## MECHANISTIC STUDY ON THE PHOTO-OXIDATION OF $\alpha$ -DIKETONES

### INTERACTION OF TRIPLET *a*-DIKETONES WITH OXYGEN

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Abstract — The mechanism for photo-oxidation of  $\alpha$ -diketones in the presence of olefins has been studied, focusing on the interaction of triplet diketones with  $O_2$ . Two types of reactions occur competitively. One is the formation of  ${}^1O_2$  by energy transfer to  $O_2$  and the other is the addition of  $O_2$  to triplet diketone, which yields acylperoxy radicals leading to the radical epoxidation of olefins. Ratios of the two reactions were determined from the yields of  ${}^1O_2$  products and epoxides. For most diketones, quantum yields for  ${}^1O_2$  formation were considerably high, in the range 0.3-0.8; but the yields for epoxides were in a wider range of 0.001-0.5. While the ratios of  ${}^1O_2$  formation and  $O_2$  addition to triplet diketones ranged from 29:71 for biacetyl to 1:99 for mesitil, the ratios remained constant by changing solvents or temperature. The latter  $O_2$  addition reaction decreased in the order of MeCOCOMe > PhCOCOMe > PhCOCOPh but the effect of *m*- and *p*-substituents on benzils was not significant, indicating the addition of  $O_2$  as a neutral biradical. In exceptional cases, the  $O_2$  addition was discussed in comparison to other carbonyl compounds.

 $\alpha$ -Diketone-sensitized photo-oxidation reported by Bartlett *et al.*<sup>1,2</sup> is interesting in relation to a Schenck mechanism (Eq. 1).<sup>3</sup>

Since triplet carbonyls are diradicals

$$\left(e.g.\right)$$
C $-O$ 

Sens  $\xrightarrow{h\nu}$  \*Sens  $\xrightarrow{O_2}$  Sens-OO·  $\rightarrow$  Oxygenation (1)

In previous papers,<sup>4.5</sup> however, we have shown that the photoepoxidation of olefins proceeds via the acylperoxy radical, 2, generated by the photo-oxidation of  $\alpha$ -diketone (1) under O<sub>2</sub>. The reasonings are based on the 1:2 stoichiometry of diketone consumed and epoxide formed, trapping of RCO<sub>2</sub>, and the formation of peroxy acid in the absence of olefins. The photoepoxidation with benzoin and O<sub>2</sub> has been capable of abstracting a H atom just as alkoxy radicals<sup>9</sup> and the addition of  $O_2$  to C-centred radicals is very fast,<sup>10</sup> the addition of  $O_2$  to the diradicals seems to be very facile. However, no detailed study is reported regarding such an interaction. Herein we report that the ratio of reactions (3) and (4) changes with the structures of diketones but is not dependent on the reaction conditions, e.g. solvents and temperature.



shown to occur likewise by way of an acylperoxy radical.<sup>6</sup>

In general, the quenching of excited states by  $O_2$  is believed to be very fast and effective, <sup>7</sup> producing  ${}^{1}O_2$ (Eq. 3).<sup>8</sup> Our interest was then focused on the interactions of excited triplet diketones with  $O_2$ , i.e. the first step in the photo-oxidation of  $\alpha$ -diketones. It is interesting to examine factors which determine the reaction courses, the formation of  ${}^{1}O_2$  (Eq. 3) or addition of  $O_2$  to triplet diketone <sup>3</sup>1 (Eq. 4).

$${}^{3}1 + {}^{3}O_{2} \rightarrow 1 + {}^{1}O_{2}$$
 (3)

#### RESULTS

 $^{1}O_{2}$  and RCO<sub>3</sub>. Formation In order to determine  $^{1}O_{2}$  formation (Eq. 3) and acylperoxy radical formation (Eq. 4),  $\alpha$ -diketones were photo-oxidized in the presence of 1,2-dimethylcyclohexene (4). That is, a benzene solution of 2–8 mM  $\alpha$ -diketone and 0.1 M 4 was irradiated at over 320 nm

under  $O_2$  and the products were detected by GLC analyses after NaBH<sub>4</sub> reduction. Since olefin 4 and  ${}^{1}O_2$  afford a characteristic ratio of allylic alcohols,<sup>11</sup> the amount of  ${}^{1}O_2$  formed may be



estimated from their yields. On the other hand, since the epoxidation of 4 via  $RCO_3$  is effective, <sup>5,6</sup> the yields of the epoxide, 5, correspond to the amount of  $RCO_3$  formation.

