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Photoepoxidation of Olefins with Benzoins and Oxygen. Epoxidation with Acylperoxy Radical[1]

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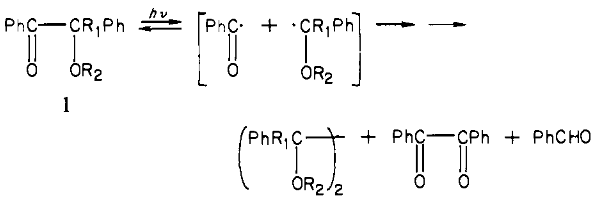
Abstract: Benzoin was photooxidized to yield benzaldehyde, peroxybenzoic acid, and hydrogen peroxide. The addition of styrenes to this photooxidation system afforded high yields of epoxides together with some C–C cleaved products. While the C–C cleavage products increased with increasing concentration of olefins, the epoxide yield was constant and nearly quantitative; the stoichiometry at the infinite olefin concentration was such that 1 mol of benzoin produces 1 mol of epoxide and 2 equiv of C–C cleaved product. The effect of olefin concentration is analyzed to show that the C–C cleavage is ascribed to benzoyloxy and α-hydroperoxy radicals, PhCH(OH)OO·. The photoepoxidation proceeds by way of acylperoxy radical, affording predominantly *trans*-epoxide (e.g., 100% *trans*-epoxide from stilbenes and 77% *trans*-epoxide from 2-octenes). The relative reactivities of olefins differ significantly from those with molecular peroxyacid; the additivity of methyl substitution does not hold, and aliphatic olefins are less reactive than the corresponding aromatic ones. The relative reactivities of photoepoxidation are explained on the basis of the stability of a resulting adduct radical between the acylperoxy radical and olefin. The peroxy radical is not reactive toward pyridine or sulfoxides. The photoepoxidation with benzoin ethers proceeds similarly except the formation of esters, which is explained by the β-scission or the 1,2-phenyl migration of intermediary α-alkoxy radical. These results are discussed in relation to practical photopolymerizations and to an origin of photoxic substances.

Benzoin and its derivatives are widely used as photoinitiators for polymerizations,[2] especially in the coatings and printings industries.[3] Although their photolysis has been extensively studied under deaerated conditions,[4] studies on the photooxidation under oxygen are few.[5] We are interested in the mechanism of photooxidation of α-acyloins in the presence of olefins (i) as a model of monooxygenase enzymes,[6] (ii) in relation to the photopolymerization of coatings and printings, and (iii) as an origin for the formation of phototoxic substances.

Oxygen atom transfer or oxenoid intermediates are interesting as a model of monooxygenase enzymes,[6] among them being carbonyl oxides,[7] pyridine *N*-oxide,[8] and unstable cyclic peroxides.[9,10] Contrary to Bartlett's original suggestion,[11] the photoepoxidation of olefins with an α-diketone and oxygen proceeds via the acylperoxy radical as the effective epoxidizing species,[12] since α-diketones are not a catalyst but a reactant consumed and converted to peroxyacid, acid, etc. We report herein that the photooxidation of benzoins produces acylperoxy radicals which can transfer an oxygen atom effectively and selectively to olefins affording predominantly *trans*-epoxides. The mechanism of the accompanying C–C cleavage of the olefin is also discussed as is its relationship to practical photopolymerizations and the origin of the photodynamic effect.

Results and Discussion

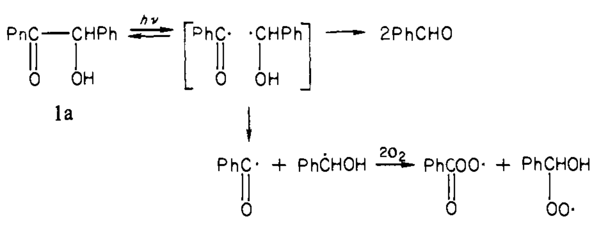
Photolysis of benzoins under deaerated conditions is known to produce acyl and α-oxy radicals, which ultimately lead to pinacols, benzil, and benzaldehyde.[4a,c,f,j] The formation of the radical pair



$$\mathrm{PhC(=O){-}CR_1Ph(OR_2)}\ (\mathbf{1}) \xrightleftharpoons{h\nu} \left[\mathrm{PhC^{\cdot}(=O)} + \mathrm{{\cdot}CR_1Ph(OR_2)}\right] \longrightarrow \longrightarrow \left(\mathrm{PhR_1C(OR_2)}{-}\right)_2 + \mathrm{PhC(=O){-}C(=O)Ph} + \mathrm{PhCHO} \quad (1)$$

was well established by CIDNP study,[4g,13] and both radicals were trapped by a spin-trapping ESR method.[14] Acetoin was also reported to exhibit CIDNP spectra,[15] products being acetaldehyde, methane, and carbon monoxide.[16]

