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Mechanism for the Oxidative Cleavage of Electron-deficient Acetylenes with Alkaline Hydrogen Peroxide[1]

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4-Phenyl-3-butyn-2-one (**1a**) was effectively cleaved by alkaline hydrogen peroxide to afford benzoic and acetic acids. The rate ratio for the addition of HOO^- and HO^- to **1a** resulted in $k_{HOO^-}/k_{HO^-}=1400$, which is comparable to that of benzylideneacetone. The major reaction of the cleavage proceeds *via* benzoylacetone. As a minor pathway, α-keto oxirene intermediate is formed and rearranges only to α-benzoylpropionate in a different way from the corresponding diketo carbene. α-Keto esters are found to be converted by HOO^- to α-alkoxy ketones *via* a novel oxidative substitution of ester group. Methyl phenylpropiolate is oxidized by HOO^- similarly as **1a**. The mechanism is discussed on the basis of oxirene intermediate inconvertible to keto carbene.

The peroxy acid oxidation of acetylenes is understood much less than that of olefins;[2] its mechanism has been discussed in relation to oxirene and keto carbene intermediates.[2,3] The two intermediates are also interested theoretically[4a,b] since oxirenes are anti-aromatic 4π-electron species.[4c] Recently, we have reported that oxirene intermediates produced from phenylacetylenes and peroxy acid are further oxidized or rearrange to ketenes (Eq. 1), but are not convertible to keto carbenes.[5]

$$RC{\equiv}CR' \xrightarrow{\text{Peroxy acid}} RC(O)CR' \longrightarrow RR'C{=}C{=}O \quad (1a)$$

$$RC(O)CR' \longrightarrow RC(=O)CR'=O \quad (1b)$$

Acetylenes are known to be less reactive toward electrophiles but more reactive toward nucleophiles than olefins.[6] Although the epoxidation of α-keto olefins with alkaline hydrogen peroxide is well known,[7] few is known about the nucleophilic oxidation of acetylenes by peroxides. We were interested in the alkaline hydrogen peroxide oxidation of electron-deficient acetylenes,[8] and herein wish to summarize our mechanistic study on the facile C-C cleavage. A study on similar cleavage of acetylenes has appeared,[9] but mechanistic details are still unclear.

Results and Discussion

Oxidative Cleavage of Acetylenes with HOO^-. An attempted oxidation of phenylacetylene with alkaline hydrogen peroxide (HOO^-) was ineffective, but electron-deficient acetylenes are smoothly cleaved by HOO^-. Thus, the oxidation of 0.1 M 4-phenyl-3-butyn-2-one (**1a**) with 1 M H_2O_2 and 0.2 M NaOH in 50% EtOH was complete within 2 h at room temperature (1 M=1 mol dm^{-3}). One molar acetylene consumed

$$\underset{\mathbf{1a}}{PhC{\equiv}CCOMe} \xrightarrow{HOO^-} \underset{95\%}{PhCO_2H} + \underset{93\%}{MeCO_2H} + \underset{48\%}{CO_2} \quad (2)$$

three moles of H_2O_2, affording high yields of benzoic and acetic acids; the yield of CO_2 was not quantitative and formic acid was detectable.

Similar oxidation of methyl phenylpropiolate ($PhC{\equiv}CCO_2Me$, **1b**) with excess HOO^- afforded $PhCO_2H$ (99%) and CO_2 (96%). Here, 96% yield of CO_2 does not mean quantitative one since **1b** possesses two carbons available for decarboxylation. As the excess amount of H_2O_2 was decreased, the hydrolysis of **1b** became a major path and the resulting propiolate ion was quite stable toward HOO^-. 55—70% yields of C-C cleavage has been reported for the case of 4-phenyl-3-butyn-2-ones,[9] but present results indicate that almost quantitative cleavage may be accomplished by using excess H_2O_2 in aqueous alcohols.