As shown in Table 1(a), a typical  ${}^{1}O_{2}$  sensitizer, such as methylene blue or Rose Bengal resulted in a characteristic ratio of allylic alcohols, 6–7–8 of 1:85:12, in accordance with that reported (i.e. 0:89:11),  ${}^{11}$  a few percent of the epoxide, 5, were also detected. On the other hand, in the radical autoxidation of 4 the epoxide, 5, was the predominant product and the ratio of allylic alcohols was quite different from the above  ${}^{1}O_{2}$  reaction (Table 1a). Such an epoxide formation as a major product is known in the autoxidation of tetrasubstituted olefins.  ${}^{12}$  Thus, the product ratio of 6–7–8 may lead to a decision on the  ${}^{1}O_{2}$ reaction or the radical autoxidation.  ${}^{11}$ 

The photo-oxidation of  $\alpha$ -diketones was most facile for biacetyl, the efficiency decreasing in the order MeCOCOMe > PhCOCOMe > PhCOCOPh (see  $\Phi_{diketone}$  in Table 1b). Since the quantum yields for the photo-oxidation of diketones remain constant in the presence of olefins, the predominant reaction is the interaction between excited diketone and O<sub>2</sub>. Exceptional cases were the photochemical reactions of phenanthrenequinone (PhQ) and acenaphthenesubstituents on benzils. There appears to be no significant effect of substituents for either  $\Phi_{epoxide}$  or  $\Phi_{allylie}$  the ratio of Eqs (4) and (3) being 0.05:0.10 for most benzils. One exceptional case here was the photo-oxidation of mesitil and 2,4,6-trimethylbenzil, where  $\Phi_{epoxide}: \Phi_{102}$  ratios were as low as typical  ${}^{1}O_{2}$  sensitizers such as methylene blue. The values of  $\Phi_{diketone}$  and  $\Phi_{102}$  for mesitil were considerably low. Another exceptional case was the inefficient photoreaction of p,p'-dihydroxybenzil, probably because of its deactivation to the ground state via an intramolecular charge-transfer state.<sup>16</sup>

#### Solvent and temperature effects

The effects of solvents and temperature on the ratio of RCO<sub>3</sub> · formation (Eq. 4) and <sup>1</sup>O<sub>2</sub> formation (Eq. 3) were determined. As listed in Table 2, the ratios were not affected by the polarity or viscosity of solvents or by changing temperature. The same was true when changing the O<sub>2</sub> atmosphere to air, i.e. by reducing P<sub>O2</sub> to 20%.

#### Comparison with other carbonyls

In order to examine the validity of the above analysis using the olefins, 4, the photo-oxidation with 2-methyl-3-phenyl-2-butene (9) was similarly undertaken.



quinone (AcQ), where the diketones react with olefins or tetrahydrofuran very fast affording 1:1 adducts<sup>13,14</sup> and the reaction with O<sub>2</sub> is not a major one.

Except for the PhQ and AcQ cases, the ratios of the allylic alcohols, 6–8, are of the typical  ${}^{1}O_{2}$  reaction, as apparent in Table 1(b). The  $\Phi_{\text{allylic}}$  in Table 1 means quantum yields for the sum of 6–8 on the basis of incident light predominantly at 366 nm. As estimated from the  $\beta$ -value of 0.03,  ${}^{15}$  0.1 M of olefin <sup>4</sup> traps 77% of the  ${}^{1}O_{2}$  formed; then the quantum yield of  ${}^{1}O_{2}$  formed may be calculated by  $\Phi_{1O_{2}} = \Phi_{\text{allylic}}/0.77$ . The  $\Phi_{1O_{2}}$  values were considerably large, i.e. in the range 0.4–0.8 for most diketones in Table 1(b). Hence, it is apparent that  ${}^{1}O_{2}$  formation (Eq. 3) is effective for most diketones except PhQ and AcQ, where the major reaction is the 1:1 formation of cycloadducts and olefins.  ${}^{14}$ 

Since the 1 mol of diketone affords 2 mol of RCO<sub>3</sub>· and, hence, 2 mol of epoxides,<sup>5</sup> the ratio of reactions (4) and (3) is  $(\Phi_{epoxide}/2): \Phi_{1O_2}$ . The ratios thus obtained, as listed in the last column in Table 1, decrease in the order of MeCOCOMe > PhCOCOMe > PhCOCOPh. This is the same order as the relative efficiency for diketone photolysis (i.e. relative  $\Phi_{diketone}$ ).

