carried out as described earlier.[6]

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**Registry No.** 1, 321-38-0; 1c, 90990-92-4; 2, 323-09-1; 3, 459-60-9; 4, 321-28-8; 6, 361-92-2.

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# Reactivities of Acylperoxy Radicals in the Photoreaction of α-Diketones and Oxygen

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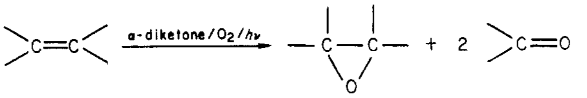
The photoepoxidation of olefins with α-diketones and oxygen has been studied mechanistically focusing on the reactivities of intermediate radicals. One mole of α-diketone resulted in the formation of 2 mol of epoxide together with 2 equiv of C–C cleavage of olefins. The photoepoxidation proceeds via acylperoxy radicals $RCO_3\cdot$ and the C–C cleavage of olefins is caused by acyloxy radical $RCO_2\cdot$. The addition of $RCO_3\cdot$ to olefins was found to be ca. $10^5$-fold faster than that of alkylperoxy radical ROO·. The relative reactivities of olefins suggest that acylperoxy radicals behave as a strongly electrophilic radical. That is, $\rho$ values of $-1$ (vs. $\sigma^+$) obtained in the photoepoxidation of substituted styrenes are of the same magnitude as those in the epoxidation with molecular peracids. Although the relative reactivities of olefins toward the photoepoxidation roughly parallel those for the peracid epoxidations, the additivity of methyl substituent is not always operative. This is explained by a steric retardation by too many substituents on the carbon attacked by $RCO_3\cdot$ in addition to the relative stabilities of resulting adduct radicals between olefins and $RCO_3\cdot$. Since acylperoxy radicals are not reactive toward sulfides, sulfoxides, or pyridine, a selective epoxidation of double bonds is possible. The relative reactivities of olefins toward benzoyloxy and methylperoxy radicals revealed a much less electrophilic nature of these oxy radicals, the $\rho$ values for styrenes being $-0.1$ to $-0.2$.

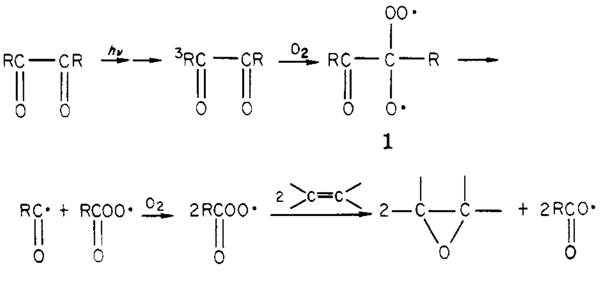
α-Diketone-sensitized photoepoxidation (eq 1) as reported by Bartlett et al.[1,2] is interesting in relation to a Schenck mechanism (eq 2)[3] in sensitized photooxidations.



(1)

$$\text{Sens} \xrightarrow{h\nu} {}^1\text{Sens} \longrightarrow {}^3\text{Sens} \xrightarrow{O_2} \dot{\text{Sens}}\text{-OO}\cdot \longrightarrow \text{Oxygenation} \qquad (2)$$

Recently we have suggested that the photoepoxidation proceeds via acylperoxy radicals $RCO_3\cdot$ generated by the photooxidation of α-diketones under oxygen.[4] That is, a reaction sequence as outlined in eq 3 is proposed from the facts that benzil is not a recycling sensitizer but photooxidized to benzoic or peroxybenzoic acid and phenyl benzoate in benzene, just as reported by Saltiel,[5] and that its photooxidation rate is not affected by the addition of olefins.



(3)

In order to ascertain whether acylperoxy radicals are the inermediary O-transfer species and to examine their reactivities, we planned to study the stoichiometry of the reaction together with relative reactivities for olefins and other substrates. Herein, we report that the photoepoxidation proceeds via acylperoxy radicals which behave as a strongly electrophilic radical toward olefins. The results are similar with those of the photoepoxidation with benzoin and oxygen,[6] suggesting the same O-transfer reagent.

## Results and Discussion

The photolysis of benzil is very slow under nitrogen but proceeds smoothly under oxygen.[4,5] The photooxidation rate was not changed by the addition of olefins and the resulting stoichiometry of epoxide:α-diketone consumed was mostly in the range of 1–2 but sometimes increased up to 3.[1a,4] The latter high ratio of 3 and the accompanying C–C cleavage of olefins could not be explained by the proposed pathway (eq 3).

**Epoxidation vs. C–C Cleavage.** The photoepoxidation with α-diketone and oxygen accompanies the C–C cleavage of olefins.[1,4] Interestingly, the epoxidation and C–C cleavage is found to be dependent on the olefin concentrations. For example, the following results were obtained

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(1) (a) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4193. (b) Bartlett, P. D.; Becherer, J. *Tetrahedron Lett.* **1978**, 2983.

(2) Recently, it has been stated that benzil is not always a sensitizer. (a) Bartlett, P. D.; Roof, A. A. M.; Shimizu, N. *J. Am. Chem. Soc.* **1982**, *104*, 3130. (b) Clennan, E. L.; Speth, D, R.; Bartlett, P. D. *J. Org. Chem.* **1983**, *48*, 1246.

(3) For example, (a) Schenck, G. O. *Angew. Chem.* **1957**, *69*, 579. (b) Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1.

(4) Sawaki, Y.; Foote, C. S. *J. Org. Chem.* **1983**, *48*, 4934.

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

(6) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 2049.

