identity of this epoxide with an authentic sample was established by TLC, IR, and GC (6% SE-30, 0.5-m column).

Epoxidation of 4,4-Dimethylcyclohex-2-en-1-one (15) in the Presence of Diethyl Methylmalonate (2) (Expts 6–8). The cathode compartment was charged with 60 mL of 0.2 M tetra-*n*-butylammonium bromide in acetonitrile, 5.0 mmol of 15, and the quantity of 2 indicated in Table I. The anolyte contained this solvent/electrolyte system and 1.0 mL of cyclohexene. The above electrolysis was carried out, monitored by GC and TLC for consumption of 2, and terminated when 2 had been totally consumed. The solvent was removed from the catholyte under reduced pressure (rotary evaporator). The residue was triturated several times with ether and filtered to remove the supporting electrolyte. The residue remaining after removal of the ether was fractionated by column chromatography (ether/Skellysolve, 1:5) into (1) the tartronate 2, (2) starting enone, and (3) the epoxide. The yields of substances in fractions 2 and 3 were determined by GC (6% SE-30, 4 mm × 5 m column) using acetophenone as an internal standard.

Epoxidation of Cyclohexenone (14) in the Presence of Diphenylacetonitrile (6) (Expts 2 and 3). The electrolysis and initial segregation of the products were carried out as above. The ether residue was partially purified by bulb-to-bulb distillation (80 °C bath temperature, 5 torr). The distillate was subjected to column chromatography (eluent Skellysolve/ether, 5:1): (a)

trace of 7, (b) recovered 14, (c) cyclohexenone epoxide.

This workup procedure was followed in expts 4, 5, 10, and 12–14.

Attempted Epoxidation of Chalcone (17) Alone. After passage of 3.0 F/mol of the enone, 17 had all been consumed. The catholyte (DMF was the solvent in this case) was poured onto ice–water and acidified with hydrochloric acid to pH 3. The solution was extracted with three 100-mL portions of ether. The extracts were washed, dried over $MgSO_4$, and taken to dryness. The residue was only benzoic acid.

Epoxidation of Chalcone (17) in the Presence of Diphenylacetonitrile (6). In view of the cleavage reaction described above, electrolyses in expts 16–18 were continued until only ca. 90% of 6 had been consumed. The workup was "normal" as defined above.

Registry No. 1, 609-08-5; 6, 86-29-3; 14, 930-68-7; 14 epoxide, 6705-49-3; 15, 1073-13-8; 15 epoxide, 1074-26-6; 16, 32264-57-6; 16 epoxide, 87482-82-4; 17, 141-79-7; 17 epoxide, 4478-63-1; 18, 94-41-7; 18 epoxide, 5411-12-1; superoxide, 11062-77-4.

Mechanism of Photoepoxidation of Olefins with α-Diketones and Oxygen

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The benzil- and biacetyl-sensitized photoepoxidation of olefins in the presence of oxygen has been studied. The photolytic loss of diketone is not affected by the presence of olefins; the ratio of epoxide formation to diketone consumption is in the range of 1–3. An ^{18}O-tracer study shows that the epoxide oxygen derives from molecular oxygen and that the recovered oxygen does not scramble. The photoepoxidation is accompanied by C–C bond cleavage; the ratio of epoxidation to C–C scission is not affected by solvent polarity and only slightly affected by the presence of diazabicyclooctane (Dabco). These results are explained by a mechanism involving the addition of oxygen to triplet diketone to give an acylperoxy radical, which is a key epoxidizing species.

Many photooxidations of olefins go by a singlet oxygen mechanism (the so-called type II photosensitized oxidation[1]). The products of this reaction are principally hydroperoxides. A second well-known process, called the type I reaction, proceeds by hydrogen atom or electron abstraction by the excited sensitizer. It has recently been reported that olefins can be photoepoxidized by diketone sensitizers and oxygen, and that the reaction is quite different from either the type I or type II photooxidation.[2a,b] More recently, α-diketone-sensitized photoepoxidation has been used as a preparative epoxidation method.[3a,b,d] Epoxide formation also accompanies the reaction of singlet oxygen with some olefins,[4a–d] although

(at least in some cases) it may not be a singlet oxygen product.[4e,f] Epoxides are also a significant byproduct in some electron transfer sensitized oxygenations.[5]

We now report a detailed study of the α-diketone sensitized photooxidation of olefins, focusing on the primary photoprocess and the epoxidizing species. After the completion of our study, a paper by Schuster et al.[3c] appeared on photoepoxidation with acenaphthenequinone as sensitizer. Bartlett et al. also reported an ^{18}O-tracer study of the photooxidation.[2c]

Results and Discussion

Stoichiometry. In benzene, benzil reacts photochemically in the presence of oxygen to give benzoic acid, phenyl benzoate, biphenyl, and benzoyl peroxide or phenol.[6] In

(1) (a) Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1. (b) Foote, C. S. *Acc. Chem. Res.* **1968**, *1*, 104. (c) Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133. (d) Foote, C. S. In "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press: New York, 1976; p 85.
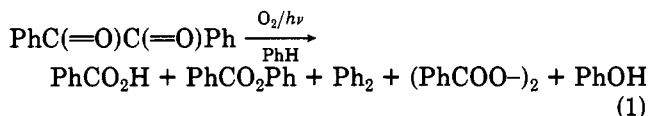
(2) (a) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4193. (b) Bartlett, P. D. In "Organic Free Radicals"; Pryor, W. A. Ed.; American Chemical Society: Washington, D.C., 1978; p 15. (c) Bartlett, P. D.; Becherer, J. *Tetrahedron Lett.* **1978**, 2983. (d) Bartlett, P. D.; Roof, A. A. M.; Shimizu, J. *J. Am. Chem. Soc.* **1982**, *104*, 3130.

(3) (a) Ryang, H.-S.; Wang, S. Y. *J. Am. Chem. Soc.* **1978**, *100*, 1302. (b) Mori, A.; Takeshite, H. *Chem. Lett.* **1978**, 395. (c) Koo, J.-Y.; Schuster, G. B., private communication; *J. Org. Chem.* **1979**, *44*, 847. (d) Buchi, G.; Fowler, K. W.; Nadzam, A. M. *J. Am. Chem. Soc.* **1982**, *104*, 544.