In Table 1(c) are listed the results for the effect of ring

In the photoepoxidation with  $\alpha$ -diketones, the olefin, 9, afforded the epoxide, 10, together with a small amount of acetophenone (i.e. 10-20% of the epoxide yield). The ratio of the allylic alcohols 11-12 was 2.5:1, which is close to the reported ratio of 2.8:1.17 The resulting ratios of reactions (4) and (3) in Table 3 are 4:96 for benzil and 34:66 for biacetyl, which are in accordance with the corresponding ratios using the olefin, 4. The consistency indicates the validity of analysis for reactions (3) and (4) using the olefins 4 or 9. The ratios of <sup>1</sup>O<sub>2</sub> formation and photoepoxidation were also determined for other carbonyl compounds using the olefin 9 (Table 3). For benzophenone, the predominant reaction was <sup>1</sup>O<sub>2</sub> formation and the photoepoxidation was ineffective. For benzaldehyde, ca 5% of epoxide was obtained, but the epoxide may also be formed via the co-autoxidation of olefin with the aldehyde.<sup>+</sup>

Benzoin resulted in a very high epoxide selectivity (Table 3). In the photolysis of benzoin, the type I  $\alpha$ scission is very fast,<sup>19</sup> producing the benzoyl radical

<sup>&</sup>lt;sup>†</sup> The olefin epoxidation is known to occur in the coauto-oxidation of the aldehyde and olefins.<sup>12,18</sup>

		Table 1. Photo	o-oxidation	of various	α-diketon	es in the pı	esence of 1,2-dim	ethylcyclohexe	ne (4)*		
RICO	COR 2 <sup>b</sup>	Conversion	H	Product dis	tribution <sup>d</sup>		Reaction for	ð	antum yield <sup>f</sup>		e
R1	R2	- of diketone <sup>2</sup> • • • • • • • • • • • • • • • • • • •	5	é	7	<b>36</b>	anync arc. formation <sup>e</sup>	<b>D</b> epoxide	<b>D</b> allylic	$\Phi_{i_{O_2}}^f$	$\frac{\mathbf{x}_{\text{crowide}}}{2}$ ; $\Phi_{1_{O_2}}$
(A) Typical <sup>1</sup> O <sub>2</sub> ar	nd radical reaction	Suc	- Andrewski and a state of the								
Rose Bengal-Me	SOH		2.4	1.3	85	12	102	I	I	1	66:
Methylene blue-	MeOH		2.0	1.0	86	12	<sup>1</sup> 02	ļ	I	-	1:99
Radical autoxids	ation <sup>b</sup>		¥.	22	14	æ	Radical	1	I	1	I
(B) Diketone phot	o-oxidation										
Me	Me	0.41	51	4	36	6	°0,	0.46	0.44	0.57	29:71
Ph	Me	0.062	33	m	2	6	<u>`</u> 0	0.14	0.29	0.38	16:84
Ł	Ph	0.035	6	7	80	90	°.	0.044	0.44	0.57	4:96
PhO	1	0.34	6	18	8	42	Radical	0.021		i	ł
PhO (0.01 M 4)		0.151	īv	0.5	61	35	<sup>1</sup> O <sub>2</sub> /radical	< 0.01	1		i
AcO	ł	0.077	Q	20	43	29	Radical	0.004	nonas	ļ	ł
AcO (0.01 M 4) <sup>j</sup>		0.012	v V	v	52	21	<sup>1</sup> O <sub>2</sub> /radical	< 0.001		I	1
g	ł	0.077	4	۳	83	10	_101	0.028	0.65	0.84	2:98
(C) Substituent eff	ect on benzil										
Ph	Ph	0.035	6	7	80	œ	•0,	0.044	0.44	0.57	4:96
P-MeOPh	p-MeOPh	0.032	21	<b>ب</b> ه	2	11	0,	0.054	0.21	0.27	16:6
PCIPh	P-CIPh	0.014	13	4	12	11	<sup>1</sup> 0 <sup>2</sup>	0.027	0.18	0.23	7:93
m-CIPh	h	-	11	1.1	78	10	°,	1	1	NANANAN I	5:95
PCIPh	p-MeOPh		16	0.9	73	10	°.	ł	ł		7:93
o-MeOPh	o-MeOPh		24	0.4	63	12	0,	I	I	ł	10:90
P-HOPh	P-HOPh	Warren		Incff	sctive			I		-	ł
2.5-Me.Ph	2.5-Me, Ph		23	0.9	69	7	°,	]	ł	1	10:90
Mesitil	Ph.	1	4	1.4	81	14	0,	!		1	2:98
Mesitil	Mesitil	0.0023	2.4	3.1	83	12	10 <sup>1</sup>	0.001	0.05	0.06	1:99