0022-3263/84/1949-3344$01.50/0

**Table I. Reciprocal Relationships between [C═C] and Product Yields for the Photooxidation in the Presence of α-Methylstyrene[a]**

| | | epoxidation | | | C–C cleavage | |
|---|---|---|---|---|---|---|
| carbonyl compds | reacting species | intercept[b] | $k_d/k_{add}$,[c] M | $k_d$,[d] $s^{-1}$ | intercept[b] | $k_d/k_{add}$,[c] M |
| benzil | $PhCO_3\cdot$ | 192% | $1.0 \times 10^{-3}$ | $1.8 \times 10^3$ | | |
| | $PhCO_2\cdot$ | | | | 167% | $32 \times 10^{-3}$ |
| biacetyl | $MeCO_3\cdot$ | 181% | $3.4 \times 10^{-3}$ | | | |
| | $MeOO\cdot$ | | | | 187% | $9 \times 10^{-3}$ |
| benzoin | $PhCO_3\cdot$ | 100% | $1.1 \times 10^{-3}$ | | | |
| | $PhCO_2\cdot$[e] | | | | 192% | $53 \times 10^{-3}$ |

[a] From the plots of 1/% yield vs. 1/[C═C] for the photooxidation of ~2 mM carbonyl compounds and 0.001–0.2 M α-methylstyrene in benzene (see Figure 1); irradiated at >320 nm for 0.5–2 h at 20 °C. Epoxide and acetophenone yields were determined by GLC. [b] % yields at the infinite olefin concentration from the intercepts. [c] Slopes of the reciprocal plots; see text for $k_d$ and $k_{add}$. [d] Calculated from $k_{add} = 1.8 \times 10^5$ $M^{-1}$ $s^{-1}$ for the addition of $PhCO_3\cdot$ in Table II. [e] $PhCO_2\cdot$ and $PhCH(OH)OO\cdot$.

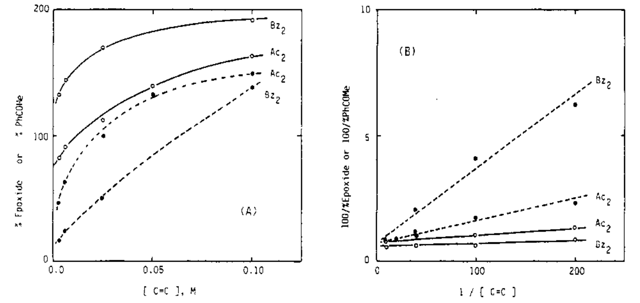
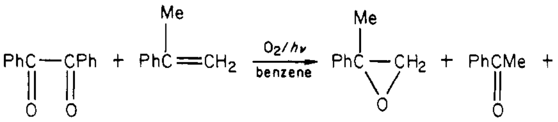


**Figure 1.** Plots (A) and reciprocal plots (B) of % epoxide (full line) and % PhCOMe (dotted line) vs. [C═C] for the photoepoxidation of α-diketone and oxygen (see footnote a in Table I for conditions); $Bz_2$ = benzil and $Ac_2$ = biacetyl.

for the oxidation of α-methylstyrene with 2 mM benzil irradiated at >320 nm in benzene under oxygen (mol % per mole of diketone consumed). The first two are



$$PhC(=O)-C(=O)Ph + PhC(Me){=}CH_2 \xrightarrow[\text{benzene}]{O_2/h\nu} PhC(Me)(-O-)CH_2 + PhC(=O)Me +$$

| | | | |
|---|---|---|---|
| 0.01 M | 170% | 24% | |
| 0.10 M | 192% | 138% | |

$$PhCO_2H + PhCO_2Ph + Ph_2 \quad (4)$$

| | | |
|---|---|---|
| 38% | 66% | 13% |
| 42% | 33% | 4% |

products from the olefin and the latter two from benzil and solvent benzene; products from allylic oxygenations were negligible for α- or β-methylstyrene which are not sensitive to singlet oxygen. Since the ratios of epoxidation and C–C cleavage change with olefin concentrations, it is apparent that the two reactions proceed via two different pathways. The sharp increase of acetophenone, a C–C cleavage product, by changing the olefin concentration from 0.01 o 0.10 M is compensated for by the decrease of phenyl benzoate and biphenyl. Since the latter two in eq 4 are the products from benzoyloxy and phenyl radicals in benzene,[5,7] it is apparent that the C–C cleavage is caused by benzoyloxy radical $PhCO_2\cdot$.

A similar dependence of product yields on the olefin concentration was also observed for the photoepoxidation with biacetyl (Figure 1). Acetophenone yields were more dependent on the concentrations of α-methylstyrene. From the intercepts of reciprocal plots, yields of epoxide and acetophenone at the infinite olefin concentration were 170–190% on the basis of α-diketone consumed (Table I). The 2:1 stoichiometry of epoxide:diketone was likewise ascertained for other olefins and α-diketones; i.e., epoxide yields of 191% ± 33% were obtained for the photoepoxidation of 0.1 M each of $Ph_2C{=}CMe_2$, $PhCH{=}CHMe$, and $PhMeC{=}CH_2$ with ~5 mM MeCOCOMe or PhCOCOMe. In the previous studies,[1a,4] most cases afforded the epoxide:diketone ratio of 2 but sometimes resulted in as high as 3. Probably, the latter high ratio is due to the accompanying coautoxidation of olefins and aldehyde R′CHO, which is produced by the C–C cleavage of olefins, according to eq 5. The epoxidation of olefins by the

$$R'CHO \xrightarrow{\text{radical}} R'\dot{C}{=}O \xrightarrow{O_2} R'CO_3\cdot \rightarrow \text{epoxidation} \quad (5)$$

coautoxidation with aldehydes is well-known.[8] The above explanation by eq 5 seems to be reasonable since the high ratios (i.e., >2) of epoxide:diketone were always observed only for olefins capable of producing aldehydes after C–C scissions and since the coautoxidation of added benzaldehyde was surely initiated under the photolysis conditions. Thus, it may be concluded that α-diketones do not act as a sensitizer according to eq 1 or 2, but olefins are epoxidized by acylperoxy radical $RCO_3\cdot$ as an intermediate in α-diketone photooxidation.