(4) (a) Bartlett, P. D.; Ho, M. S. *J. Am. Chem. Soc.* **1974**, *96*, 627. (b) Jefford, C. W.; Boschung, A. F. *Helv. Chim. Acta* **1974**, *57*, 2257. (c) Jefford, C. W.; Boschung, A. F. *Tetrahedron Lett.* **1976**, 4771. (d) Bartlett, P. D.; Landis, M. E. *J. Am. Chem. Soc.* **1977**, *99*, 3033. (e) Foote, C. S.; Wong, S. *Am. Chem. Soc., Div. Pet. Chem. Prep.* **1969**, *14*, A93. (f) Jefford, C. W.; Boschung, A. F. *Helv. Chim. Acta* **1976**, *59*, 2542; *Ibid.* **1977**, *60*, 2673.

(5) (a) Eriksen, J.; Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455. (b) Eriksen, J.; Foote, C. S. *Ibid.* **1980**, *102*, 6083.

(6) Saltiel, J.; Curtis, H. C. *Mol. Photochem.* **1969**, *1*, 239.

$$PhC(=O)C(=O)Ph \xrightarrow[\text{PhH}]{O_2/h\nu}$$
$$PhCO_2H + PhCO_2Ph + Ph_2 + (PhCOO-)_2 + PhOH \quad (1)$$

contrast, Bartlett and Shimizu reported that benzil is recovered in high yield in the sensitized photooxidation of olefins.[2a] In the latter case, benzil was used in a 1:1 molar

$$PhC-CPh + C=C \xrightarrow{O_2/h\nu} PhC-CPh + -C-C- \quad (2)$$
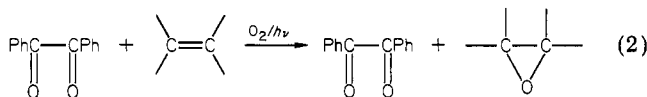
ratio with olefin and the recovery of benzil was 62–94%. This report has recently been corrected, and a considerably lower recovery of benzil reported.[2d] In the case of acenaphthenequinone, anhydride is produced from the diketone in 80% yield regardless of the presence of olefins.[3c]

In the absence of olefin, a considerable amount of a previously unreported product, perbenzoic acid, (44%) is formed (Table I). The yield of this product decreases to <5% when olefins are present, while that of phenyl benzoate is increased, all other factors remaining constant (runs 2 and 9). This product suggests the intermediate formation of benzoyloxy radicals. Benzoyl chloride was obtained in the presence of carbon tetrachloride, suggesting the intermediacy of benzoyl radical as well; this compound was identified by GLC after conversion to methyl benzoate by methanol/pyridine; benzoic anhydride was not detected by GLC. Similar formation of benzoyl radical has been reported in the photolysis of α-hydroperoxy ketones.[7a]

The addition of a high concentration of Dabco (1,4-diazabicyclo[2.2.2]octane), a well-known singlet oxygen quencher, inhibited the photooxidation (run 5) as reported.[2a] However, the retardation is probably caused by an internal filter effect caused by formation of colored byproducts[8a] rather than singlet oxygen quenching, because DABCO at 0.005 M concentration, enough to quench any singlet oxygen reaction,[8b] has no significant effect either on the conversion of benzil or on the product distribution (runs 5 and 6). In addition, the photooxidation of benzil is actually retarded in the presence of singlet oxygen sensitizers such as methylene blue. Both benzophenone and benzaldehyde are much less efficient sensitizers of the photooxidation than benzil (runs 7 and 8).

A key question is whether the diketone is recovered unchanged or consumed. This question was investigated and our results show that benzil is destroyed both in the presence and absence of olefins (Table I). The ratios of epoxide formed to benzil consumed are in the range of 1.1–1.6 (Table I). A similar ratio (1–2) is also obtained for other olefins, e.g., 1,1-diphenylethylene or 1,1-diphenyl-2-methylpropene. The ratio of epoxide formed to biacetyl sensitizer consumed has been reported to be 1.9 for the case of 1,1-diphenyl-2-methylpropene.[2a] A similar ratio (2:1) is obtained for the reaction of 0.28 M biacetyl and 0.1 M α-methylstyrene with intense irradiation (1.5 cm distance from the lamp) at 0 °C. However, the ratio is 3.3 for the reaction with 0.0125 M biacetyl and a 0.05 M

concentration of the same olefin under weaker irradiation (10 cm from the lamp). The other products are 9% anisole (see discussion), 102% acetic acid, 34% acetone, 23% methanol, 13% methane, and 1% ethane. The ratio of epoxide formed to diketone consumed was also reported to be 3 for the case of phenylmethylglyoxal.[2a] From these results, it is apparent that α-diketone is not a sensitizer or catalyst but is a reactant, and that the ratio of the amount of epoxide formed to diketone consumed is in the range of 1–3, depending on reactants and conditions.

Epoxidation vs. C–C Cleavage. The data in Table I also show a significant amount (20–30%) of C–C cleavage products accompanying the epoxidation. The selectivity does not change much in the presence of DABCO (run 6).

A more detailed study of the selectivity is summarized in Table II. Again, the oxidative C–C cleavage in aprotic solvents is considerable (20–30%), regardless of the type of olefin or α-diketone or the presence of Dabco (cf. runs 15–18). The C–C cleavage is significantly decreased only for the reaction in alcohols. Run 15, with biacetyl, appears to have an anomalously high cleavage ratio.[8c] The mechanism of the cleavage is not yet clear, but it is not a singlet oxygen reaction (via dioxetanes) because the cleavage is not inhibited by the presence of Dabco. Furthermore, the two olefins studied in Table II are nearly inert to singlet oxygen. A possible mechanism for the cleavage could be electron transfer, as in the dicyanoanthracene–O_2–olefin system.[5] However, the electron transfer oxidation reaction requires extremely polar solvents, and the fact that there is no effect of solvent polarity (Table II) seems to rule out this mechanism in this case. A preliminary study indicates that the C–C cleavage is caused by acyloxy radicals.[7h]

Tracer Study. An oxygen-18 tracer study was carried out to establish whether the epoxide oxygen derives from O_2 or diketone. The results in Table III clearly show that it is derived from atmospheric oxygen. Moreover, the remaining labeled oxygen gas does not exchange with unlabeled O_2. One oxygen of the product phenyl benzoate, which is scrambled between acyl O and alkyl O, is also derived from O_2 (see Experimental Section for details).

$$PhC-CPh + {}^*O_2 + C=C \xrightarrow{h\nu} -C-C- +$$
$$PhC-OPh + {}^*O_2 \quad (3)$$
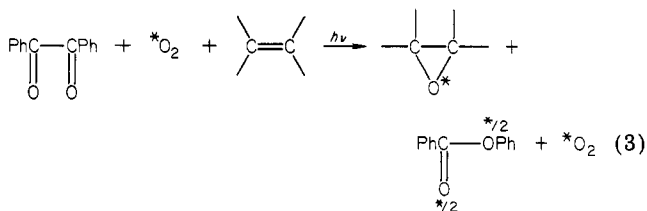
Since phenyl benzoate is known to be formed from benzoyloxy radical and benzene,[9] the scrambling in the phenyl ester is easily understood.