• Irradiation of 2-8 mM  $\alpha$ -diketones and 0.1 M 4 in benzene under O<sub>2</sub> at over 320 nm at 20°; products were determined by GLC after reduction with NaBH<sub>4</sub> and the intensity of incident light was determined by ferrioxalate actinometry.

Mesitil

• Ph is C<sub>6</sub>H., C<sub>6</sub>H. or C<sub>6</sub>H., i PhQ, phenanthrenequinone; AcQ, acenaphthenequinone; CQ, camphoroquinone; mesitil, 24,6-trimethylphenyl.

• Quantum yields for the diketone decomposition as determined by UV.

<sup>4</sup> Product distributions from the olefin as determined by GLC after reduction with NaBH<sub>4</sub>.

\*Types of major reaction for the formation of three allylic alcohols (6-8); i.e. <sup>1</sup>O<sub>2</sub> reaction or radical auto-oxidation.

 $^{t}\Phi_{alplue}$  is quantum yield for the formation of allylic alcohols (i.e. 6 + 7 + 8). Then, the quantum yield for  $^{1}O_{2}$  formation may be calculated from  $\Phi(^{1}O_{2}) = \Phi_{alyluc}/0.77$ , since 77% of  $^{1}O_{2}$  formed reacts with 0.1 M 4 as calculated from its  $\beta$ -value of 0.03.<sup>3b</sup>

\*The ratio of the addition of O<sub>2</sub> to triplet diketone vs <sup>1</sup>O<sub>2</sub> formation; i.e. the ratio of reactions (3) and (4) or (14) and (15).

The radical auto-oxidation of 4 initiated by AIBN in MeCN at 60°.

The predominant reaction is the 1:1 addition between quinone and olefin.<sup>14</sup>

Reaction in dichloromethane and AcQ was determined by GLC.

\* Ineffective in comparison to other benzils (i.e. below 10%)

Solvent (η, cp) <sup>b</sup>	With benzil (epoxide-allylics) <sup>c</sup>	With biacetyl (epoxide-allylics) <sup>c</sup>	
Benzene (0.65)	[1:89	57:43	
CCL (0.97)	9:91	51:49	
MeCN (0.35)	12:88	42:58	
i-PrOH (2.86)	12:88	58:42	
MeOH (0.55)	11:89	58:42	
PhH-CH <sub>2</sub> Cl <sub>2</sub> (1:3), 0°	13:87	_	
$PhH-CH_{2}Cl_{2}(1:3), -65^{\circ}$	14:86	43:57	

Table 2. Effect of solvents and temperature on the ratios of photoepoxidation and the <sup>1</sup>O<sub>2</sub> reaction of 4<sup>a</sup>

\* Irradiation of 2-4 mM diketone and 0.1 M 4 at over 320 nm under O<sub>2</sub> at 20°. Products at the initial stage (i.e. 5-10% conversion of diketone) were determined by GLC after reduction with NaBH<sub>4</sub>.

Viscosity of solvents.

<sup>c</sup> Allylics are the sum of 6-8; the typical ratios of 6-7-8 are 2:78:1 for benzil and 2:36:10 for biacetyl. The latter case is not of a typical <sup>1</sup>O<sub>2</sub> reaction, suggesting the significant contribution of a radical auto-oxidation of 4.