Photooxidation of Benzoin. The photooxidation of benzoin **1a** under oxygen was effective (i.e., Φ = ca. 0.2) and afforded benzaldehyde, perbenzoic acid, and hydrogen peroxide (Table I). The high-yield formation of benzaldehyde might indicate an in-cage H atom transfer from α-hydroxybenzyl to the benzoyl radical (eq 2a). However, the concurrent formation of relatively high yields



$$\mathrm{PnC(=O){-}CHPh(OH)}\ (\mathbf{1a}) \xrightleftharpoons{h\nu} \left[\mathrm{PhC^{\cdot}(=O)}\ \ \mathrm{{\cdot}CHPh(OH)}\right] \longrightarrow 2\mathrm{PhCHO} \quad (2a)$$

$$\downarrow$$

$$\mathrm{PhC^{\cdot}(=O)} + \mathrm{Ph\dot{C}HOH} \xrightarrow{2\mathrm{O_2}} \mathrm{PhC(=O)OO^{\cdot}} + \mathrm{PhCH(OH)OO^{\cdot}} \quad (2b)$$

of peroxybenzoic acid and H_2O_2 suggests the formation of the two free radicals which are effectively trapped by oxygen (eq 2b). This scheme is consistent with no formation of benzaldehyde from α-phenylbenzoin (**1b**).

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Table I. Photooxidation of Benzoins under Oxygen[a]

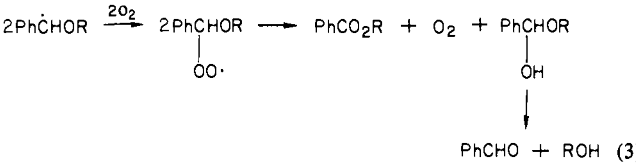
	$PhC(=O)-CR_1Ph(OR_2)$					products,[c] %				
	R_1	R_2	additive	solvent	Φ[b]	PhR_1-C=O	$PhCO_3$-H	H_2-O_2	$PhCO_2$-Ph	others[d]
1a	H	H		MeOH	0.16	100	60	95		
				PhH	0.21	95	35	60	8	
			0.01 M olefin[e]	PhH		89	<2	50	30	epoxide (90%), PhCOMe (17%)
			0.1 M olefin[e]	PhH	0.25	92	<2	55	15	epoxide (100%), PhCOMe (114%)
1b	Ph	H		PhH	0.24	98	50	45	9	
				MeCN		99	23	26		
1c	H	Ph		PhH	0.23	86	60	65	20	PhOH (45%)
				MeCN		60	18	14	12	PhOH (38%)
			0.1 M olefin[e]	MeCN		50	<2	22	27	epoxide (81%), PhCOMe (100%), PhOH (29%)
1d	Ph	Me		MeCN	0.39	21	41	35		$PhCO_2Me$ (66%), PhOH (10%)
			0.1 M olefin[e]	MeCN		14	<2	9		$PhCO_2Me$ (51%), PhOH (0%), epoxide (72%), PhCOMe (122%)

[a] Irradiation of 2 mM benzoin solutions at over 320 nm (mainly at 366 nm) for 2 h at 20 °C under O_2. [b] Quantum yield of benzoin decomposition was determined by GLC after 20–30% conversions. [c] Yield of major products based on benzoins (mol % per mole of benzoin) as determined by GLC and iodometry. [d] A few percent of biphenyl was always detected in the reaction in benzene. Benzoic acid was not determined. [e] α-Methylstyrene.

The addition of olefin suppresses peracid formation, giving instead a high yield of epoxide. This epoxidation is not due to molecular peracid, since the yield of epoxide was not affected by the addition of Me_2SO, a much more reactive substrate for peracid. The concomitant C–C cleavage (e.g., acetophenone from α-methylstyrene) suggests a radical mechanism for the epoxidation,[17] this mechanism being substantiated by the accompanying formation of phenyl benzoate, a product from the benzoyloxy radical and the solvent benzene. Thus, it may be concluded that epoxidation proceeds by way of the acylperoxy radical as is the case in the coautoxidation of olefins with aldehydes.[18] Details of this photoepoxidation will be discussed later.

