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PHOTOOXIDATION AND PHOTOOXYGENATION OF α-DIAZOKETONE IN ALCOHOL

Hideo Tomioka,* Shingo Kondo, Kiyotsugu Misaki, and Yasuji Izawa
Department of Industrial Chemistry, Faculty of Engineering,
Mie University, Tsu, Mie 514 Japan

Summary. The investigation of the mechanism of oxidative-cleavage reaction of azibenzil in alcohol to give benzoates revealed the role of oxygen (either $^1O_2$ or $^3O_2$) in the photolysis of α-diazoketone.

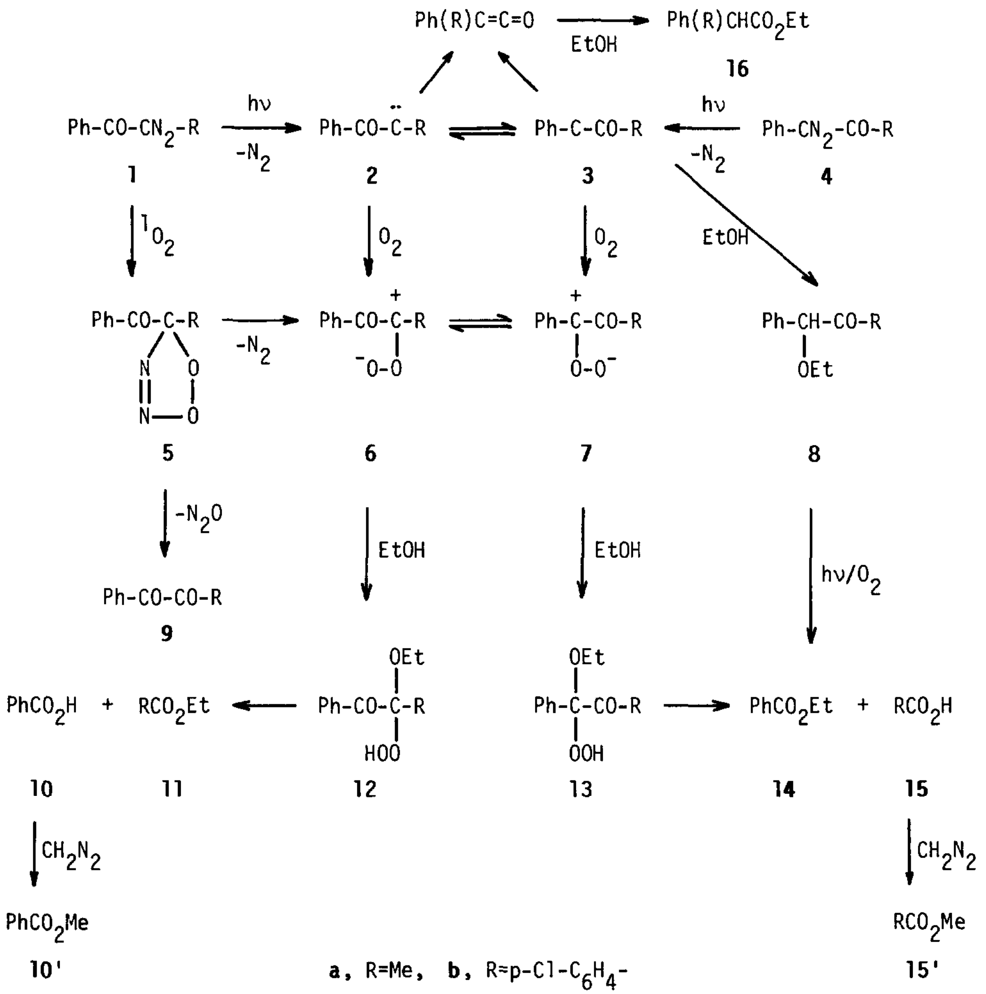
Recently we have obtained compelling evidence for the ketocarbene-ketocarbene interconversion (e.g , **2** $\rightleftarrows$ **3**) in the photochemical decomposition of isomeric α-diazoketones (**1** and **4**) in alcohol [1,2] For example, comparable formation of OH insertion product (**8a**) in the photolysis of either **1a** or **4a** in ethanol support the idea that the isomeric singlet carbenes are actually in equilibrium (Scheme I). We have found[1] that when the photolysis is carried out in the presence of oxygen, alkyl benzoates (e.g., **14**) were formed at the expense of 8a. Formation of **14** in the photolysis of 1 is of special interest since the process must include either ketocarbene-ketocarbene rearrangement (**1** → **2** → **3** → **8** → **14** or **1** → **2** → **3** → **7** → **13** → **14**) or carbonyl carbonyloxide-carbonyl carbonyloxide rearrangement (**1** → **2** → **6** → **7** → **13** → **14** or **1** → **5** → **6** → **7** → **13** → 14). In order to elucidate these possibilities we have examined the photooxidation and photooxygenation of pairs of unsymmetrical azibenzils (**1b** and **4b**)[3] in alcohol.