Table 3. Photo-oxidation of 9 with some carbonyl compounds under O<sub>2</sub>\*

Carbonyl compounds	$E_T^{\mathbf{b}}$ (kcal/mol)	Ф <sub>зт</sub> ь	Product ratio (epoxide-allylics) <sup>e</sup>	$\frac{\text{epoxide}}{2}: {}^{1}\text{O}_{2}{}^{d}$
PhCOCOPh	53	0.92	13:87	4:96
PhCOCOPh, air		_	13:87	4:96
MeCOCOMe	56	1.0	64:36	34:66
Ph <sub>2</sub> C=O	69	1.0	2:98	1:99*
PhCHO	72	—	~5:95	~3:97°
PhCOCH(OH)Ph		-	88:12	81:19°

Irradiation of 2-5 mM carbonyl compounds and 0.05 M 9 in benzene at over 320 nm under

 $O_2$  at 20°. <sup>b</sup>  $E_7$ , Energy of  $T_1$ ;  $\Phi_{sr}$  quantum yields of intersystem crossing from  $S_1$  to  $T_1$ .<sup>38</sup> <sup>c</sup> Allylics are the sum of 11 and 12 (Eq. 6). <sup>d</sup> See footnote g in Table 1. Yields of <sup>1</sup>O<sub>2</sub> formation were calculated from 0.05 M 9 with <sup>c</sup>  $A = 10^{-1} T_{11} + 50\%$  of <sup>1</sup>O<sub>2</sub> is transed by the 0.05 M olefin.  $\beta = 0.035$ ;<sup>17</sup> i.e. 59% of <sup>1</sup>O<sub>2</sub> is trapped by the 0.05 M olefin.

• The ratio of epoxide $-{}^{1}O_{2}$ .

$$\begin{array}{c|cccc} PhC & \xrightarrow{h\nu} & PhC \cdot + \cdot CHPh & \xrightarrow{20_2} & PhCOO \cdot & (+PhCHOO \cdot) & \longrightarrow & O- \ transfer \\ | & | & | & | & | & | & | \\ O & OH & O & OH & O & OH \end{array}$$
(7)

and, hence, PhCO<sub>3</sub>· by O<sub>2</sub> trapping.<sup>6</sup> This pathway (Eq. 7) is significantly different from the present case of diketones, as discussed later. Hence, it is not certain whether the 12% formation of allylic alcohols from benzoin and 9 are produced from  ${}^{1}O_{2}$  via energy transfer from excited benzoin, or produced from benzaldehyde or from by-products.<sup>†</sup>

#### DISCUSSION

Since excited triplet carbonyl is a diradical

$$(i.e.)$$
C $-O$ 

capable of abstracting  $H^9$  and the addition of  $O_2$  to carbon-centred radicals is very fast,<sup>10</sup> the addition of  $O_2$  to the diradicals may be expected to be facile. This corresponds to a formation of 'moloxide' in a Schenck mechanism.<sup>3</sup> a-diketone-sensitized photo-The epoxidation of olefins reported by Bartlett et al.<sup>2</sup> seemed to be the first clear example of such a Schencktype oxygenation (Eq. 1). Indeed, although the photolysis of benzil in benzene is very slow under nitrogen and does not yield the benzoyl radical,<sup>20</sup> the reaction under  $O_2$  proceeds smoothly yielding benzoic acid, phenyl benzoate and biphenyl.<sup>21</sup> Here, phenyl benzoate is produced from the benzoyloxy radical and solvent benzene. However, our recent studies<sup>4,5</sup> revealed that the photo-oxidation rate of  $\alpha$ -diketones is independent of olefins and that the stoichiometry of diketone-epoxide is 1:2.1 Photo-oxidation in the absence of olefin affords a significant amount of peroxy

<sup>†</sup> The major products of benzoin photolysis are PhCO<sub>2</sub>H and PhCHO, but unknown coloured products were also detected by examining UV spectra.6

<sup>&</sup>lt;sup>‡</sup>In the photoepoxidation of 0.1 M PhMeC==CH<sub>2</sub> or Ph<sub>2</sub>C=CMe<sub>2</sub> with PhCOCOPh, PhCOCOMe and MeCOCOMe, the amount of epoxides formed was  $2.0 \pm 0.1$ mol per mol of diketone consumed.<sup>5</sup> One mol of diketone yields 2 mol of epoxide.

acid.<sup>4</sup> Thus, it is apparent that  $\alpha$ -diketones under  $O_2$  are photo-oxidized according to Eq. (4) to yield the acyl peroxy radical RCO<sub>3</sub>, affording *trans*-epoxides predominantly via radical epoxidation. That is, the diketones do not recycle as a sensitizer but decompose photochemically under  $O_2$ . Alternatively, the photooxidation is not a  ${}^1O_2$  reaction since it is not sensitized by methylene blue or Rose Bengal which absorb over 98% of the light.