Photooxidation of Benzoin Ethers. The photooxidation of benzoin methyl ethers in methanol has been reported to afford methyl benzoate (50–85%) in addition to peracid and H_2O_2.[5] The results, in Table I, show that the major products from benzoin phenyl ether (**1c**) are benzaldehyde (50–85%), phenol (30–50%), and a rather low yield (10–30%) of phenyl benzoate. The reported high yield of methyl benzoate (50–85%)[5] may be partly due to the subsequent photooxidation of benzaldehyde to methyl benzoate in methanol.[19]

Russell's mechanism[20] suggests the origin of the esters as shown in eq 3. This path should lead to a molar ratio of PhCHO:

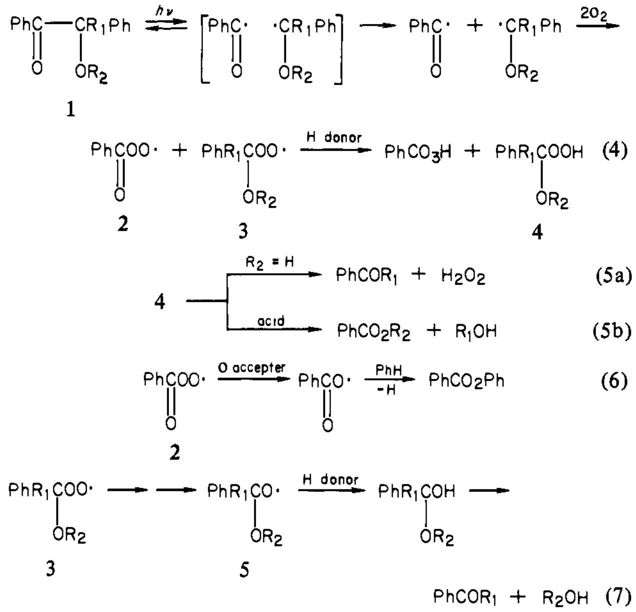


$$2Ph\dot{C}HOR \xrightarrow{2O_2} 2PhCH(OO\cdot)OR \longrightarrow PhCO_2R + O_2 + PhCH(OH)OR \longrightarrow PhCHO + ROH \quad (3)$$

$PhCO_2R$ = 1:1. Instead the yield of $PhCO_2Ph$ from **1c** was low compared with that of PhCHO, indicating the pathway cannot be a major one. The mechanism (eq 3) is also inconsistent with the fact that a higher yield (50–60%) of methyl benzoate was obtained from α-phenylbenzoin (**1b**) which has no α-hydrogen.

A more reasonable mechanism for the photooxidation of benzoins is shown in Scheme I. As discussed above, the formation of the radical pair in the solvent cage is apparent from CIDNP spectra,[4g] and benzaldehyde is not formed via H transfer in the cage such as the case for eq 2a. Hence, the two radicals diffuse out of the cage and are effectively trapped by oxygen, affording peroxy radicals and peroxides. Here, H donor means solvents, aldehydes produced, or the precursor of phenyl benzoate in eq 6.

Scheme I



$$PhC(=O)-CR_1Ph(OR_2)\ (\mathbf{1}) \underset{}{\overset{h\nu}{\rightleftharpoons}} [PhC(=O)\cdot\ \ \cdot CR_1Ph(OR_2)] \longrightarrow PhC(=O)\cdot + \cdot CR_1Ph(OR_2) \xrightarrow{2O_2}$$

$$PhC(=O)OO\cdot\ (\mathbf{2}) + PhR_1C(OR_2)OO\cdot\ (\mathbf{3}) \xrightarrow{\text{H donor}} PhCO_3H + PhR_1C(OR_2)OOH\ (\mathbf{4}) \quad (4)$$

$$\mathbf{4} \xrightarrow{R_2 = H} PhCOR_1 + H_2O_2 \quad (5a)$$

$$\mathbf{4} \xrightarrow{\text{acid}} PhCO_2R_2 + R_1OH \quad (5b)$$

$$PhC(=O)OO\cdot\ (\mathbf{2}) \xrightarrow{\text{O accepter}} PhC(=O)O\cdot \xrightarrow[-H]{PhH} PhCO_2Ph \quad (6)$$

$$PhR_1C(OR_2)OO\cdot\ (\mathbf{3}) \longrightarrow \longrightarrow PhR_1C(OR_2)O\cdot\ (\mathbf{5}) \xrightarrow{\text{H donor}} PhR_1C(OR_2)OH \longrightarrow PhCOR_1 + R_2OH \quad (7)$$

In the absence of olefins the yield of peroxyacid was considerably high, but α-alkoxy hydroperoxide **4** was not detected in the reaction at room temperature. The photooxidation of **1c** in CH_2Cl_2-*i*-PrOH at 0 °C, however, gave a low yield (10%) of the hydroperoxide **4c** (R_1 = H, R_2 = Ph) in addition to peroxyacid (57%), PhCHO (32%), PhOH (27%), $PhCO_2Ph$ (50%), and H_2O_2 (~250%).[21] The formation of **4c**, though it could not be isolated, was supported by its NMR spectra (i.e., a singlet at δ 6.24) and by a facile reaction with triphenylphosphine, yielding benzaldehyde and phenol. Similarly, hydroperoxide **4d** (R_1 = Ph, R_2 = Me)[22] was obtained in 20% yield in addition to $PhCO_2Me$ (52%) and $Ph_2C = O$ (22%) from the photooxidation of **1d** in CH_2Cl_2-*i*-PrOH at 0 °C.