A test for the possible incorporation of ${}^{18}O$ into benzil was difficult because the molecular ion of benzil in the mass spectrum in weak, and the exchange of carbonyl oxygen with any water in the mixture would be facile. Water could be produced in the reaction, for example, via HOO· or H_2O_2 from O_2 and cyclohexadienyl radicals, since oxygen is well-known to be an efficient oxidant for the latter radical.[9] In agreement with these results, an ${}^{18}O$-tracer study using GC–MS has recently been reported which showed that the oxygen atom of the epoxide comes from O_2 and that incorporation of oxygen from O_2 into α-diketone is rather small (≤10%).[2c]

First Step in the Photooxidation of Benzil. It is known that α-diketones add photochemically to olefins,

(7) (a) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7324. (b) Sawaki, Y., unpublished results.

(8) (a) A charge transfer complex between DABCO and phenanthrenequinone is formed and inhibits the photoreaction of the quinone: Sawaki, Y., unpublished results. A similar situation probably occurs with benzil. (b) ca. 90% of the singlet oxygen reaction should be quenched with 0.005 M DABCO. Foote, C. S.; Peterson, E. R.; Lee, K.-W. *J. Am. Chem. Soc.* **1972**, *94*, 1032. (c) 1,1-Diphenylethylene oxide is gradually degraded to benzophenone under the photolysis conditions. This is probably an acid-catalyzed reaction. Inhibition of this degradation by the basic DABCO may account for the modest effect of DABCO on the epoxide/cleavage ratio. (runs 15 and 16, Table II).

(9) (a) Nakata, T.; Tokumaru, K.; Simamura, O. *Tetrahedron Lett.* **1967**, 3303. (b) Saltiel, J.; Curtis, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 2056.

Table I. Photooxidation of Benzil in the Presence of Olefins[a]

run	conditions[a]	conversion of Bz$_2$, %	products, mol%/mol of Bz$_2$ consumed[b]					
			epoxide	PhCHO	PhCO$_2$Ph	PhCO$_2$H	Ph$_2$	others
1[c]		54.9			34	78	0	PhCO$_3$H (44%)
2[d]		53.9	136	33	46	28	1	(PhCO$_2$)$_2$
3[d]	25 °C	54.4	106	36	35	50	6	
4[d]	25 °C CCl$_4$	52.7	32	15	7	15	9	
5[d]	0.05M Dabco	5.5	2.8	0	0	f	0	
6[d]	0.005M Dabco	46.5	132	23	51	f	0	
7[d]	Ph$_2$C=O[g]	g	3	9	0	f	0	
8[d]	(Ph$_2$C=O + PhCHO)[g]	g	3	f	0	f	0	
9[e]		46.8	162		69	f	0	

[a] Benzil 0.05M, Bz$_2$ and 0.10 M olefin irradiated in benzene for 40 min at 0 °C, except as noted. Oxygen was bubbled through a capillary into a 10-mL Pyrex test tube. Ph = C$_6$H$_5$ and Dabco = diazabicyclo[2.2.2]octane. [b] Determined by GLC. Peroxides were titrated. A small amount of perbenzoic acid (<5%) could be detected in all runs but is listed only in the run in which larger amounts were produced. [c] No olefin. [d] β-Methylstyrene. [e] Norbornene. [f] Not determined. [g] Benzophenone and/or benzaldehyde (0.05 M) in place of benzil. The carbonyl compounds were recovered in 91-95% yields. The yields of runs 7 and 8 are based on charged carbonyl compound.
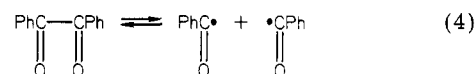
Table II. Comparison of Epoxidation and C-C Cleavage[a]

run	olefin	conditions[b]	epoxide: cleavage[c]
10[d]	Ph$_2$C=CMe$_2$		80:20
11[d]	Ph$_2$C=CMe$_2$	40 min	82:18
12[d]	Ph$_2$C=CMe$_2$	75% MeCN	76:25
13[d]	Ph$_2$C=CMe$_2$	75% i-PrOH	94:6
14[d]	Ph$_2$C=CMe$_2$	75% MeOH	96:4
15[d]	Ph$_2$C=CH$_2$		45:55[e]
16[d]	Ph$_2$C=CH$_2$	0.005 M Dabco	70:30[f]
17[g]	Ph$_2$C=CH$_2$		67:33
18[g]	Ph$_2$C=CH$_2$	75% MeCN	70:30

[a] Reaction of 0.05 M Bz$_2$ (benzil) or 0.10 M Ac$_2$ (biacetyl) with 0.10 M olefin irradiated for 25 min at 0 °C unless otherwise noted. [b] Solvent is benzene unless otherwise noted, % means volume % in benzene. [c] Cleavage is percent yield of benzophenone; the material balance for starting olefin is excellent (>90%) for runs 10-14 and good (>70%) for runs 15-18. [d] Biacetyl. [e] 38% epoxide and 47% benzophenone (recovered olefin 4%). [f] 43% epoxide and 18% benzophenone (recovered olefin 35%). [g] Benzil.

affording 1,2- and 1,4-cycloaddition[10a] or allylic addition[11] (in the sense of an ene reaction). The photochemical reaction of α-diketones in solution mostly involves intra-, or intermolecular hydrogen abstraction.[10b] The major products from the photolysis of benzil under anaerobic conditions in hydrogen-donating solvents are the corresponding pinacol, benzoin, and benzoin benzoate.[12] This reaction always contains products (benzaldehyde, benzoin benzoate, and benzoic acid) from the acyl radical in 10–30% yields.[12] Benzoic acid was reported to be the sole product from the photolysis of benzil in i-PrOH under O$_2$,[12a] but the present results show that the photolysis yields a considerable amount of perbenzoic acid as well. In addition, photolytic α-cleavage of benzoins occurs very rapidly to form a radical pair, which is efficiently trapped by thiol (the quantum yield for the cleavage increases from 0.05 to 0.35 in the presence of 10^{-3} M thiol).[13a] These facts

and considerations suggest a possible mechanism involving dissociation of benzil into two benzoyl radicals:

$$\text{PhC}\!-\!\text{CPh} \rightleftharpoons \text{PhC}{\cdot} + {\cdot}\text{CPh} \qquad (4)$$
$$\underset{\text{O} \quad \text{O}}{\|\quad\|} \qquad\qquad \underset{\text{O}}{\|} \quad \underset{\text{O}}{\|}$$

To test the possibility of this dissociation, the relative quantum yield of benzil decomposition was determined under various conditions (Table IV). The quantum yield in benzene under O$_2$ is 0.039, which is close to the literature value (ϕ = 0.030)[6]. The value (0.067) in i-PrOH– (3:1) is slightly lower than the literature one (ϕ = 0.11)[12a,c] in i-PrOH.