The slopes for the plots of 1/epoxide or 1/acetophenone vs. 1/[C═C] in Figure 1 differ significantly from each other, indicating intermediates of different reactivities. The similar dependence on olefin concentrations was also observed for the coautoxidation of benzaldehyde and α-methylstyrene (AIBN initiated at 60 °C); e.g., the yield of acetophenone increased from 25% to 47% by increasing the olefin concentration form 0.01 to 0.1 M. Likewise, the photolysis of benzoyl peroxide, which yields benzoyloxy radical in benzene, exhibited a similar dependence on the olefin concentration under oxygen.

These facts may well be understood by assuming the epoxidation with $RCO_3\cdot$ (eq 6) and the C–C scission via $RCO_2\cdot$ (eq 7). Since the epoxide yields are lowered only slightly by the decrease of olefin concentrations and are practically the same in air or under oxygen, the addition of $RCO_3\cdot$ to C═C and the following cyclization of adduct **2** to afford epoxide (eq 6) are fast and effective. The insensitivity of epoxide yields on the partial pressure of oxygen suggest that the cyclization is much faster than the addition of $O_2$ to **2**. This is in contrast to the polyperoxide forming autoxidation of olefins where epoxide formations, although as a minor reaction, are increased significantly by the decrease of oxygen pressure.[9] The effective cyclization of **2** reflects a potent departing ability of acyloxy radicals.[8]

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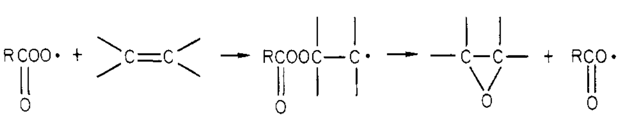
(7) (a) Nakata, T.; Tokumaru, K.; Simamura, O. *Tetrahedron Lett.* **1969**, 3303. (b) Saltiel, J.; Curtis, H. C. *J. Am. Chem. Soc.* **1971**, 91, 2056.

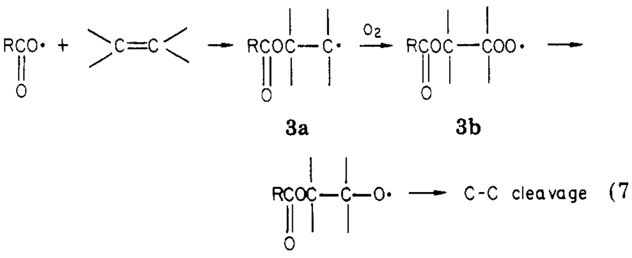
(8) (a) Van Sickle, D. E.; Mayo, F. R.; Gould, E. S.; Arluck, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 977. (b) Tsuchiya, F.; Ikawa, T. *Can. J. Chem.* **1969**, *47*, 3191. (c) Diaz, R. R.; Selby, K.; Waddigton, D. J. *J. Chem. Soc., Perkin Trans. 2* **1975**, *758*; **1977**, 360.

(9) Mayo, F. R. *Acc. Chem. Res.* **1968**, *1*, 193.



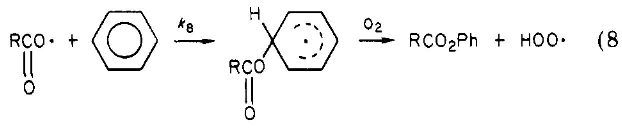
2

(6)



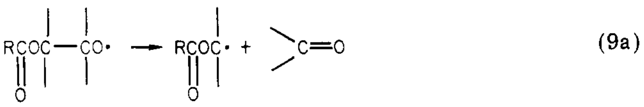
3a 3b

3c

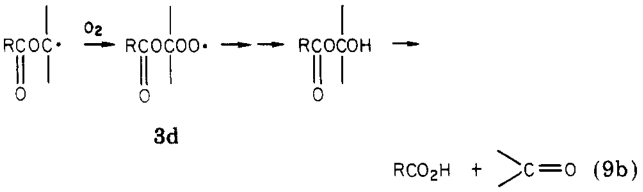


4

On the other hand, the C–C cleavage of olefins proceed via the addition of benzoyloxy radical (R = Ph, eq 7). The addition of $PhCO_2\cdot$ to olefins is not so fast and hence the decrease of olefin concentrations resulted in the shift of major reaction from eq 7 to eq 8. Similar dependences on olefin concentrations for the C–C cleavage obtained in the coautoxidation with benzaldehyde or the photooxidation with benzoyl peroxide strongly suggest that the C–C cleavages are equally caused by benzoyloxy radical (eq 7). The cleavage proceeds probably via the β-scissions of alkoxy radical **3c**, since β-scission of alkoxy radicals (eq 9a) are well-known.[10a] Although a detailed mechanism cannot be given,[10b] a likely one is shown in eq 9b.



3c



3d

For the case of biacetyl, the C–C scission of olefins is probably via MeOO· formed from Me· and $O_2$ (i.e., MeOO· in place of $RCO_2\cdot$, eq 7), since the decarboxylation of acetoxy radical $MeCO_2\cdot$ is vary fast.[10c] In fact, the dependence of C–C cleavage on [C=C] is quite different from the benzil case (Figure 1), suggesting a different species for the cleavage. The addition of MeOO· to C=C is competitive to the known disproportionation to afford MeCHO and MeOH.[11] The assumption of C–C cleavage caused by peroxy radical is in accordance with the results of benzoin photooxidation (Table I); 1 mol of benzoin resulted in 1 mol of epoxide and 2 equiv of C–C cleavage. In this case, the C–C cleavage is caused both by $PhCO_2\cdot$ and peroxy radical PhCH(OH)OO· which is formed according to eq 10.[6]

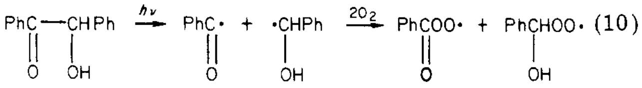


Table II. Rate Constant for the Addition of $RCO_3\bullet$ to Olefins at 20 °C

| radical | olefin | $k_{add}/k_{abstr}$[a] | $k_{add}$,[b] $M^{-1}\ s^{-1}$ |
|---|---|---|---|
| $PhCO_3\cdot$ | $PhMeC{=}CH_2$ | 5.48 | $1.81 \times 10^5$ |
| | $Ph_2C{=}CMe_2$ | 4.04 | $1.33 \times 10^5$ |
| t-BuOO· | $PhMeC{=}CH_2$ | | 2.85[c] |
| ROO·[d] | $PhMeC{=}CH_2$ | | $10$[d] |