Direct irradiation of p-chlorophenylbenzoyldiazomethane (**1b**, 10^{-2} M) in oxygen-saturated ethanol using 300-W mercury lamp filtered by Corning CS-052 (>350 nm), followed by passing diazomethane into the reaction mixture gave four benzoates (**10'**, **11b**, **14**, and **15'b**), diketone (**9b**) and Wolff rearrangement product (WR, **16b**). Similar irradiation of isomeric azibenzil (**4b**) resulted in the formation of the same products but in different ratios (Table).

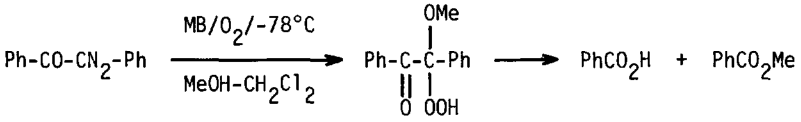
Photooxygenation of either **1b** or **4b** (10^{-2} M) in EtOH with methylene blue (10^{-3} M) sensitizer using a tungsten lamp filtered by Na_2CrO_4 (>550 nm)[4] followed by treatment with diazomethane also gave four possible benzoates (**10'**, **11b**, **14**, and **15'b**) along with large amount of diketone (**9b**) (Table). Almost complete elimination of the Wolff rearrangement product (**16**) indicates that free carbene is not involved in the present reaction

It has been shown[4,5] that carbonyl carbonyloxide (e g., **6b** and/or **7b**) generated by photosensitized oxygenation of azibenzil at -78°C is trapped by methanol to give α-ketomethoxy hydroperoxide which spontaneously decomposes to methyl benzoate and benzoic acid upon warming to room temperature (eq 1) Bailey et al[6] have studied the thermal decomposition of α-ketoethoxy hydrogenperoxide (**12a**) in EtOH (Scheme II) and have shown that **12a** rearranges to intermediate (**17a**) which then decomposes either (a) to give benzoic acid (10) and ethyl acetate (**11**) or (b) to give alcohol and a mixed anhydride (**18a**), which then undergoes alcoholysis to 10 and **11** or to ethyl benzoate (**14**) and acetic acid (15) Although the major reaction (path a, >85%) results

Scheme I



in **10** and **11**, a minor reaction (<15%) giving **14** and **15** also occurs. This implies that **14** and **15b** could be formed from 12b via alcoholysis of a mixed anhydride (18b). Control experiments showed, however, that trace (<1%) of ethyl benzoates (**11b** and **14**) were detected in ethanolic solution of **18b** even under irradiation Direct alcoholysis[6] of 12a to give 11 and 14 is also reduced since this could not explain that the yield of **11** (or 14) equals that of 10 (or 15). Thus, it appears adequate to suggest that the formation of **14** and **15** (or **10** and **11**) in the photooxygenation of



$$\text{Ph-CO-CN}_2\text{-Ph} \xrightarrow[\text{MeOH-CH}_2\text{Cl}_2]{\text{MB/O}_2\text{/-78°C}} \text{Ph-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-}\overset{\overset{\text{OMe}}{|}}{\underset{\underset{\text{OOH}}{|}}{\text{C}}}\text{-Ph} \longrightarrow \text{PhCO}_2\text{H} + \text{PhCO}_2\text{Me}$$

(1)[4]