In contrast to the case of benzoins, which yield a trappable benzoyl radical,[13] thiol addition to the benzil photolysis under N$_2$ did not result in the formation of much benzaldehyde (run 27); the decreased quantum yield of benzil loss could be due to the formation of light-absorbing products, since the UV showed considerable new absorbance around 368 nm after irradiation. Trapping of the benzoyl radical by carbon tetrachloride also failed under nitrogen; no benzoyl chloride was formed. Cross-coupling experiments using benzil and p,p'-dimethoxybenzil or with p-methoxybenzil under N$_2$ gave negative results; no products of cross coupling of benzoyl radicals could be observed. No benzoyl radical could be detected even with esr using the sensitive spin-trapping method with nitroxides.[14] Thus it is concluded that benzoyl radical (eq 4) is *not* formed as the primary photolysis product.

Thus, the formation of peroxy acid under O$_2$ must be explained by another scheme than eq 4. In the past, the photooxidation of α-diketones has sometimes been explained by hydrogen abstraction from solvent followed by the addition of oxygen to the resulting ketyl radical.[15] The present results, however, show that the decomposition of benzil under O$_2$ is rather insensitive to the presence of abstractable allylic hydrogen atoms (runs 29–31) or solvent (i-PrOH) hydrogen. These facts suggest that the primary process is a direct interaction between oxygen and diketones, as suggested previously.[6]

The rate of loss of benzil is not altered by the presence of various olefins except trans-stilbene (runs 32 and 33). Since stilbene is known to be an efficient quencher of triplet benzil,[13b] this result suggests that triplet benzil is involved in the photolysis. Since the quantum yield for

(10) (a) Pfundt, G.; Schenck, G. O. In "1,4-Cycloadditions"; Hamer J., Ed.; Academic Press: New York, 1967; p 345. (b) Monroe, B. M. *Adv. Photochem.* **1971**, *8*, 77.
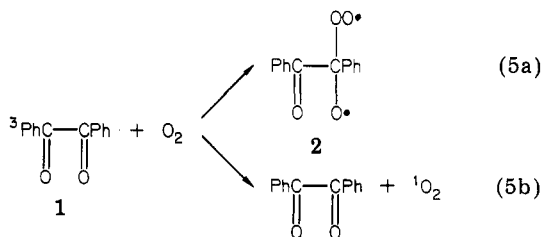
(11) (a) Ryang, H.-S.; Shima, K.; Sakurai, H. *J. Am. Chem. Soc.* **1971**, *93*, 5270. (b) *J. Org. Chem.* **1973**, *38*, 2860. (c) Ryang, H.-S., private communication.

(12) (a) Bunbury, D. L.; Chuang, T. T. *Can. J. Chem.* **1969**, *47*, 2045. (b) *Ibid.* **1972**, *50*, 2499. (c) Ogata, Y.; Takagi, T.; Fujii, Y. *J. Org. Chem.* **1972**, *37*, 4026.

(13) (a) Lewis, F. D.; Lauterbach, R. T.; Heine, H.-G.; Hartmenn, W.; Rudolph, H. J. *J. Am. Chem. Soc.* **1975**, *97*, 1519. (b) Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, C. *J. Am. Chem. Soc.* **1964**, *86*, 3197. (c) Sawaki, Y.; Ogata, Y. *Ibid.* **1981**, *103*, 2049.

(14) Ledwith, A.; Russell, P. J.; Sutcliffe, L. M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1925.

(15) (a) Gream, G. E.; Paice, J. C.; Ramsay, C. C. *Aust. J. Chem.* **1969**, *22*, 1229. (b) Stevens, B.; Dubois, J. T. *J. Chem. Soc.* **1962**, 2813. (c) Maruyama, K.; Ono, K.; Osugi, J. *Bull. Chem. Soc., Jpn.* **1972**, *45*, 847.
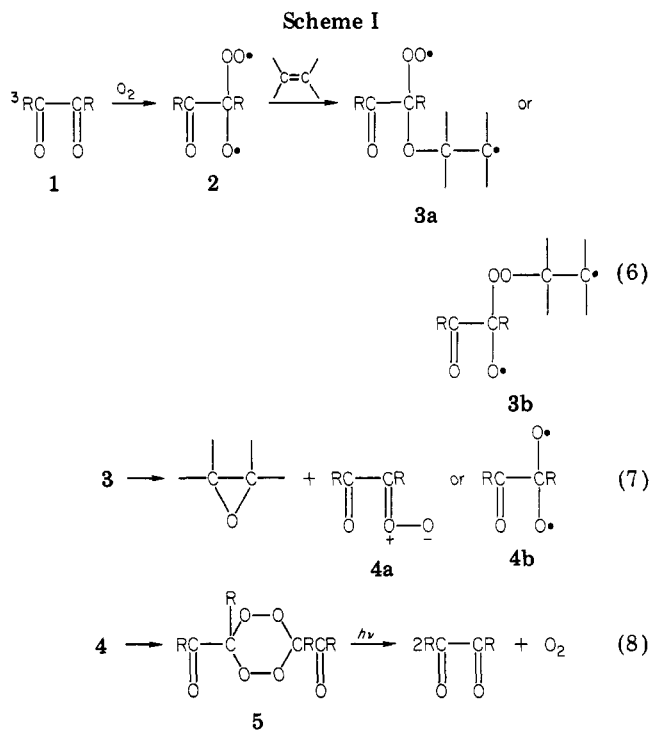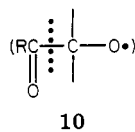
$$^3PhC-CPh + O_2 \left\{ \begin{array}{l} PhC-CPh \quad (5a) \\ \quad 2 \\ PhC-CPh + {}^1O_2 \quad (5b) \end{array} \right.$$