Kinetics. The rate of addition of HOO^- to acetylene **1a** was determined in water by following the decrease of **1a** using excess H_2O_2. The rate increased linearly with $[HO^-]$ up to pH 11, reaching a constant value at pH>12 and pK_a of H_2O_2 is 11.37; hence the rate quation satisfies Eq. 3.

$$v = k_2[PhC{\equiv}CCOMe][HOO^-] \quad (3)$$

The rate constants, $10\,k_2$, for **1a** are 1.04, 1.39, 1.97, 2.50, and 3.47 $M^{-1}\,s^{-1}$ at 15.0, 20.0, 25.0, 30.0, and 35.0 °C, respectively, at pH 11.2 (Na_2CO_3 buffer). For comparison, the epoxidation rate of benzylideneacetone (**2**) was also determined; $10\,k_2$=1.40, 1.76, 2.32, 3.03, and 3.79 $M^{-1}\,s^{-1}$, respectively. The resulting activation parameters are listed in Table 1.

The addition rate of HO^- (0.05—0.28 M) for **1a** to form benzoylacetone was found to be a combination of two- and third-order kinetics (Eq. 4).

$$v = \{k_2[HO^-]+k_3[HO^-]^2\}[PhC{\equiv}CCOMe] \quad (4)$$

The third-order kinetics suggest a base-catalysis by second HO^- ion, *i.e.*, an attack with $HO^-\cdots HO^-$. Similar third-order kinetics are known for nucleophilic additions[11] such as hydrolysis[12] and aminolysis[13] of esters.

It is generally accepted that acetylenes are more susceptible to nucleophilic attacks than olefins.[6] But acetylene **1a** and olefin **2** have rates of similar magnitude for both additions of HOO^- and HO^-. A small kinetic differences between **1a** and **2** lies in the change in activation parameters; while the activation enthalpy (ΔH^*) for acetylene **1a** is slightly higher than olefin **2**, entropy requirement for **1a** is substantially smaller. The larger entropy loss for olefin **2** is probably due to the rather restricted orientation in the Michael addition

Table 1. Kinetic data for the addition of HOO^- and HO^- to PhC≡CCOMe (**1a**) and PhCH=CHCOMe (**2**) in water at 25.0 °C[a)]

Substrate	Nucleophile	k_2 / $M^{-1}\,s^{-1}$	k_3 / $M^{-2}\,s^{-1}$	ΔH^* / kcal mol^{-1}	ΔS^* / e.u.	α-Effect
1a	HOO^-	1.67×10^{-1}		11.0	−18	1.39×10^3
	HO^-	1.20×10^{-4}	8.5×10^{-3}			
2	HOO^-	2.20×10^{-1}		9.1	−24	1.92×10^3
	HO^-	1.14×10^{-4}	2.2×10^{-4}			

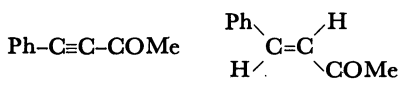
a) The oxidation was conducted with 5×10^{-5} M substrate and 2—10 mM H_2O_2 in an aqueous buffer of 0.1 M Na_2CO_3. The addition reaction of HO^- was carried out with 5×10^{-5} substrate and and 0.05—0.3 M NaOH. The rates were monitored by the decrease of UV absorbance of **1a** or **2**. Notations for k_2 and k_3 are shown in Eqs 3 and 4.