Thus, the following processes (Eqs 8-12) are expected as a dominant photochemical event.

$$1 \xrightarrow{\text{nv}}{1} 1 \xrightarrow{\text{ost}}{3} 1 \tag{8}$$

$$^{3}1 \rightarrow 1 + hv \text{ or heat}$$
 (9)

$${}^{3}1 + O_2 \rightarrow 1 + {}^{3}O_2 \tag{10}$$

$${}^{3}\mathbf{1} + \mathbf{O}_{2} \rightarrow \mathbf{1} + {}^{1}\mathbf{O}_{2} \tag{11}$$

<sup>3</sup>1+O<sub>2</sub> 
$$\rightarrow$$
 RC-C  $\rightarrow$  RC-C scission) (12)  
 $\parallel \mid \mid$   
O O

Here,  ${}^{3}O_{2}$  is  $O_{2}$  and  $\Phi_{sT}$  is quantum yield for intersystem crossing. In Eq. (9),  $h\nu$  corresponds to the phosphorescence from  ${}^{3}1$  and heat to radiationless deactivation. For the case of  $\alpha$ -diketones, the intersystem crossing from  ${}^{1}1$  to  ${}^{3}1$  is effective (i.e.  $\Phi_{sT}$ ~ 1),  ${}^{22.23}$  and the lifetimes of  ${}^{3}1$  are as long as 1–10 ms.<sup>24</sup> Since the quenching of triplet diketones by  $O_{2}$  is fast (i.e.  $k_{q} = 10^{7}-10^{9} \text{ M}^{-1} \text{ s}^{-1}$ ),<sup>8</sup> the quenching of  ${}^{3}1$  is expected to be almost quantitative under air (*ca* 2 mM  $O_{2}$  in solution) or under  $O_{2}$  (*ca* 10 mM). Actually, quantum yields for the diketone photo-oxidation are practically the same in air or under  $O_{2}$ , indicating no significance of Eq. (9).

Reaction (10) is the perturbed intersystem crossing assisted by  $O_2$ , but it seems not to be a major path, at least in the cases of biacetyl and benzil, since the combined quantum yield of Eqs (11) and (12) is significantly high. For example the sum of  $\Phi_{exoside}/2\Phi_{1O_2}$   $^{1}O_{2}$  Formation and  $O_{2}$  addition to  $^{3}C=O$ 

The O<sub>2</sub> quenching of triplet carbonyls is known to be fast and effective, <sup>7,8,25,26</sup> the quenching rates for most carbonyls are of the order of 10<sup>9</sup> M<sup>-1</sup>s<sup>-1</sup>, whereas they are ca 10<sup>8</sup> for some ketones.<sup>†</sup> A recent study in the vapour phase<sup>28</sup> resulted in small negative activation energies for the quenching rate with O<sub>2</sub> suggesting the existence of a weakly bound complex between excited carbonyls and O<sub>2</sub>. The O<sub>2</sub> quenching for excited  $\alpha$ diketone in solution is, likewise, fast; e.g.  $1 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> for benzil<sup>27</sup> and  $5 \times 10^9$  for biacetyl.<sup>26</sup> In fact, relatively high yields of <sup>1</sup>O<sub>2</sub> formation resulted for most diketones, i.e.  $\Phi_{1O_2} = 0.2-0.8$  (Table 2). Three mechanisms are conceivable for the formation of <sup>1</sup>O<sub>2</sub> from <sup>3</sup>1 and O<sub>2</sub> (Eqs 13a-c).<sup>8</sup>

Electron transfer:

$${}^{9}1 + O_2 \rightarrow 1^{++} + O_2^{-+} \rightarrow 1 + {}^{1}O_2$$
 (13a)