1

intersystem crossing of benzil (ϕ_{ST}) is 0.92 and the triplet energy (E_T) is 53 kcal/mol,[16] the quenching of triplet benzil by *trans*-stilbene ($E_T < 50$ kcal/mol)[16] should be an efficient process. Quenching of triplet benzil by 1,3-cyclohexadiene ($E_T = 54$ kcal/mol) is not effective, since its reaction with oxygen is much faster. As would be expected for the intermediacy of benzil triplet, the major process (93%) reported for tetramethylethylene is reaction with singlet oxygen;[2a] in the presence of 0.025 M olefin, the loss of benzil is still constant in spite of the fact that the yield of ene product hydroperoxide is 66% based on the initial amount of benzil (run 34). (Singlet oxygen products are 93% of the mixture for tetramethylethylene[2a] and 11% for 1,1-diphenyl-2,2-dimethylethylene at 0.1 M initial concentrations.) However, the loss of benzil is significant even under nitrogen (run 36), and, although products were not investigated, it is likely that this reaction is an ene reaction between triplet benzil and the olefin,[11c] such as occurs in the case of biacetyl.[11]
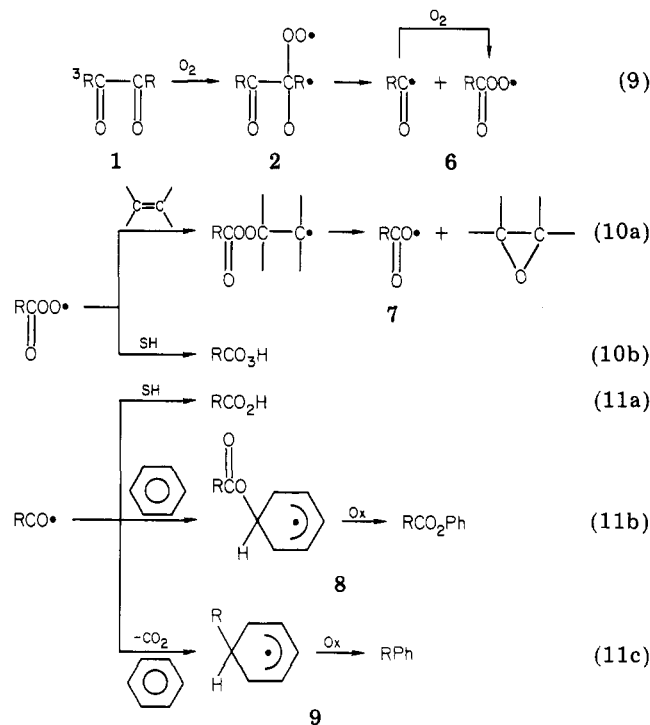
Mechanism. As discussed above, all the facts argue against the preliminary formation of two benzoyl radicals (eq 4). Thus, there remain two conceivable schemes for the photoepoxidation with benzil (Schemes I and II).

Scheme I was originally suggested by Shimizu and Bartlett to explain the benzil-sensitized photoepoxidation[2a] and was based on the reported high recovery of benzil. However, the present results indicate that benzil is photodecomposed regardless of the presence of olefins, and the ratio of epoxide formed to benzil consumed is in the range of 1.1–1.6. These results are inconsistent with Scheme I alone. Moreover, this scheme does not explain the lack of scrambling in the recovered O_2 (Table III and eq 8) and the lack of [18]O incorporation in benzil.[2c] Another point not easy to understand is the driving force for the conversion of **3a** to epoxide and how it is possible that an intermediate as unstable as **4a** or **4b** has a long enough lifetime to dimerize to **5** with high efficiency.

On the other hand, Scheme II is consistent with all the results. The addition of oxygen to triplet benzil (eq 5a) is competitive with the physical quenching to yield singlet oxygen (eq 5b), and the ratio is not affected by added olefins. Other competitive primary pathways for triplet benzil are the quenching by olefins with low-lying triplets (such as *trans*-stilbene) and the addition to olefins such as tetramethylethylene.[11] Except in these two cases, the photodecomposition of benzil (eq 9) is rather constant under various conditions (Table IV). The predominant formation of peroxyacid in the absence of olefins is explained by eq 9 and 10b. A facile acyl scission from acyl alkoxy radicals (**10**) has recently been established.[17]

$$(RC\overset{\cdot\cdot}{\underset{\parallel}{\,}}\overset{|}{\underset{|}{C}}-O\cdot)$$

10

Scheme I

$$^3RC-CR \xrightarrow{O_2} RC-CR \xrightarrow{\backslash C=C /} RC-CR \quad or$$

1   **2**   **3a**

(6)

3b

$$3 \longrightarrow -C-C- + RC-CR \quad or \quad RC-CR \quad (7)$$

4a   **4b**

$$4 \longrightarrow RC-C \quad CRCR \xrightarrow{h\nu} 2RC-CR + O_2 \quad (8)$$

5

Scheme II

$$^3RC-CR \xrightarrow{O_2} RC-CR\cdot \longrightarrow RC\cdot + RCOO\cdot \quad (9)$$

1   **2**   **6**

$$RCOO\cdot \left\{ \begin{array}{l} \xrightarrow{\backslash C=C/} RCOOC-C\cdot \longrightarrow RCO\cdot + -C-C- \quad (10a) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad 7 \\ \xrightarrow{SH} RCO_3H \quad (10b) \end{array} \right.$$

$$RCO\cdot \left\{ \begin{array}{l} \xrightarrow{SH} RCO_2H \quad (11a) \\ \xrightarrow{} 8 \xrightarrow{Ox} RCO_2Ph \quad (11b) \\ \xrightarrow{-CO_2} 9 \xrightarrow{Ox} RPh \quad (11c) \end{array} \right.$$

8

9

The competition of reactions 10a and 10b explains the decrease of peroxy acid formation in the presence of olefins. Phenyl benzoate (eq 11b) and biphenyl neq 11c) are products of the well-known homolytic aromatic substitution of benzoyloxy and phenyl radicals, respectively, on benzene.[18] This conclusion is also confirmed by the fact that the photooxidation of benzil in acetonitrile yields no phenyl benzoate, and that the photolysis of *p*-anisil in aerated benzene affords phenyl *p*-anisoate. The small amount of benzoyl peroxide formation is due to either the