That the α-alkoxy hydroperoxide **4** was not isolable from the photolysis at room temperature could be due to the acid-catalyzed decomposition (eq 5) of **4**.[23] It is well-known that peroxide

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(17) The autoxidation of olefins results in the epoxidation and the C–C cleavage in addition to polyoxide formation: (a) Van Sickel, D. E.; Mayo, F. R.; Gould, E. S.; Arluck, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 977. (b) Mayo, F. R. *Acc. Chem. Res.* **1968**, *1*, 193.

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(21) The yields are based on benzoin **1c**; the high-yield formation of H_2O_2 (~250%) indicates that isopropyl alcohol was autoxidized to yield H_2O_2 and acetone.

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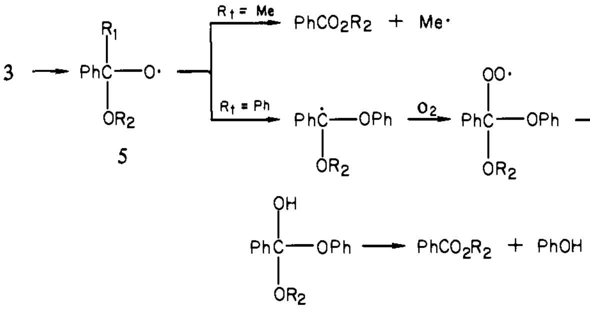
Table II. Photoepoxidation of Olefins with α-Acyloins and Oxygen[a]

			products,[b] %		
α-acyloin	olefin	solvent	PhCHO[c]	epoxide (trans:cis)	others[d]
1a	none	MeOH	100		$PhCO_3H$ (60%)
	trans-PhCH=CHMe	MeOH	~100	111 (95:5)	PhCHO (~34%)
	cis-PhCH=CHMe	MeOH[e]	*f*	*f* (97:3)	*f*
	trans-PhCH=CHPh	MeOH	~100	57 (100:0)	PhCHO (~130%), PT[g] (10%)
	cis-PhCH=CHPh[h]	MeOH	~100	24 (100:0)	PhCHO (~90%), PT[g] (3%)
	2-octenes[i]	MeOH	*f*	*f* (74:26)	
	cis-2-octene	MeOH	*f*	*f* (79:21)	
	$PhMeC=CH_2$	MeOH	102	85	PhCOMe (72%)
	$Ph_2C=CMe_2$	MeOH	73	113	$Ph_2C=O$ (38%)
1c	$PhMeC=CH_2$	PhH	93	97	PhCOMe (88%)
	trans-PhCH=CHMe	PhH	~92	119 (97:3)	PhOH (74%),[j] $PhCO_2Ph$ (20%)[j]
acetoin	$PhMeC=CH_2$	MeOH[k]		86	PhCOMe (70%)
	cis-PhCH=CHPh	MeOH[k]		20 (100:0)	PhCHO (25%)
PhCHO[l]	*cis*-PhCH=CHMe	PhH[e]		*f* (96:4)	*f*

[a] Irradiation of 2–4 mM acyloin through Pyrex filter under oxygen for 2 h; ca. 0.1 M of olefin was added. [b] Yields were determined by GLC and iodometry; mole % per mole of acyloin. [c] Benzaldehyde from benzoins. Other products from benzoins (e.g., benzoic acid) was not determined except for peroxyacid. [d] C–C cleaved products from olefins. The yield of PhCHO was calculated by subtracting 100% from the total yield, assuming a quantitative formation of PhCHO from benzoins. [e] 0.1 M of Me_2SO was added. [f] Not determined. [g] Phenanthrene. [h] 0.04 M of olefins. [i] Trans:cis is ca. 1:1. [j] Product from benzoin ether 1c. [k] Irradiation time 6 h. [l] Autoxidation (60 °C, 2 h) of 0.2 M PhCHO and 0.1 M olefin in benzene initiated by AIBN (ca. 0.01 M) under O_2. Me_2SO was added to suppress the epoxidation by way of peroxybenzoic acid formed.

rearrangements are dramatically accelerated by the α-oxy substituent.[24] However, the hydroperoxides **4c** and **4d** were stable in benzene containing a comparable concentration (i.e., ~2 mM) of benzoic acid at room temperature. Moreover, the reported formation of methyl benzoate (72%) and acetophenone (18%) from α-methylbenzoin methyl ether (**1e**, $R_1 = R_2 = Me$)[5] cannot be explained by the rearrangement mechanism such as the case for eq 5b. That is, the predominant formation of $PhCO_2Me$ from **4e** ($R_1 = R_2 = Me$) could be hardly understood by eq 5b, since the order of migratory aptitude is surely Ph ≫ Me in heterolytic peroxide rearrangements.[25]