[a] Rate ratios (see eq 11 for notations) were obtained competitively from the initial stage (i.e., within 15% conversion) in the photooxidation of 5 mM diketone in the presence of 5–10 mM each of PhCHO and olefin in benzene. The decrease of PhCHO and epoxide yields were determined by GLC. [b] Calculated by using the reported $k_{abstr}$ value of 33 000 $M^{-1}\ s^{-1}$ at 30 °C. Korcek, S.; Chenier, J. H. B.; Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1972**, *50*, 2285. [c] At 30 °C. Reference 19. [d] Rate constant for the addition of polyperoxide radical at 40 °C. Howard, J. A. Reference 10a, p 28.

All of the above facts suggest that the C–C cleavage is caused by $RCO_2\cdot$ or ROO·. The alternative C–C scission via a polyperoxide formation is of no importance under these low concentrations of olefins (i.e., up to 0.2 M), since the plots of 1/acetophenone vs. 1/[C=C] are linear and diketones affect just 2 equiv of C–C cleavage of olefins.

**Rate Constants of the Addition to Olefins.** The hydrogen abstraction with acylperoxy radical $RCO_3\cdot$ is known to be about 1000-fold faster than alkylperoxy radical ROO·.[12] But the rate constant of its addition to olefins is not known in solutions,[13a] so the rate constants were determined as follows. Since the cyclization of adduct **2** to epoxide is fast and effective (eq 6), the rate constant for addition $k_{add}$ (eq 11a) may be obtained in competition with the H abstraction from benzaldehyde (eq 11b). The

$$RCO_3\cdot + {>}C{=}C{<} \xrightarrow{k_{add}} \mathbf{2} \xrightarrow[\text{fast}]{} \text{epoxide} \quad (11a)$$

$$RCO_3\cdot + PhCHO \xrightarrow{k_{abstr}} RCO_3H + Ph\dot{C}{=}O \quad (11b)$$

addition to C=C was estimated from the epoxide yield and the H abstraction from the decrease of benzaldehyde.[14a] Since the $k_{add}/k_{abstr}$ ratios were not affected by the addition of dimethyl sulfoxide, a more reactive substrate toward peroxy acid, the effect of $RCO_3H$ formed was negligibly

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(10) (a) Kochi, J. K. "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, p 677. (b) Tracer experiments with $^{16}O_2$–$^{18}O_2$ may clarify the fate of **3b** or **3d**, since the scrambling of $O_2$ gas according to 2ROO· → 2RO· + $O_2$ is known. But such a scrambling was not significant.[4] A tentative explanation is that the life times of peroxy radical **3b** and **3d** are too short to affect such a bimolecular reaction under the reaction conditions. (c) Kochi, J. K. Reference 10a, p 698.

(11) (a) Clinton, N. A.; Kenley, R. A.; Traylor, T. G. *J. Am. Chem. Soc.* **1975**, *97*, 3746, 3752, 3757. (b) Kenley, R. A.; Traylor, T. G. *Ibid.* **1975**, *97*, 4700.

(12) (a) Niki, E.; Ukegawa, K.; Kamiya, Y. *Kogyo Kagaku Zasshi* **1971**, *74*, 1354. (b) Haward, J. A. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 28.

(13) (a) The rates of addition of $RCO_3\cdot$ to olefins in vapor phase have been determined for the coautoxidation of aldehydes and olefins.[8c,13b] In solutions, the relative rates for the addition to and allylic hydrogen abstraction of cyclohexene was reported; the reported ratio of $k_{add}/k_{abstr}$ with $RCO_3\cdot$ was 0.67 in the coautoxidation with valeraldehyde at 60 °C.[13c] But, the present photooxidation of 0.01 M cyclohexene with benzil and oxygen resulted in 216% epoxide and 26% allylic oxygenation (% based on benzil); the resulting high ratio (i.e., 8.3) of $k_{add}/k_{abstr}$ reflects the fast addition rate ($k_{add}$) of $RCO_3\cdot$. Again the ratios were dependent on the concentrations of cyclohexene. The ratio decreased to 2.1 with 0.1 M cyclohexene (i.e., 268% epoxide and 125% allylic oxygenation); thus the decrease of the ratio is based on the increase of allylic oxygenation initiated by $PhCO_2\cdot$. (b) Selby, K.; Waddington, D. J. *J. Chem. Soc. Perkin Trans. 2* **1980**, 65. (c) Simmons, K. E.; Van Sickle, D. E. *J. Am. Chem. Soc.* **1973**, *95*, 7759.

(14) (a) The resulting benzoyl radical (eq 11b) and oxygen yields another molecule of $PhCO_3\cdot$, which in turn reacts either via eq 11a or 11b. Thus, the yield of epoxide and the decrease of benzaldehyde reflect the $k_{add}/k_{abstr}$ ratio by benzoylperoxy radical. (b) Calculated from $k_{add}$ = 3 × $10^4$ $M^{-1}\ s^{-1}$ at 80 °C and $E_a$ = 7 kcal/mol. Berington, J. C.; Toole, J. *J. Polym. Sci.* **1958**, *28*, 415.