Table   Photolysis of Azibenzil in O_2/EtOH

		yield, %[d]					
		benzoates				diketone	WR
Azibenzil	Conditions	**10'**	**11b**	**14**	**15'b**	**9b**	**16b**
1b	a	25.8	26.8	4.8	4.1	7.1	35.9
	b	e	15.2	5.9	e	trace	34.2
	c	25.3	27.5	5.0	5.2	44.4	trace
4b	a	4.9	5.6	24.5	23.0	6.0	29.9
	b	e	9.2	10.7	e	trace	33.1
	c	1.8	2.9	20.2	23.0	39.5	trace

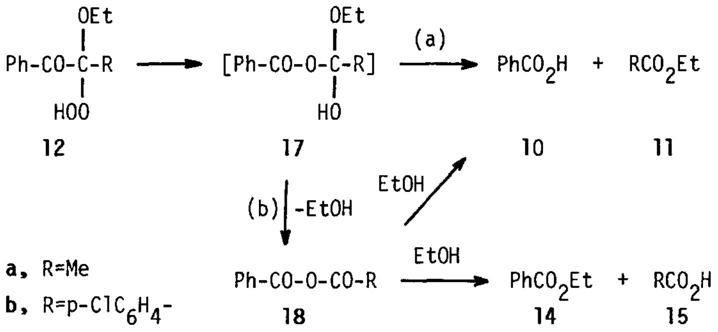
a) Direct irradiation using 300-W Hg-lamp filtered by Corning CS-052 (>350 nm)

b) About 10-fold excess of dabco was added to a)

c) Methylene blue-sensitized photooxygenation using a 150-W tungsten lamp filtered by Na_2CrO_4 (400 g/L).[4]

d) Determined by GC   e) Not determined

Scheme II



1b (or **4b**) involves, at least in part, carbonyl carbonyloxide rearrangement (**6** $\rightleftarrows$ **7**).[7]

Now what is an intermediate leading to benzoates in the direct photooxidation of azibenzil, then? OH insertion products (**8b**) were not detected in the reaction mixture, although control experiments showed that **8b** was stable under these conditions. This eliminates photooxidative cleavage[8] of 8b in alcohol as a possible route to benzoate. Inspection of the Table reveals that the ratio of diketone to benzoate is much larger in the dye-sensitized photooxygenation than in the direct photooxidation. Moreover, when dabco was added as a singlet oxygen quencher to the direct photolytic run, only diketone (**9**) was almost completely eliminated while benzoates were still formed (Table). It is immediately clear that, in protic media, the diketone is not formed from carbonyl carbonyloxide (**6** or **7**), which should be trapped efficiently by nucleophiles (e.g., EtOH) to give adduct (e.g., **12** and **13**) and that it should be formed only via elimination of N_2O from an adduct of $^1O_2$ and azibenzil, e.g., dioxapyrazoline (**5**),[9] under these conditions

If this is indeed so, using the amount of diketone formed in the direct photooxidation, it can be calculated that only ca 15% of benzoate is formed in the reaction of azibenzil with $^1O_2$ Thus most of benzoate should result from the reaction of molecular oxygen with free carbene It is well known that triplet carbenes react quite efficiently with oxygen This would lead to a diradical form of carbonyloxide, which would not be trapped by nucleophiles Presumably, a portion of the diradical carbonyloxide would be converted to the dipolar form which reacts with alcohol. It is not clear at present whether or not ketocarbene-ketocarbene rearrangement (2 $\rightleftarrows$ 3) is involved in formation of **14** (or **11**) in the direct photooxidation of **1** (or **4**) since carbonyl carbonyloxide rearrangement (6 $\rightleftarrows$ 7) has been shown to occur.

References and Notes

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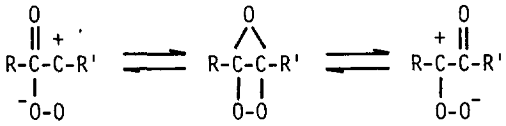
(7) (a) Ando et al have reported direct evidence for the dioxetane (A) intermediate in the low temperature photooxygenation of 2-diazo-3-butanone It is quite probable to assume that such



(A)

intermediate is involved in the carbonyl carbonyloxide rearrangement, W Ando, H Miyazaki, K. Itoh, and D Auchi, Tetrahedron Lett , 23, 555 (1982).

(b) Attempts to detect the hydrogenperoxide (**12** or **13**) by NMR at -78°C were unsuccessful by our hands

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(9) See for example, D P Higley and R. W Murray, J Am Chem Soc., 96, 3330 (1974)

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