An alternative mechanism for the ester formation from benzoin ethers is a radical reaction via alkoxy radical **5**. The reported



(8a)

(8b)

formation of $PhCO_2Me$ from **1e** ($R_1 = R_2 = Me$) is explicable only by the β-scission of the methyl radical from **5e** ($R_1 = R_2 = Me$) according to eq 8a like the well-known case of cumyloxy radical. The formation of $PhCO_2Me$ from **1d** ($R_1 = Ph$, $R_2 = Me$) can be understood by a 1,2-migration of phenyl group in **5d** ($R_1 = Ph$, $R_2 = Me$) according to pathway 8b. Such a facile 1,2-migration of phenyl is known in the diphenylalkoxy radical.[26] The formation of $PhCO_2R_2$ via and α-alkoxy radical intermediate, **5**, when $R_1 = H$, is understandable in view of the reported fact that the Fenton reaction of PhCH(OMe)OOH afforded $PhCO_2Me$ in 67% yield.[23b] Thus, the ester formation in these photooxidations of benzoin ethers is probably via the reaction of alkoxy radical **5** (eq 8a and 8b) as a major pathway.

Photoepoxidation. The most interesting point in the photooxidation of benzoins is the efficient oxygen atom transfer to olefins, i.e., epoxidation. As shown in Table II, high yields of epoxides and benzaldehyde were obtained. It is interesting to note that the stereochemistry of epoxides was predominantly trans: 100% trans from *cis*- or *trans*-stilbene and ~77% trans from *cis*- or *trans*-2-octene. These results suggest a radical epoxidation by benzoylperoxy radical (**2**), since a similar formation of *trans*-epoxides is known in the coautoxidation of the aldehyde and olefins.[18] The sequence as outlined in eq 6 is supported by the fact that in the photooxidation of benzoin **1a** in benzene (Table I) the addition of olefin caused a high-yield formation of epoxide, at the expense of peracid formation, accompanying the significant increase in the yield of phenyl benzoate, a product from the benzoyloxy radical and benzene.[27]

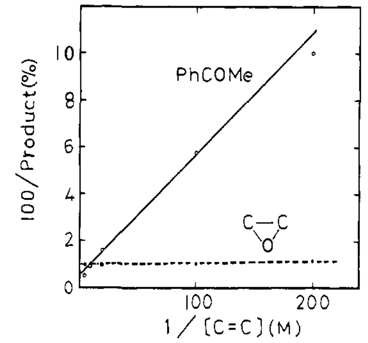


Figure 1. Effect of olefin concentration on the photoepoxidation of α-methylstyrene with benzoin; irradiation of 0.005–0.40 M olefin and 2.5 mM benzoin in benzene (Pyrex filter, 2 h). Yields are based on the charged benzoin; other products not shown are PhCHO (80–95%), Ph_2 (1–11%), and $PhCO_2Ph$ (3–25%).

The photoepoxidation is accompanied by C–C cleavage of olefins. Interestingly, this cleavage reaction depends on the olefin concentration. For example, in the photooxidation of **1a** in the presence of 0.01, 0.1, and 0.2 M α-methylstyrene under oxygen in benzene, the yields of acetophenone were 17, 114, and 216% and those of phenyl benzoate were 34, 15, and 1%, respectively, while the epoxide yield was high and constant (i.e., over 90%). This clearly indicates that benzoylperoxy radical **2** is effectively trapped by and epoxidizes olefins (eq 9), whereas the benzoyloxy radical reacts competitively with the olefin and the solvent benzene (eq 10 and 11). Since the epoxide yields are high and constant