**Table III. Substituent Effect on the Addition to Styrenes**[a]

| substituent in styrene | photoepoxidation | | C–C cleavage[b] | | addition of $t$-BuOO·[c] | epoxidation with PBA[d] |
|---|---|---|---|---|---|---|
| | $PhCO_3$· | $MeCO_3$· | $PhCO_2$· | MeOO· | | |
| | | | Relative Rates[a] | | | |
| $p$-MeO | 5.20 | 5.80 | 1.48 | 1.09 | 1.83 | 4.58 |
| $p$-Me | 1.80 | 1.31 | 0.91 | 1.13 | 1.65 | 1.36 |
| H | (1.00) | (1.00) | (1.00) | (1.00) | (1.00) | (1.00) |
| $p$-Cl | 0.61 | 0.72 | 0.86 | 0.84 | 0.92 | 0.69 |
| $m$-Cl | 0.38 | 0.33 | 0.82 | 1.06 | 0.92 | 0.31 |
| | | | $\rho$ Value | | | |
| $\rho$ ($\sigma^+$) | –0.99 | –1.02 | –0.20 | –0.08 | –0.30 | –0.96 |
| ($\gamma$)[e] | (0.997) | (0.984) | (0.87) | (0.72) | (0.915) | (0.987) |

[a] Relative rates were determined competitively from the initial photooxidation (i.e., <15% conversion) of 2 mM benzil or biacetyl in the presence of 0.02–0.1 M styrenes under oxygen in benzene at 20 °C. Products, styrene oxides, and benzaldehydes were determined by GLC, affording the relative reactivities as an average of two or three times determinations. [b] Benzaldehyde formation. [c] Reference 10a, p 28. [d] From rate measurement of the epoxidation with perbenzoic acid in benzene at 25 °C. [e] Correlation coefficient.

small. The absolute values of $k_{add}$ may be obtained from $k_{add}/k_{abstr}$ ratios and the reported $k_{abstr}$ value (Table II). Thus, the resulting $k_{add}$ values are $\sim 10^5$ $M^{-1}/s^{-1}$, which is higher by $10^5$-fold compared to the corresponding $k_{add}$ value of $t$-BuOO·. Consequently, the effective epoxidation with $RCO_3$· is due to the very fast addition to olefins.

In the absence of aldehyde, the effect of olefin concentrations may be analyzed by the following:

$$RCO_3\cdot + \ >C{=}C< \ \xrightarrow{k_{add}} \text{epoxidation} \qquad (12a)$$

$$RCO_3\cdot \xrightarrow{k_d} \text{other reactions} \qquad (12b)$$

Then

$$\frac{\text{epoxidation}}{\text{other reactions}} = \frac{k_{add}[RCO_3\cdot][C{=}C]}{k_d[RCO_3\cdot]} = \frac{k_{add}}{k_d}[C{=}C] \qquad (13a)$$

or

$$\frac{100}{\%\ \text{epoxide}} \propto \frac{k_d}{k_{add}}\left(\frac{1}{[C{=}C]}\right) \qquad (13b)$$

That is, the slopes for plots of 1/% epoxide vs. 1/[C=C] give the values of $k_d/k_{add}$. The slope in Figure 1 and the $k_{add}$ value in Table II afford $k_d = 2 \times 10^2$ $s^{-1}$ for $PhCO_3$· in benzene at 20 °C (Table I). In other words, the life time (i.e., $1/k_d$) is $5 \times 10^{-3}$ s for $PhCO_3$·. The detailed mechanism for the decomposition of $RCO_3$· (eq 12b) is complex and involves many reactions.[11] The fact that the slope or $k_d/k_{add}$ for the photoepoxidation with benzoin is identical with the case of benzil (Table I) substantiates the same epoxidizing species, i.e., $RCO_3$·, for the two reactions.

A quite similar analysis is possible for the C–C cleavage of olefin only by substituting $RCO_2$· or ROO· in place of $RCO_3$· in eq 12. The resulting $k_d/k_{add}$ values are listed in the last column in Table I. The rate for addition of benzoyloxy radical to styrene is $k_{add} = 5.4 \times 10^3$ $M^{-1}$ $s^{-1}$ as calculated from the reported data.[14b] The $k_{add}$ value for $\alpha$-methylstyrene is then estimated to be $1.5 \times 10^4$ $M^{-1}$ $s^{-1}$ from the rate ratio of 2.8 for $\alpha$-methylstyrene/styrene in Table III. Thus, $k_d$ for $PhCO_2$· is calculated to be 480 $s^{-1}$ from the $k_{add}$ value and $k_d/k_{add} = 3.2 \times 10^{-2}$ M in Table I. Since the major reaction of $PhCO_2$· in aerated benzene is the formation of $PhCO_2Ph$ (eq 8), the calculation results in $k_8 = 480/11 = 44$ $M^{-1}$ $s^{-1}$, benzene ring of 11 M concentration. The $k_8$ value is of the same magnitude with the reported one (35 $M^{-1}$ $s^{-1}$) estimated from product ratios from the thermal decomposition of benzoyl peroxide in benzene at 80 °C.[15] The coincidence indicates the validity of the above analysis for the C–C cleavage.

**Relative Reactivities of Olefins and Other Substrates.** As shown in Table III, acylperoxy radicals $RCO_3$· are found to be a strongly electrophilic oxidant toward olefins like molecular peracids. That is, the substituent effect for the photoepoxidation of styrenes shows relatively large negative $\rho$ values (vs. $\sigma^+$); i.e., $\rho = -0.99$ and $-1.02$ for $PhCO_3$· and $MeCO_3$·, respectively (first and second columns in Table III), which are of the same magnitude with the epoxidation with perbenzoic acid ($\rho = -0.96$, last column). In Table IV are listed the relative rates of various olefins for epoxidations. The radical epoxidation with $RCO_3$· is roughly parallel to peracid epoxidations, but the additivity of methyl substitution is not always operative for the case of $RCO_3$·. For example, there do not appear large differences between relative rates of mono-, di-, and trimethylstyrenes. This is in contrast to the epoxidation with molecular peracids where one methyl group accelerates the rate by 5–10 folds (Table IV). Singlet oxygen is also an electrophilic reagent;[16] the accelerating effect by the methyl group is significantly large for aliphatic olefins (Table IV). Interestingly, the $^1O_2$ reactions of substituted $\alpha,\beta,\beta$-trimethylstyrenes afforded $\rho = -0.93$ (vs. $\sigma$),[16b] which is of the same magnitude as the epoxidation of styrenes with $RCO_3$· and $RCO_3H$.