Table 2. Oxidation: of acetylenes and related compounds with alkaline H_2O_2[a)]

Substrate (S)	S : H_2O_2	Products (%)[b)]					
		$PhCO_2H$	**3**	**4**	**5**	**6a**	Others
PhC≡CCOMe (**1a**)	1 : 1	46	24	3	2	2	$PhCO_2Me$ (1%), Adducts (28%)[c)]
	1 : 5	92	5	6	2	1	
	1 : 0	0	12	0	0	0	MeOH adducts (70%)[c)]
	1 : 1[d)]	40	22	6	2	<1	e)
	1 : 1[f)]	50	17	6	2	<1	e)
$PhCOCH_2COMe$ (**3**)	1 : 1	27	73[g)]	0	0	0	
	1 : 5	71	14[g)]	0	0	0	
PhCOCH(Me)CO_2Me (**7a**)	1 : 1	19	0	11	17	33	
	1 : 5	32	0	11	16	16	
	1 : 0	0	0	≈10	10	0	Recovered **7a** (80%)
McCOCH(Ph)CO_2Me (**7c**)	1 : 5	22	0	0	0	39[h)]	$PhCH_2COMe$ (16%); $PhCH_2CO_2Me$ (2%)
	1 : 0	0	0	0	0	0[h)]	$PhCH_2CO_2Me$ (85%)
PhC≡CCO_2Me (**1b**)	1 : 1	45			1[i)]	5[j)]	$PhCO_2Me$ (22%); PhC≡CCO_2H (20%)
	1 : 5	56			1[i)]	0[j)]	$PhCO_2Me$ (6%); PhC≡CCO_2H (25%)
	1 : 0	0			0[i)]	0[j)]	Adduct[k)] (10%); **1b**[g)] (90%)
$PhCOCH_2CO_2Me$ (**7b**)	1 : 1	34			3[i)]	19[j)]	Recovered **7b** (33%)
	1 : 5	70			3[i)]	14[j)]	
	1 : 0	0			0[i)]	0[j)]	Recovered **7b** (100%)

a) Reaction with 0.02 M substrate and 0.1 M MeONa at 20—25 °C for 1 h. b) Products were determined by GLC and/or NMR. c) Ph(MeO)C=CHCOMe; cis : trans ratio being 7 : 3. d) Reaction in EtOH. e) Not determined. f) Reaction in *i*-PrOH. g) Recovered. h) **6c**. i) Acetophenone. j) **6b**. k) Ph(MeO)C=$CHCO_2Me$; cis : trans ratio of *ca.* 1 : 1.

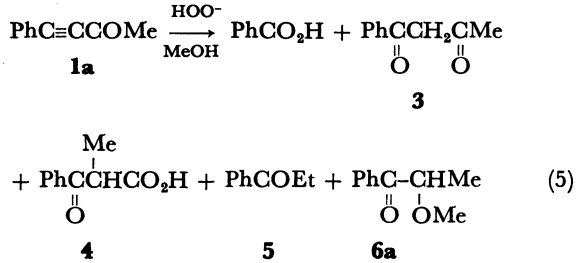
to the planar olefin. On the other hand, the addition to linear acetylenic moiety of **1a** requires smaller restriction on orientation, thus lowering entropy loss in attaining the transition state.



1a **2**

The rate ratio of HOO^- *vs* HO^- is known to exhibits a large α-effect;[14] *e.g.*, the α-effect in the addition to nitriles is in the range of 3000—10000.[15] The ratios k_{HOO^-}/k_{HO^-} for the present reaction are 1400 and 1900 for acetylene **1a** and olefin **2**, respectively (Table 1). A trend has been noted that nucleophilic additions to sp carbon exhibit a larger α-effect than addition to sp^2 carbon.[16] But no significant difference was found between acetylene **1a** (*i.e.*, sp carbon) and olefin **2** (*i.e.*, sp^2 carbon). It seems that there is no single factor to govern the α-effect, although several explanations have been noted on the origin of the effect.[17]

Intermediates. In order to clarify the oxidation mechanism, searches for intermediates were carried out with 1 h reaction in MeOH. GLC, NMR, and GC-MS analyses indicated several intermediates during the oxidation with HOO^- (Table 2). Considerable amounts of adducts with solvent MeOH were produced when **1a** : H_2O_2 was 1 : 1, but became negligible with **1a** : H_2O_2 = 1 : 5. Products from **1a** and HOO^- are shown in Eq. 5; major intermediates were benzoylacetone **3** and α-benzoylpropionic acid **4**. Minor by-products were propiophenone **5** and α-methoxypropio-

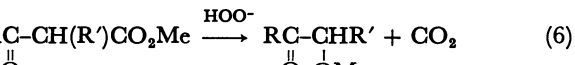


1a **3**

4 **5** **6a** (5)

phenone **6a**, both of which were shown to be produced from methyl α-benzoylpropionate (**7a**) by a control experiment.