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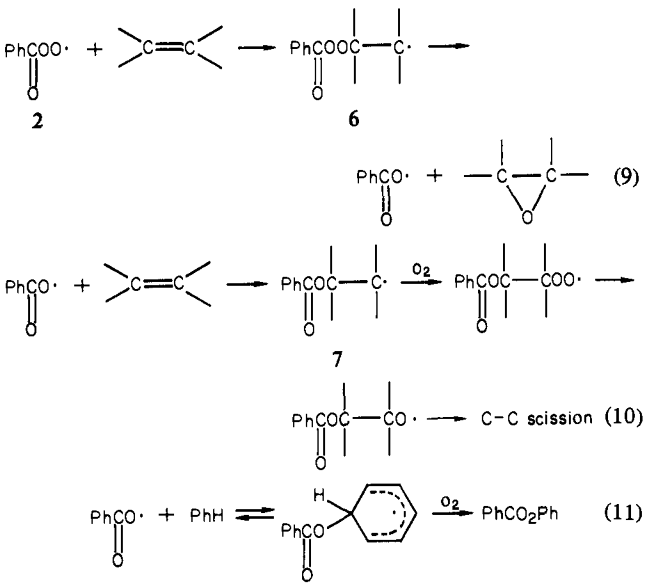
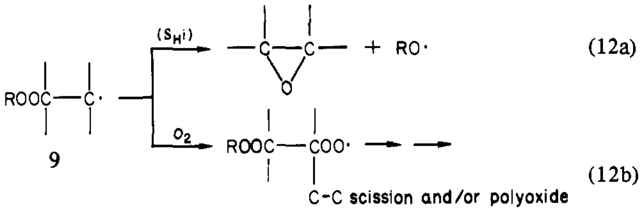
(27) It is known that the benzoyloxylation of benzene is effective in the presence of oxygen: (a) Nakata, T.; Tokumaru, K.; Simamura, O. *Tetrahedron Lett.* **1967**, 3303. (b) Saltiel, J.; Curtis, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 2056.



(i.e., 100 ± 10%) with methylstyrene = 0.004–0.4 M in benzene, the epoxidation reaction (eq 9) is fast and effective; i.e., the intramolecular cyclization in **6** is very fast. On the other hand, the reactions of the benzoyloxy radical (eq 10 and 11) are competitive, and the high concentration of olefin reduces the benzoyloxylation of benzene.

This relation may be analyzed by a reciprocal correlation of product yields and olefin concentrations (Figure 1). On the intercept at 1/[C═C] = 0, the epoxide yield is 100%, suggesting the formation of 1 mol of epoxide from 1 mol of benzoin. But the corresponding yield of acetophenone, a C—C scission product, is 196%, which indicates that 1 mol of benzoin causes 2 equiv of C—C cleavage. Probably, PhCH(OH)OO· (**3**, $R_1 = R_2 = H$) is another reagent for the C—C scission along with the benzoyloxy radical in eq 10. Since the plot of 1/[PhCOMe] vs. 1/[C═C] gives a straight line, the C—C cleavage via polyoxide[17] seems to be unimportant under these conditions in diluted olefin. Indeed, GLC and NMR studies suggest that such a polyoxide is not formed in the present reaction with ~0.1 mol of α-methylstyrene. Although the details of the C—C cleavage are not clear, one possible pathway is the cleavage via β-scission in the intermediary β-benzoyloxyalkoxy radical as shown in eq 10.

Stereochemistry and Relative Reactivity in the Photoepoxidation. An intramolecular cyclization (S_Hi) reaction in the adduct of the cumylperoxy radical (**9**, R = cumyl) is known to be relatively slow compared with the addition of oxygen, and hence the epoxide yield (i.e., reaction 12a) is only 3% under 1 atom of oxygen.[17] The present results show that when R = acyl, the S_Hi cyclization (eq 9 or 12a (R = acyl)) is very fast and quantitative. Assuming a diffusion-controlled rate (~10^{10} M^{-1} s^{-1}) for the addition of O_2 to **9** (eq 12b), the rate of the intramolecular cyclization should then be $>10^9$ s^{-1}.[28] The C—C cleavage proceeds probably via a path similar to eq 10.

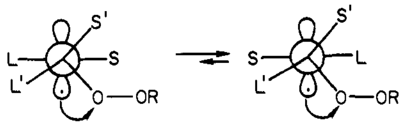


Here, the rotation around the C—C bond in **6** or **9** should be much faster than the cyclization to epoxide because both *cis*- and *trans*-olefins gave epoxides of the same stereochemistry, predominantly trans (see Table II). This trans stereochemistry may be easily understood on the basis of relative stability of cis and trans in the cyclization intermediates. Here, L or L′ and S or S′ mean the larger and the smaller substituents in the olefin, respectively. In the transition state for the S_Hi cyclization, the substituents of the olefin, L, S, L′, and S′, should become eclipsed as shown above; the *trans*-**10** is surely more stable than the cis isomer. Indeed, the resulting epoxides from stilbenes, β-methylstyrenes, and 2-octenes are 100, 97, and 77% trans, respectively, reflecting a decrease in the energy differences between the *cis*- and the *trans*-**10**.