Another characteristic point in Table IV is the fact that acylperoxy radicals are not reactive toward sulfides, sulfoxides, and pyridine, which are highly reactive toward peracids. Thus, $RCO_3$· may be a selective epoxidzing agent for double bonds in molecules possessing such groups. The stereochemistries of resulting epoxides are predominantly trans; 100% trans from stilbenes and 80% trans from 2-octenes. These stereochemistries were not altered by the temperature change from 40 to –70 °C.

The relative reactivities of olefins and the stereochemistries of epoxides with diketones are practically the same with the photoepoxidation with benzoin (Table IV). The photoepoxidation of substituted styrenes with benzoin affords $\rho = -1.14$ ($\sigma^+$, $\gamma = 0.988$), which is very close to the results with $\alpha$-diketones in Table III. Again these facts suggest the common inermediate, i.e., $RCO_3$·, between the photoepoxidation with $\alpha$-diketones and benzoin.

**Epoxidation Mechanism.** As described above, acylperoxy radical epoxidize double bonds selectively and are not reactive toward sulfides, sulfoxide, and pyridine. This is due to the inferior abilities of the radical to add to these substrates. Since $RCO_3$· affords 1 equiv of epoxide and the epoxide yields are not affected by oxygen pressure, the cyclization of adduct radical **5** is much faster than the addition of $O_2$ to **5**.[17a] Moreover, in the photoepoxidation

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(15) DeTar, D. F. *J. Am. Chem. Soc.* **1967**, *89*, 4058.

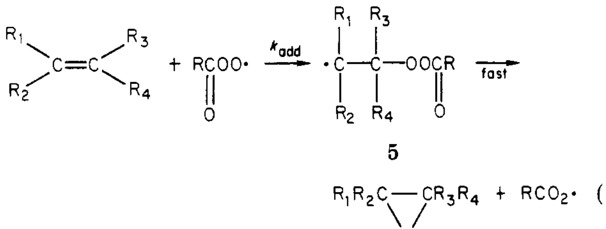
(16) (a) Foote, C. S. *Acc. Chem. Res.* **1968**, *1*, 104. (b) Foote, C. S.; Denny, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5162.

**Table IV. Relative Rates for the Photoepoxidation and Oxidation with α-Diketone and Oxygen in Comparison with Other Related Reactions**[a]

| substrate | photooxidation: benzil[a] ($PhCO_3\cdot$) | photooxidation: biacetyl[a] ($MeCO_3\cdot$) | photooxidation: benzoin[b] ($PhCO_3\cdot$) | $^1O_2$[c] | $PhCO_3H$[d] | *t*-BuOO·[e] | Me·[f] |
|---|---|---|---|---|---|---|---|
| | | | Aromatic Olefins | | | | |
| $PhCH{=}CH_2$ | 0.135 | 0.132 | 0.123 | | 0.140 | 0.46 | 0.86 |
| $PhMeC{=}CH_2$ | (1.00) | (1.00) | (1.00) | | (1.00) | (1.00) | (1.00) |
| *trans*-$PhCH{=}CHMe$ | 1.94 | 1.80 | 1.95 | | 1.59 | 0.88 | 0.10 |
| $PhCH{=}CMe_2$ | 0.64 | | 0.92 | | 3.37 | | |
| $PhMeC{=}CMe_2$ | 1.22 | 1.32 | 1.86 | 740[g] | 20.2 | | 0.022 |
| *trans*-$PhCH{=}CHPh$ | ~0.6[h] | 0.64[h] | 0.76[h] | | 0.064[h] | 0.16 | 0.11 |
| (cis/trans)[i] | (10.2)[i] | (2.1)[i] | (0.15)[i] | | (0.00)[i] | | |
| *trans*-$PhCH{=}CHCOMe$ | | 0.088[h] | | | 0.055[h] | | |
| | | | Aliphatic Olefins | | | | |
| 1-octene | | 0.006 | 0.010 | 0.16 | 0.13 | | 0.02 |
| *cis*-2-octene | | 0.09[j] | 0.08[k] | 2.2[l] | 2.73 | | 0.04 |
| cyclohexene | | 0.09 | 0.14 | (1.00) | 2.79 | | |
| 1-methylcyclohexene | | 0.96 | 1.04 | 22 | 13.6 | | |
| 1,2-dimethylcyclohexene | | 1.69 | ~2 | 1900 | 63.2 | | |
| $CH_2{=}CHCN$ | | <0.001 | | | <0.001 | 0.004 | 1.66 |
| $CH_2{=}CHCO_2Et$ | | <0.001 | | | <0.001 | 0.007 | 1.11 |
| $CH_2{=}CHOCOMe$ | | 0.001 | | | 0.009 | 0.007 | 0.04 |
| | | | Other Substrates | | | | |
| $Ph_2S$ | | <0.01 | <0.01 | | 1900 | | |
| $Ph_2SO$ | | <0.01 | <0.01 | | 23 | | |
| $Me_2SO$ | | <0.1 | <0.1 | | 64 | | |
| pyridine | | <0.01 | <0.01 | | 1.3 | | |

[a] Relative rates were determined competitively for the photooxidation of 2 mM diketone in the presence of 0.05–1 M concentrations of two olefins in benzene at 20 °C. Yields were determined by GLC. [b] Reaction of benzoin in benzene–acetone (3:1). Reference 6. [c] Gollnick, K.; Kuhn, H. J. In "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Ed.; Academic Press: New York, 1979; p 289. [d] From rate measurements for the oxidation with perbenzoic acid in benzene at 25 °C. [e] Addition of *t*-BuOO· to olefins. Reference 19. [f] Addition of Me· to olefins. Reference 21. [g] Substituent effect: $\rho = -0.93$. Reference 16b. [h] *trans*-Epoxide. [i] Ratios of cis/trans for the recovered stilbene. [j] Epoxide: cis/trans = 80/20. [k] Epoxide: cis/trans = 79/21. [l] Value of *cis*-2-butene.

of *cis*-stilbene with biacetyl and oxygen (irradiated at over 320 nm) the recovered olefin after 60% conversion was unchanged cis only;[17b] i.e., the reverse reaction of **5** to regenerate olefins was not appreciable. Hence, the rate-determining step is the addition of $RCO_3\cdot$ to C=C (eq 14).