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Table III. ^{18}O Study on the Photooxidation of Olefins with α-Diketones[a]

run	reactants			product	^{18}O excess, %
	olefin	O_2 excess, $^{18}O\%$			
19[b]	$Ph_2C=CMe_2$	2.46 ± 0.15		Ph_2COCMe_2 O_2	2.55 ± 0.41 no scrambling[d]
20[c]	$Ph_2C=CMe_2$	3.06 ± 0.08		Ph_2COCMe_2	3.28 ± 0.38
21[c]	$PhCH=CHMe$	3.19		$PhCO_2Ph$	1.32[e]

[a] α-Diketone (0.2 mmol) and olefin (0.2 mmol) were irradiated under oxygen containing ^{18}O for 40 min at 0–5 °C. For the analysis see Experimental Section. [b] Benzil. [c] Biacetyl. [d] Starting oxygen gas contained $O_2^{16,18}:O_2^{18,18} = 100:50.7$. After ca. 70% conversion of oxygen, the composition of remaining oxygen was 100:50, which indicates no scrambling of $O_2^{18,18}$ with excess $O_2^{16,16}$. Similar results were obtained for the biacetyl case (run 20). [e] Benzoic acid from alkaline hydrolysis of $PhCO_2Ph$ in aqueous dioxane contains 0.61% excess ^{18}O.
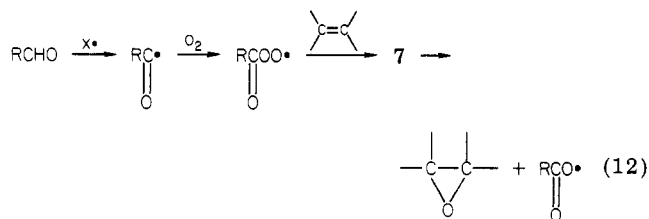
Table IV. Quantum Yields and Products for the Photolysis of Benzil under Various Conditions[a]

run	conditions[a]	conversion of benzil, %	Φ[b]	products, %[c]		
				Ph_2	$PhCO_2Ph$	others
22		24.6 ± 0.9	0.039[d,e]	8	77	$PhCO_3H$ (60%)
23	air	19.4	0.031	32	27	f
24	N_2	3.6	0.005[e]	0	0	f
25	75% i-PrOH	32.9	0.057	0	0	$PhCO_3H$ (50%)
26	N_2, 75% i-PrOH	37.6	0.067[g]	0	0	f
27	N_2, 75 mM p-MePhSH	9.7	0.015	0	0	PhCHO (<5%)
28	0.1 M norbornene	27.4	0.043	14	50	f
29	0.1 M 1,3-cyclohexadiene	34.6	0.060	6	11	f
30	0.5 M 1,3-cyclohexadiene	26.9	0.043	9	27	f
31	0.1 M $PhCH=CHCH_3$	23.3	0.037	7	35	epoxide (180%)
32	0.01 M trans-stilbene	12.1	0.018	2	f	h
33	0.1 M trans-stilbene	10.2	0.015	trace	trace	i
34	0.025 M $Me_2C=CMe_2$	27.6	0.047	trace	trace	j
35	0.1 M $Me_2C=CMe_2$	42.4	0.077	trace	trace	k
36	N_2, 0.1 M $Me_2C=CMe_2$	36.3	0.063	trace	trace	l

[a] Photolysis of 0.0125 M benzil in benzene under O_2 unless otherwise noted. The conversion of benzil was determined by GLC; results are an average of two to four sums. % means volume % in benzene. $Ph = C_6H_5$ or C_6H_4. [b] The quantum yields for benzil decomposition were determined relatively using a merry-go-round, irradiating 15 min through a Pyrex filter with a Hanovia medium pressure 450-W Hg lamp at room temperature. See Experimental Section. [c] Products were determined by GLC or iodometrically and percent yields are based on consumed benzil. Benzoic acid was not determined. [d] This value was determined by irradiating at 366 nm with ferrioxalate actinometry. [e] Reference 6 gives 0.03 and 0.003 for O_2 and N_2. [f] Not determined. [g] References 12a,c give 0.11 for i-PrOH. [h] cis-Stilbene 66% (cis/trans > 8), epoxide 7%, and PhCHO 5%. [i] cis-Stilbene 402% (cis/trans = 0.77). [j-l] From the NMR spectra, 3-hydroperoxy-2,3-dimethyl-1-butene could be determined (66%, 52%, and 0% yields for j, k, and l, respectively). Another major product was detected which is probably an ene adduct of benzil with olefin in trace, 31%, and 25% yields by NMR, respectively (cf. ref 11).

coupling of benzoyl and benzoylperoxy radical (6, R = Ph) or the bimolecular reaction of 6, as in the case with acetylperoxy radical.[19]

The key steps in the photoepoxidation are the addition of acylperoxy radical 6 to olefin, and the cyclization of adduct to epoxide (eq 10a). Epoxide formation by this mechanism has been long known in the autoxidation of olefins[20] and for the reaction of alkylperoxy radicals (e.g., t-BuOO·) and olefins.[21] In the coautoxidation of aldehydes and olefins, the same reaction occurs.[22] Free radical ep-

$$RCHO \xrightarrow{X \cdot} RC \cdot \xrightarrow{O_2} RCOO \cdot \xrightarrow{\text{C=C}} 7 \rightarrow$$

$$\xrightarrow{\quad} \text{epoxide} + RCO \cdot \quad (12)$$

oxidation affords predominantly trans epoxides, as in the

present case. It is apparent from the product stereochemistry that the adduct radical 7 (eq 10a or 12) has a long enough lifetime to rotate to the favored trans conformation prior to cyclization. The accompanying C–C cleavage (Table I and II) could be explained by a scheme assuming a competitive addition of O_2 to 7:
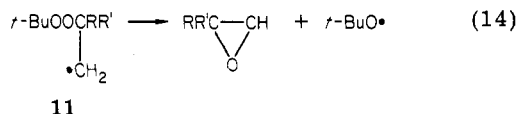
$$(13a)$$

$$7 \quad (13b)$$
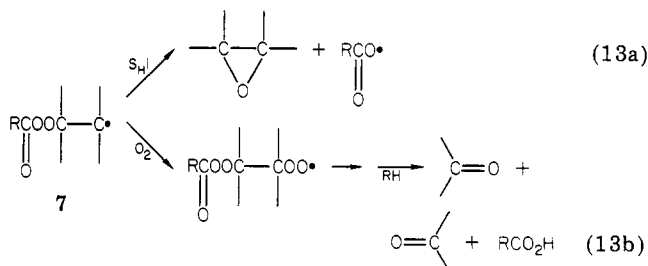
However, the lack of dependence of epoxide yields on oxygen pressure is not consistent with this scheme. A recent preliminary study indicates that the C–C cleavage is caused by acyloxy radical.[7b] The formation of C–C fission products along with epoxide has often been observed in the autoxidation of olefins[20b] and also in the coautoxidation of aldehyde and olefins.[23] Predominant formation of trans epoxide was also reported for direct photooxidation of olefin.[24] Although the author suggested