Table III. Relative Rates of Epoxidation and Oxidation

substrate	relative rate: photoepoxidation with benzoin[a]	relative rate: epoxidation with PBA[b]
$PhC(Me)=CH_2$	(1.00)	(1.00)[c]
$PhCH=CH_2$	0.123	0.140
trans-PhCH=CHMe	1.95	1.59
$PhCH=CMe_2$	0.92	3.37
$PhC(Me)=CMe_2$	1.86	20.2
trans-PhCH=CHPh	0.76	0.064
1-octene	0.0099	0.13
cis-2-octene	0.11	2.73
cyclohexene	0.143	2.79
1-methylcyclohexene	1.04	13.6
1,2-dimethylcyclohexene	~2	63.2
Me_2SO	<0.1[d]	64[d]
pyridine	<0.01[e]	1.33[e]

[a] Relative rate of photoepoxidation obtained by competitive reaction with 0.02–0.2 M substrate and 2.5 mM benzoin in benzene–acetone (3:1) at 20 °C. [b] Relative rates obtained for the epoxidation of olefins (0.02–0.2 M) with perbenzoic acid (0.005–0.01 M) in benzene at 25 °C. [c] Second-order rate constant is 6.77×10^{-3} M^{-1} s^{-1}. [d] Sulfone formation. [e] Pyridine *N*-oxide formation.

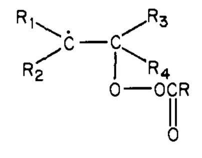


(13)

cis-10 *trans*-10

So far, a similar epoxidation with RCO_3· has been demonstrated in the coautoxidation of RCHO and olefin.[18] However, it was not possible to study quantitatively the stereochemistry and the relative reactivity in the radical epoxidation, since a significant amount of peroxyacid was concomitantly formed because of the presence of large amount of the aldehyde.

The relative reactivity of olefins is another characteristic point in the epoxidation with acylperoxy radical (Table III). Aliphatic olefins are less reactive than aromatic ones. The radical epoxidation is rather insensitive to the second or third methyl substituent, which is in contrast with the molecular epoxidation with peroxyacid where the additivity of methyl substituents is operative (i.e., ca. tenfold increase in rate by one methyl). The peracid epoxidation may be explained on the basis of nucleophilic π-bond basicity of olefins. On the other hand, the relative reactivity in the present radical epoxidation is probably determined by the addition step of RCO_3· to C═C, since the peroxidic adduct **6** cyclizes, as discussed above, fast and effectively to afford epoxide. The addition step, in turn, seems to be governed by the stability of resulting radical (**6** or **11**). For example, styrenes are much more reactive than the corresponding aliphatic olefins because of the formation of much more stable benzyl radicals (**11**, R_1 or R_2 = Ph). The stabilization of radical **11** is sufficient when the



11

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[28] Since the epoxide yield was over 90%, $k_{S_Hi}[9] > 10 \times 10^{10}[9][O_2]$, which leads to $k_{S_Hi} > 10^9$ s^{-1} under 1 atom of oxygen (i.e., $[O_2] \approx 0.01$ M).

radical is tertiary or benzyl, i.e., there is no effect of a second or third methyl substituent on the β-carbon. This explanation seems to be consistent with the major tendency of the relative reactivity in Table III. One open question is why the terminal olefins are 1 order less reactive than the corresponding internal olefins (e.g., compare sytrene and β-methylstyrene or 1- and 2-octenes). This significant difference could not be explained only on the basis of radical stability of **11** and needs a more detailed study.

Interestingly, acylperoxy radical is rather unreactive to sulfur and nitrogen compounds. As exemplified at the bottom of Table III, Me_2SO and pyridine, which are quite reactive to molecular peracid, are not oxidized to sulfone or *N*-oxide in the presence of olefin. This implies that a selective epoxidation of double bond is possible in an olefin possessing a sulfide, sulfinyl, or pyridyl group. The lower reactivity of the nitrogen or sulfur group is probably due to its inability to participate in the addition reaction of acylperoxy radical.

Aliphatic Acyloins. The photolysis of acetoin under deaerated conditions exhibits CIDNP spectra,[15] products being acetaldehyde, methane, and carbon monoxide.[16] Under oxygen acetoin undergoes the similar photoepoxidation of olefins as benzoin does (Table II). These results indicate similar sequences as outlined in Scheme I; one small difference is the facile decarboxylation of aliphatic $RCO_2\cdot$ to $R\cdot$ and CO_2.

Photodynamic effect is a complex phenomenon, and its origin is not clarified.[29] Singlet oxygen might be a candidate, but organisms possess some protective substances;[30] the same is true for the case of superoxide or hydrogen peroxide.[31] An important intermediate of metabolism of carbohydrates is α-oxy ketones, including glyceraldehyde or dihydroxyacetones.[32] Since acyloins, RCOCH(OH)R′, have absorbance at around 300 nm, their photooxidation by sun light may yield several peroxidic intermediates or products such as $RCO_3\cdot$, RCO_3H, $R'CH(OH)OO\cdot$, $ROO\cdot$, or H_2O_2. Especially, $RCO_3\cdot$ and/or RCO_3H possess high chemical reactivities and hence might be candidate for an origin of photodynamic effect. Indeed, we have experienced that peracids are severely irritant and inflammatory to skin even as a diluted solution.