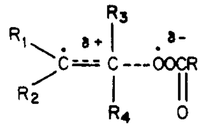


**5**

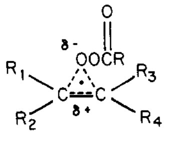
(14)

The trans stereochemistry of resulting epoxides is understood by the free rotation of the C–C bond in adduct radical **5**. Since the stereochemistries of epoxides were not altered by the stereochemistries of starting olefins, solvents, or reaction temperatures (from 40 to −78 °C), equilibriums between *trans*-**5** and *cis*-**5** are established and the resulting cis/trans ratio reflects a energy difference between the two rotational forms of **5**.[6]

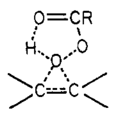
The substituent effect of $\rho \simeq -1$ ($\sigma^+$) for the photoepoxidation of styrenes indicated a polar transition state **6** involving electrophilic attack of $RCO_3\cdot$. The $10^5$-fold faster addition of $RCO_3\cdot$ compared with ROO· suggests the importance of electrophilicity in the radical addition of peroxy radicals and supports the polar transition state **6**. Substituents such as Ph and Me groups are necessary to stabilize the developing carbon radical in **6**. But the additivity of methyl group is not always operative, which is probably due to the following two factors. One is the stability effect of substituents in the adduct radical **5**; i.e., the stabilization by the 1-substituents, $R_1$ and $R_2$, is apparently large in comparison to the 2-ones, $R_3$ and $R_4$. This will lead to a break in the additivity of methyl substitutions. The second factor is a steric retardation by substituents on the carbon attacked, i.e., $R_3$ and $R_4$, which will also cancell out the accerelating polar effect of a methyl group. In contrast, such a steric retardation is not significant in the peracid epoxidations where the peroxidic oxygen attacks symmetrically π-electrons of olefins as shown in **8**. A similar symmetrical transition state **7** for the $RCO_3\cdot$ addition is not appropriate in view of the observed leveling effect of methyl substitutions.



**6**



**7**



**8**

Additions of radicals to olefins are mostly correlated with stabilities of resulting adduct radicals,[18,19] but somtimes steric[20a] or polar effects[20b] dominate. Methyl radical behaves as a weakly nucleophilic radical; the addition to styrenes is rather retarded by methyl substituents,[21] and the characteristic point of this radical is its high reactivity toward ethylenic monomers with electron-attracting groups (see Table IV). Polar effects on the radical additions to C=C are known in many cases of radical polymeriza-

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(17) (a) It is well-known that the addition of $O_2$ to carbon-centered radicals is almost of diffusion-controlled rate. (b) Energy transfer from $^3$biacetyl to stilbenes was not so effective in contrast to the benzil case.

(18) (a) Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; p 97. (b) Walling, C. *J. Phys. Chem.* **1960**, *64*, 166.

(19) Howard, J. A. *Can. J. Chem.* **1972**, *50*, 2298.

(20) (a) Sakurai, H.; Hosomi, A.; Kumada, M. *J. Org. Chem.* **1969**, *34*, 1764. (b) Tedder, J. M.; Walton, J. C. *Tetrahedron* **1980**, *36*, 701.

(21) (a) Leavitt, F.; Levy, M.; Szwarc, M.; Stannett, V. *J. Am. Chem. Soc.* **1955**, *77*, 5493. (b) Szwarc, M. J. *Polym. Sci.* **1955**, *16*, 367. (c) Carrock, F.; Szwarc, M. *J. Am. Chem. Soc.* **1959**, *81*, 4138.

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tions,[18a] additions of thiyl radicals to styrenes ($\rho \sim -0.4$ vs. $\sigma^+$),[22] and additions of $Cl_3C\cdot$ to styrenes ($\rho = -0.42$ vs. $\sigma^+$)[23] and aliphatic olefins ($\rho^* = -0.2$ to $-0.4$ vs. $\sigma^0$ or $\sigma^*$).[24] As shown in Table III, the substituent effects for additions of $PhCO_2\cdot$, $MeOO\cdot$, and $t\text{-}BuOO\cdot$ to styrenes also resulted in small negative $\rho$ values ($\rho = -0.1$ to $-0.3$ vs. $\sigma^+$) with poor correlations. That is, these oxy radicals add to styrenes as a weak electrophile. In contrast, acylperoxy radicals afford large negative $\rho$ values ($\rho = -1$ vs. $\sigma^+$), indicating the importance of polar effects in the radical additions to olefins.[25] The coincidence of $\rho$ values between the reactions of $RCO_3\cdot$, $RCO_3H$, and $^1O_2$ is interesting. It is also interesting to recall that similar polar effects (i.e., $\rho = -0.3$ to $-1.1$ vs. $\sigma^+$) are known in benzylic hydrogen abstractions[27] where benzyl radicals are being formed.

In conclusion, $\alpha$-diketones are photooxidized to 2 equiv of acylperoxy radical, which add to olefins $10^5$-fold faster than alkylperoxy radicals and lead to effective epoxidations. Selective epoxidation of double bonds is possible since $RCO_3\cdot$ is not reactive to sulfides, sulfoxides, and pyridine. The photoepoxidation proceeds at low temperature or in the presence of pyridine; then is application to acid-sensitive or unstable epoxides may be possible.[26] The accompanying C–C cleavage of olefins proceeds via the addition of $RCO_2\cdot$ or $ROO\cdot$.