Diradical formation:

$$^{3}1 + O_{2} \rightarrow 1 - OO \rightarrow 1 + ^{1}O_{2}$$
 (13b)

Electron exchange:

$${}^{3}1 + O_2 \rightarrow 1 + {}^{1}O_2.$$
 (13c)

The first mechanism via electron transfer (Eq. 13a) is not appropriate in view of the constant photooxidation rates and constant ratios of epoxide– ${}^{1}O_{2}$ when changing to polar or protic solvents. The second mechanism of  ${}^{1}O_{2}$  formation via a diradical adduct (e.g. 3) is not acceptable on the basis of the fact that  ${}^{1}O_{2}$  is similarly produced from mesitil where the addition to C=O is sterically inhibited.<sup>‡</sup> Hence, the only mechanism possible for  ${}^{1}O_{2}$  formation is that of energy transfer via electron exchange (Eq. 13c). Electron exchange is believed to be operative for most cases of  $O_{2}$ quenching.<sup>8,26</sup>

The above consideration leads to a scheme, as a reaction of encounter complex 13, involving energy transfer from <sup>3</sup>1 to  $O_2$  (Eq. 14) and competitive addition of  $O_2$  to the excited carbonyl in <sup>3</sup>1 (Eq. 15). The photo-



is 0.80 for biacetyl (Table 1b). The combined quantum yields are lower for p,p'-dichloro- and p,p'dimethoxybenzils and much lower for mesityl and p,p'dihydroxybenzil. In these cases, processes (9) and/or (10) would be significant owing to a heavy atom effect, intramolecular charge-transfer or other process, but it is not the purpose of this study to deal with these effects. Hence, in the following discussion only processes (11) and (12) are considered to be major interactions between <sup>3</sup>I and O<sub>2</sub>. Discussion about PhQ and AcQ is excluded since their interaction with O<sub>2</sub> is minor owing to the occurrence of fast reactions with solvents or olefins.<sup>13,14</sup>

† The quenching rate of  ${}^{3}C = O$  with  $O_{2}$  is slower, by a factor of 10, than the diffusion rate. This was explained by assuming that  ${}^{3}(n\pi^{*})$  state carbonyls are less accessible for  $O_{2}$ . However, this explanation is not appropriate since  ${}^{3}(n\pi^{*})$  state carbonyls (e.g. 4-phenylbenzophenone) are quenched much more slowly, i.e. 1% of the diffusion rate.<sup>8</sup> The reason for this is not clear at present.<sup>27</sup>

<sup>†</sup> The slightly lower yield of <sup>1</sup>O<sub>2</sub> from mesitil (i.e.  $\phi_{1O_2} = 0.06$ ) might be due to either the lower  $\phi_{ST}^{-13e}$  or competitive intramolecular H abstraction from o-Me as has frequently been observed for ketones.<sup>29</sup> The irradiation of mesitil, however, in aerated MeOD afforded no detectable deuterized diketone so ruling out the latter possibility.

Y. SAWAKI

oxidation rate of  $\alpha$ -diketones was constant in different solvents and at various temperatures (from 20 to  $-60^{\circ}$ ), which suggests activation energies and the dependence on solvent polarity are practically identical between reactions (14) and (15). Here, the  $\beta$ -scission of the alkoxy radical, 3, is assumed to be very fast since the scission of the acyl radical in the  $\beta$ -acyl alkoxy radical is known to be very facile.<sup>30</sup> Moreover, since the triplet diketone, <sup>31</sup>, possesses excited energies of 50–60 kcal/mol, the diradical adduct, 3, might retain a significant amount of energy from its precursor.<sup>13</sup> This would accelerate the  $\beta$ -scission of the acyl radical from 3 and, hence, make the above assumption likely, i.e. that the radical, 3, decomposes immediately after its formation.<sup>†</sup>