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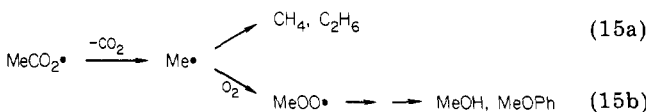(24) Petterson, R. C. *Angew. Chem. Int. Ed. Engl.* 1970, 9, 644.

direct addition of oxygen to the excited olefin, the subsequent epoxidation step proposed is similar to the above reaction. It is noteworthy that cyclization to epoxides has been shown to be greatly accelerated by steric effects.[25] For example, the relative rates of cyclization of 11 with R,R′ = H,H; H,Me; and Me,Me are 1, 20, and 350, respectively.[25]

$$t\text{-BuOOCRR'} \longrightarrow RR'C\overset{\displaystyle O}{\underset{}{\diagup\!\diagdown}}CH + t\text{-BuO}\bullet \qquad (14)$$

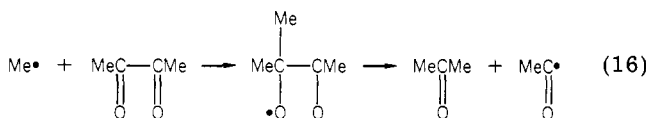$$\overset{\displaystyle |}{\underset{\displaystyle \bullet CH_2}{}}$$

11

This large steric acceleration may be related to the fact that significant epoxide formation occurs during singlet oxygen reactions only for hindered olefins[4] (probably as a side reaction).

Photoepoxidation with Biacetyl. Biacetyl fluorescence can be quenched by olefins,[26] but quenching is negligible under the present conditions (0.1 M olefin). In a kinetic study of the biacetyl-sensitized photooxidation of diphenylanthracene, a biacetyl–oxygen complex (called an "oxciplex") has been suggested.[27] Although 15% of biacetyl fluorescence is quenched by atmospheric oxygen,[28] the major reaction is probably via triplet biacetyl. This suggestion is based on the fact that the amount of biacetyl destroyed is 43% (12% under N_2), which is much larger than in the benzil case, 25% (4% under N_2) under the conditions of Table IV. Since the absorption coefficient of the biacetyl is less than that of benzil in the irradiation range, the quantum yield of biacetyl decomposition is much higher that that of benzil (0.04 under O_2). The amount of photolysis of biacetyl in the presence of 0.1 M tetramethylethylene is the same as that in the absence of the olefin. All the results are quite similar to those in the case of benzil, e.g., the large accelerating effect of oxygen in the photolysis, the ratio of epoxide formed to diketone consumed, the results of the $^{18}O_2$ study (Table III), and the accompanying C–C cleavege (Table I and II). Thus, the mechanism for photoepoxidation with biacetyl is probably the same as that with benzil.

A minor difference from the benzil case is the facile decarboxylation of acetoxy radical to give methyl radical (Me·). Anisole, a minor product in this reaction, is known to be formed from Me· and O_2 in benzene.[29]

$$MeCO_2\bullet \xrightarrow{-CO_2} Me\bullet \begin{cases} \nearrow CH_4, C_2H_6 & (15a) \\ \searrow_{O_2} MeOO\bullet \longrightarrow \longrightarrow MeOH, MeOPh & (15b) \end{cases}$$

Acetone may be formed either by the coupling of Me· and Me·C(=O) or by the reaction of Me· with biacetyl:

$$Me\bullet + \underset{\underset{O}{\|}}{Me}C\!\!-\!\!\underset{\underset{O}{\|}}{C}Me \longrightarrow \underset{\underset{\bullet O}{|}}{Me}\overset{\overset{Me}{|}}{C}\!\!-\!\!\underset{\underset{O}{|}}{C}Me \longrightarrow \underset{\underset{O}{\|}}{Me}CMe + \underset{\underset{O}{\|}}{Me}C\bullet \qquad (16)$$

The latter photoacylation reaction, previously described by Bentrude,[30] is a useful synthetic reaction in some cases.[31] This reaction becomes a complicating factor when

determining accurate quantum yields.

Experimental Section

Melting points are corrected. NMR spectra were recorded on a Varian T-60 and mass spectra on an AEI MS-9 for organic compounds and a Consolidated Electrodynamics 21-620 mass spectrometer for O_2 gas. GLC analysis was done on a HP Model 5720A using a 50-cm column packed with 10% UC W982 on Chromosorb W (AW, DMCS), a 75-cm column packed with Carbowax 20 M on Anachrom, and a 180-cm column with Porapack Q (180–100 mesh). Bibenzyl was used as an internal standard.

Materials. p-Anisil was obtained by a 2-h reflux of SeO_2 and anisoin (1:1 molar ratio) in AcOH and recrystallized from benzene–MeOH, 40% yield, mp 132–133 °C (lit.[32] mp 133 °C). 1,1-Diphenyl-2-methylpropene was synthesized according to a literature method,[34] bp 123–124 °C (3mm) (lit.[34] 150–155 °C (4mm)), 70% yield. Other diketones and olefins are from commercial sources. ^{18}O-enriched gas was purchased from Research Products Divisions, Miles Lab., Inc., IN.

Photooxidation of Benzil and Olefins. A typical procedure for experiments in Table I and II is as follows. A total of 4 mL of a benzene solution of benzil (0.05 M) and olefin (0.10 M) was placed in a 10-mL Pyrex test tube at 0–3 °C and, with oxygen being bubbled through a capillary, irradiated for 40 min with a Hanovia medium pressure 450-W Hg lamp in a water-cooled Pyrex jacket (1.5 cm distance). Products were determined by GLC using bibenzyl as an internal standard; the retention time of each product was identical with those of authentic samples on two columns, carbowax 20 M and UC W982.

The peroxidic mixture was determined as follows: An aliquot (1 mL) was added to a mixture of MeOH (5 mL) and Me_2SO (0.5 mL); peracid was completely consumed in 5 min of standing, and the remaining benzoyl peroxide was titrated by iodometry. The total peroxide (peracid + benzoyl peroxide) was titrated iodometrically with KI in MeOH without the preliminary treatment with Me_2SO. The difference between the two titrations corresponds to the amount of peracid.