In conclusion, the photooxidation of acyloins effectively produces acylperoxy radicals which could selectively transfer the oxygen atom to olefins affording predominantly *trans*-epoxide. In the practice of making aerated coatings and printings with benzoin photolysis, the first reaction is the radical epoxidation with acylperoxy radical; then polymerization is probably initiated by benzoyloxy and peroxy radicals (**3**).

Experimental Section

Melting points were corrected and boiling points were uncorrected. IR spectra were recorded with a Perkin-Elmer 337 grating spectrometer, UV spectra with a Hitachi 124 spectrophotometer, and ^1H NMR spectra with a Hitachi R-24B spectrometer. GLC analyses were performed with a Yanagimoto G180 gas chromatograph with a flame ionization detector by using two different columns: PEG 20M, 20% on Chamelite CK; Silicone OV-17, 5% on Shimalite W.

Materials. α-Phenylbenzoin (**1b**) and its methyl ether (**1d**) were described previously.[22] Benzoin phenyl ether (**1c**) was synthesized according to the literature method,[33] mp 85–86 °C (lit.[33] 85 °C). *cis*-Stilbene was obtained by sensitized isomerization from the trans isomer and was ca. 95% pure. 2-Methyl-3-phenyl-2-butene,[34] 1,1-diphenyl-2-methylpropene,[35] and 1,2-dimethylcyclohexene[34] were reported elsewhere; other olefins are of commercial source.

General Procedure of Photooxidation. A 5-mL benzene solution of 2 mM benoin in 20-mL test tube was saturated with oxygen by bubbling its stream for 5 min and irradiated with a 300-W medium-pressure Hg lamp through a Pyrex filter at ca. 20 °C. After 1- or 2-h irradiatin, perbenzoic acid and hydrogen peroxide were titrated as described previously.[36] The peroxyacid was characterized by the extraction with aqueous alkali and by the instant oxidation of Me_2SO to sulfone, yielding benzoic acid. Benzaldehyde was identified by GLC and NMR and by $NaBH_4$ reduction to benzyl alcohol; phenyl benzoate was done by GLC and by the reaction with sodium methoxide to afford methyl benzoate and phenol.

The photoepoxidation of olefins was carried out similarly, and epoxides were identified and determined by GLC analysis in comparison with the corresponding authentic samples obtained by epoxidation with perbenzoic acid.

The quantum yields for the photooxidation of benzoins were determined by using ferrioxalate actinometry[37] and/or a merry-go-round apparatus. The conversion of benzoins (20–30%) was determined by GLC analysis; the determination by means of UV spectra was not appropriate because of the formation of a small amount of colored product(s).

Photooxidation of α-Phenylbenzoin Methyl Ether (1d). The ether **1d** (100 mg, 0.33 mmol) and Me_2SO (0.2 g) were dissolved in CH_2Cl_2 (18 mL)–*i*-PrOH (2 mL) and irradiated through Pyrex glass with oxygen bubbling at 0 °C for 1 h. After the mixture was washed with water, the solvent was evaporated under slightly reduced pressure. The GLC and NMR spectra of the crude product mixture showed the formation of $PhCO_2Me$ (52%), $Ph_2C{=}O$ (22%), and α-(hydroperoxy)-α-methoxydiphenylmethane (**4d**)[22] in 20% yield. This hydroperoxide has a NMR signal of the methyl group at δ 3.22 (singlet) and could be purified by extraction with aqueous alkali followed by neutralization with AcOH as described previously.[22]

Photooxidation of Benzoin Phenyl Ether (1c). The ether **1c** (100 mg, 0.35 mmol) was dissolved in CH_2Cl_2 (15 mL)–*i*-PrOH (1.5 mL) and irradiated, under oxygen bubbling, through Pyrex glass at 0 °C for 1 h. After the mixture was washed with aqueous bicarbonate, the solvent was evaporated at a slightly reduced pressure. The iodometric titration, NMR, and GLC analyses indicated the formation of $PhCO_3H$ (57%), PhCHO (32%), PhOH (27%), $PhCO_2Ph$ (50%), H_2O_2 (~250%), and α-hydroxybenzyl hydroperoxide (**4c**) in 10% yield. The hydroperoxide **4c** could not be isolated but could be identified by the facile reduction with triphenylphosphine to benzaldehyde and phenol and also by its NMR spectra, where the methylene proton appeared at δ 6.24 (s), the corresponding proton of the starting ether **1c** being at δ 6.13.

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