What is the determining factor for selectivity of energy transfer (Eq. 14) or O<sub>2</sub> addition (Eq. 15)? While the yields of  ${}^{1}O_{2}$  are relatively high and constant (i.e.  $\Phi_{10} = 0.2-0.8$  in most cases, epoxide yields (i.e. Eq. 15) change with the structure of the diketones. The ratios of epoxide to <sup>1</sup>O<sub>2</sub> (i.e. ratios of Eqs 15-14) decrease the order of MeCOCOMe > PhCOCOMe in > PhCOCOPh » CQ, indicating a very facile addition of O2 to aliphatic acetyl group. This is the same order as the addition of nucleophiles to carbonyl compounds such as in hydration equilibria.<sup>31</sup> For example, 67% of biacetyl is hydrated in water but benzil is not hydrated appreciably. As for the reaction ratio of Eqs (15)-(14), the effect of ring substituents on benzil is mostly of no effect (i.e.  $\rho \sim 0$ ); the exception is that of diketones possessing a sterically inaccessible mesitoyl group. In sharp contrast, the addition of ROO<sup>-</sup>, a peroxidic nucleophile, to benzils exhibits a large polar effect (i.e.  $\rho \sim 3$ )<sup>32</sup> and the relative reactivity of CQ > PhCOCOMe > MeCOCOMe > PhCOCOPh is quite different from the present reaction (Y. Sawaki, unpublished). Since reaction (15) is the addition of neutral radical  $O_2$  to  ${}^{3}C==O$ , the polar effect of the ring substituents is not important. The resulting order of MeC=O > PhC=O is readily understood on the basis of an unfavourable decrease in resonance stabilization in the latter PhC=O group on going from 1 to 3.

In the case of unsymmetrical PhCOCOMe, the excitation might be expected to be located at the benzoyl group in view of its lower  $E_T$  energy (by 3-4 kcal/mol) compared to the aliphatic carbonyl.<sup>23</sup> But the resulting  $\Phi_{epoxide}$  is not close to that of benzil but between biacetyl and benzil (Table 1b). Judging from this, the excitation of PhCOCOMe seems to be on both groups; in other words, the two carbonyls conjugate each other. It is known that the dihedral angles between the two carbonyls in  $\alpha$ -diketones change from 90° for benzil to 180° for biacetyl and mesitil.<sup>33</sup> In view of the data in Table 1, there appears to be no relationship between the dihedral angles and  $\Phi_{1Q_2}$  or  $\Phi_{epoxide}$ .

Finally, benzophenone is efficient for  ${}^{1}O_{2}$  formation but inefficient for the photoepoxidation of olefin (Table 3). It is not certain whether or not a small amount of epoxide is formed via the adduct radical 14 (Eq. 16). This is because epoxides are often produced as a byproduct in the radical auto-oxidation of olefins.<sup>12</sup> In the case of benzaldehyde, 5% epoxide was obtained

# † In fact, no energy minimum could be attained for the calculated energies of $H_2C(OO^{\circ})(O^{\circ})$ by the MINDO/3 or INDO methods (Y. Sawaki and H. Kato, unpublished).

$${}^{3}R_{2}C = 0 \xrightarrow{O_{2}} R_{2}C \xrightarrow{OO}_{O_{1}} \xrightarrow{OO}_{O_{2}} Epoxidation (16)$$

from the olefin, 9. Again, epoxidation via 14 was not always ascertained owing to likely epoxide formation via the coauto-oxidation of aldehyde and olefin.<sup>18</sup> Any conclusion regarding the occurrence of O-transfer via 14, although of low efficiency, is not possible without more detailed studies.

#### **EXPERIMENTAL**

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

Materials. Compounds 4 and 9 were described previously.<sup>34</sup> Mesitil<sup>13e</sup> and 4,4'-dihydroxybenzil<sup>35</sup> were obtained as described in the lit. Substituted benzils have been described previously.<sup>4,29b,36</sup> Other materials were from commercial sources.

Photoepoxidation. Procedures for photoepoxidations were as noted previously.<sup>4</sup> A typical procedure for the determination of quantum yields is as follows. A 4 ml benzene soln of 2 mM  $\alpha$ -diketone and 0.1 M 1,2-dimethylcyclohexane in a Pyrex tube was irradiated under O<sub>2</sub> at over 320 nm for 1 hr at 20° using a 300 W medium pressure Hglamp. As a filter soln, 5% NaNO<sub>3</sub> aq was used. The mixture, after reduction with NaBH<sub>4</sub> and MeOH, was analysed by GLC using propiophenone or biphenyl as an internal standard. The incident light was determined using ferrioxalate actinometry.<sup>37</sup> The results are listed in Table 1. The quantum yields for the diketone disappearance were determined by UV absorbance.

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