Benzoyl peroxide could be easily isolated from the photooxidation of benzil on a scale four times that of run 1; after evaporation of solvent under reduced pressure, the addition of a small amount of MeOH started the crystallization of benzoyl peroxide in 9% yield, mp 105–107 °C dec. (lit.[35] 106 °C).

^{18}O-Tracer Study. A 10-mL round-bottomed flask with a magnetic stirrer was filled with a benzene solution of 0.05 M benzil and 0.05 M $Ph_2C=CMe_2$, fitted with a serum cap and flushed with N_2 gas. After inserting a 10-mL syringe filled with $^{18}O_2$, about 5 mL of the benzene solution was taken out by another syringe. The reaction mixture was irradiated, stirring magnetically, at 0–3 °C for 40 min with a Hanovia medium-pressure 450-W Hg lamp. About 5 mL of O_2 was absorbed; the remaining gas above the solution was purified and analyzed by mass spectroscopy and found to contain 2.46% excess ^{18}O. Solvent was evaporated under reduced pressure and the residue was chromatographed on an alumina column (5 g) with hexane to afford pure epoxide. The excess ^{18}O content of the epoxide was determined, as described elsewhere,[36] in comparison to the M + 1 peak as a reference. A similar procedure was applied to the biacetyl-olefin-*O_2 system (run 20).

For the case of α-methylstyrene (run 21), repeated mass spectral measurements were unsuccessful with the available spectrometer because of excessive volatility of the epoxide. Phenyl benzoate was purified by converting unreacted benzil to benzoic acid with a small amount of alkaline H_2O_2 ($NaHCO_3$, 50% aqueous dioxane), then extracted with CH_2Cl_2, and dried over Na_2SO_4. The evaporation of solvent afforded pure phenyl benzoate; mass spectral analysis showed 1.32% excess ^{18}O. The ester was then hydrolyzed to benzoic acid by NaOH in 50% dioxane, neutralized with

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aqueous HCl, extracted with ether, and then recrystallized from ether–CCl$_4$; the benzoic acid was shown to contain 0.61% excess ^{18}O, about half of that in phenyl benzoate.[37] These results show that one oxygen atom in PhCO$_2$Ph is incorporated from *O$_2$ gas, half in each oxygen.

Attempted mass spectral analyses of unreacted benzil were all unsuccessful because of the small parent peak of benzil and difficulty in purification; chromatographic purification was not applicable since the oxygen exchange with water is very facile for the carbonyl oxygen in benzil.

Quantum Yield Determinations. Quantum yields were determined for the photolysis of 5 M benzil in benzene saturated with oxygen (3 mL of solution in a 1-cm Pyrex cell), irradiating at 366 nm with a Hitachi MPF-2A fluorescence spectrometer (Xe lamp). The irradiation was carried to less than 20% conversion, as determined by UV. The incident light intensity was determined by ferrioxalate actinometry.[39] The result was ϕ = 0.039 as listed in Table IV (run 22).

For the other runs in Table IV, relative yields were determined by irradiating benzene solutions through a Pyrex filter with a Hanovia medium-pressure 450-W Hg lamp using a water cooled merry-go-round for 15 min at room temperature (10 cm distance from the lamp). The solutions were of 4-mL volume in 10-mL Pyrex test tubes fitted with serum caps and were saturated with O$_2$ or N$_2$ by flushing through syringe needles. The conversions of benzil were determined after 15 min irradiation. The results in Table IV are mostly means of two or three determinations.

Cross Experiments. To test the possible intermediacy of the benzoyl radical, cross experiments were undertaken between 0.01 M p-anisil and 0.01 M benzil under nitrogen. No cross product (p-methoxybenzil) was detected by repeated irradiations; the conversion of the benzil was as high as 33–81% and 0.5% of the cross product could easily have been detected.

A similar attempt failed to detect benzil or p-anisil from irradiation of a 0.01 M benzene solution of p-methoxybenzil under N$_2$ or O$_2$. In contrast to the results under O$_2$, attempted trapping of the benzoyl radical by CCl$_4$ failed to afford benzoyl chloride under N$_2$.

(37) It was assumed that no exchange of oxygen between H$_2$O and phenyl benzoate occurs during the alkaline hydrolysis. This assumption is based on the fact that, although *O exchange occurs in the hydrolysis of PhCO$_2$R (R = Me or Et),[38] the exchange is only 10–20% of the hydrolysis and that for the present case of the phenyl ester (R = Ph), the exchange should be much slower because PhO$^-$ is a much more effective departing group than MeO$^-$ or EtO$^-$.

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Oxidation of Alkyl Trimethylsilyl Ketene Acetals with Lead(IV) Carboxylates

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Alkyl trimethylsilyl ketene acetals generated from either esters or lactones react with lead(IV) acetate (LTA) or lead(IV) benzoate (LTB) to afford useful yields of the corresponding α-carboyloxy esters and α-carboyloxy lactones. Yields of the reaction products are optimized by use of the appropriate solvent (methylene chloride or benzene) during oxidation. Alkyl groups such as methyl, ethyl, and tert-butyl are all compatible with the procedure, and lactones containing five-, six-, and seven-membered rings give good yields of oxidation products.

The direct oxygenation of ester enolates,[1] treatment of ester enolates with MoOPh (MoO$_5$·py·HMPA),[2] and the treatment of alkyl trimethylsilyl ketene acetals with m-chloroperbenzoic acid (MCPBA)[3] or singlet oxygen[4] have been used as methods for the placement of oxygen on the α-carbon adjacent to a carboxy unit. We have previously reported that enol silyl ethers react smoothly with lead(IV) carboxylates to afford the corresponding α-acetoxy[5] and α-benzoyloxy[6] carbonyl compounds in high yield. Although accounts in the literature concerned with the lead(IV) acetate (LTA) oxidation of esters do exist,[7] the inability of esters to enolize readily under the conditions normally used for LTA oxidation places a severe limitation on this method of α-position functionalization. This being the case, we felt that preformed ester enols or analogues of these species should react rapidly with lead(IV) carboxylates to afford α-carboyloxy esters. Further, it might also be possible to modify this approach to give a useful synthetic method for the preparation of α-carboyloxy lactones.

We report here that alkyl trimethylsilyl ketene acetals 1 or 2, derived from esters and lactones, respectively, react with either LTA or lead(IV) benzoate (LTB). When the crude reaction product is treated with triethylammonium

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