## Experimental Section

GLC analyses were performed with a Yanagimoto G180 gas chromatograph using two different columns: PEG 20M, 20% on Chromosorb WAW; Silicon OV-17, 5% on Shimalite W. $^1H$ NMR spectra were recorded with a Hitachi R24B spectrometer.

**Materials.** Ring-substituted styrenes,[28] $\beta,\beta$-dimethylstyrene,[29] $\alpha,\beta,\beta$-trimethylstyrene,[28] and 1,2-dimethylcyclohexene[30] were described previously. Other olefins were of commercial sources. Authentic epoxides were obtained by the epoxidations of olefins with perbenzoic acid.

**Typical Photoepoxidation.** General procedures were noted previously.[4] A 4 mL benzene solution of 2 mM benzil and 0.1 M $\alpha$-methylstyrene in a Pyrex tube was irradiated under oxygen at over 320 nm with a 300-W medium-pressure Hg lamp for 1 h at 20 °C (water bath). As a filter solution, 5% aqueous sodium nitrate was used. GLC analysis showed 192% $\alpha$-methylstyrene oxide, 138% acetophenone, 33% phenyl benzoate, 4% biphenyl, and 42% benzoic acid. % yields are mole % per mole of $\alpha$-diketone consumed and benzoic acid was determined after the methylation with diazo methane. Acetophenone was also identified by $NaBH_4$ reduction to $\alpha$-phenylethyl alcohol.

Relative rates of the olefin photoepoxidation were determined competitively by using 2 mM $\alpha$-diketone and 0.02–1 M olefins. The relative yields of epoxides were determined by GLC analyses, affording the relative reactivities as listed in Tables III and IV.

Formaldehyde and methanol were detected for the photooxidation of biacetyl, but the reliable determination of their yields could not be attained by GLC analysis.

**Registry No.** $PhCH{=}CH_2$, 100-42-5; $PhMeC{=}CH_2$, 98-83-9; *trans*-$PhCH{=}CHMe$, 873-66-5; $PhCH{=}CMe_2$, 768-49-0; $PhMeC{=}CMe_2$, 769-57-3; *trans*-$PhCH{=}CHPh$, 103-30-0; *trans*-$PhCH{=}CHCOMe$, 1896-62-4; $CH_2{=}CHCN$, 107-13-1; $CH_2{=}CHCO_2Et$, 140-88-5; $CH_2{=}CHOCOMe$, 108-05-4; $Ph_2S$, 139-66-2; $Ph_2SO$, 945-51-7; $Me_2SO$, 67-68-5; $Ph_2C{=}CMe_2$, 781-33-9; $PhCO_3\cdot$, 35683-46-6; $PhCO_2\cdot$, 766-76-7; $MeCO_3\cdot$, 36709-10-1; $MeOO\cdot$, 2143-58-0; 1-octene, 111-66-0; *cis*-2-octene, 7642-04-8; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; 1,2-dimethylcyclohexene, 1674-10-8; pyridine, 110-86-1; *p*-methoxystyrene, 637-69-4; *p*-methylstyrene, 622-97-9; *p*-chlorostyrene, 1073-67-2; *m*-chlorostyrene, 2039-85-2; benzil, 134-81-6; biacetyl, 431-03-8; benzoin, 119-53-9.

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(22) (a) Cadogan, J. I. G.; Sadler, I. H. *J. Chem. Soc. B* **1966**, 1191. (b) Church, D. F.; Gleicher, G. J. *J. Org. Chem.* **1975**, *40*, 536. (c) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1982**, *104*, 1701.

(23) Sakurai, H.; Hayashi, S.; Hosomi, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1945.

(24) Martin, M. M.; Gleicher, G. J. *J. Am. Chem. Soc.* **1964**, *86*, 233, 238, 242.

(25) (a) The observed preference of the addition of $RCO_3\cdot$ to C=C over H abstraction for cyclohexene has been explained by its highly electrophilic character.[13c,25b] (b) Zaikov, G. E.; Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1969**, *47*, 3017.

(26) Such applications have been reported. (a) Malacria, M.; Goré, *J. Org. Chem.* **1979**, *44*, 885. (b) Büchi, G.; Fowler, K. W.; Nadzan, A. M. *J. Am. Chem. Soc.* **1982**, *104*, 544.

(27) Russell, G. A. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 293.

(28) Ogata, Y.; Sawaki, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 194.

(29) Ogata, Y.; Sawaki, Y.; Shimizu, H. *J. Org. Chem.* **1978**, *43*, 1760.

(30) Sawaki, Y.; Ogata, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 793.

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# Photoreduction of Triplet Thioxanthone by Amines: Charge Transfer Generates Radicals That Initiate Polymerization of Olefins

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Thioxanthone triplet is photoreduced by amines via a charge-transfer or exciplex intermediate to thioxanthyl ketyl radical. This ion pair can be observed by nanosecond laser spectroscopy in polar solvents with easily oxidized dimethylaniline as reductant. The intermediacy of this species in benzene was indicated by the correlation of triplet quenching rates with amine ionization potential and by the absence of a significant isotope effect in triplet quenching by *tert*-butylamine-$d_2$. In contrast, tri-*n*-butylstannane reacts more rapidly than its ionization potential would dictate and exhibits a larger isotope effect. Addition of methyl methacrylate does not significantly alter the rates of decay for the ion pair of ketyl radical. Product studies show that the aminomethyl radical $PhN(CH_3)CH_2\cdot$ is the principal initiator of olefin polymerization.

## Introduction

Mixtures of aromatic ketones with amines have acquired importance as photoinitiators of olefin polymerization.[1,2] It has normally been assumed that reduction of the excited state of the ketone by amine results in radicals which

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(1) Amirzadeh, G.; Schnabel, W. *Makromol. Chem.* **1981**, *182*, 2821.

(2) Davidson, R. S.; Goodin, J. W. *Eur. Polym. J.* **1982**, *18*, 597; Sandner, M. R.; Osborn, C. L.; Trecker, D. J. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *108* 3173.

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