The reaction of methyl phenylpropiolate (**1b**) with HOO⁻ afforded, in addition to benzoic and phenylpropiolic acids, methyl benzoate, acetophenone, and α-methoxyacetophenone in MeOH (Table 2). Again, control experiments revealed that the latter two products



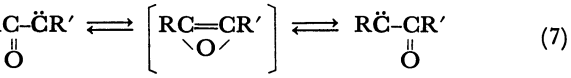
(6)

7 **6**

a, R=Ph, R′=Me
b, R=Ph, R′=H
c, R=Me, R′=Ph

are formed from methyl benzoylacetate (**7b**) and HOO⁻. Thus the formation of α-alkoxy ketones (**6**) from β-keto esters is a novel oxidative substitution of ester group (Eq. 6). The yield of **6** is 33, 19, and 39% from **7a**, **7b**, and **7c**, respectively. For the case of **7b**, its reaction with MeONa alone yielded methyl phenylacetate *via* MeO⁻-catalyzed deacylation.

Decomposition of Diazo Diketone. In the decomposition of α-diazo ketones, ketocarbene-ketocarbene interconversions have been proved experimentally, where oxirenes are often supposed to be an intermediate (Eq. 7).[18] On the other hand, it is reasonable to assume



(7)

8a **8b**

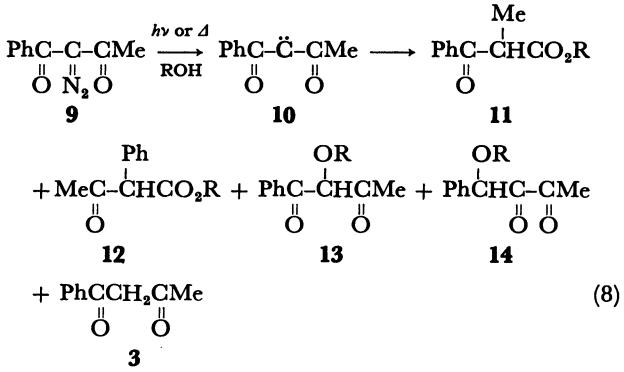
that acetylenes are attacked electrophilically by peroxy acid to form oxirenes in analogy with olefin epoxidation.[3,5] Likewise, a generation of oxirene intermediate is conceivable in the present nucleophilic oxidation of acetylene **1a** or **1b** with HOO⁻.[9] In order to check the intermediacy of oxirene and/or keto carbene, the decomposition of 2-diazo-1-phenyl-1,3-butanedione (**9**) was carried out in alcohols (Table 3). Major products *via* carbene **10** were rearranged esters (**11** and **12**), O–H inserted diketones **13** and **14** (Eq. 8), diketone **14** being formed *via* O–H insertion of isomerized keto carbene from **10**. Benzoylacetone **3**, a hydrogen abstraction

Table 3. Photolysis and thermolysis of diazo ketone (**9**)[a]

Solvent	Conditions	Products (%)[b]				
		11	**12**	**13**	**14**	**3**
MeOH	*hν*(>290 nm)/8 h	26	13	26	≈10	0
	hν(290 nm)/N_2/8 h	26	11	28	≈13	0
	hν(254 nm)/4 h	21	11	20	≈3	0
	Δ(80 °C)/4 h	15	28	21	≈10	<1
EtOH	*hν*(>290 nm)/5 h	30	11	17	≈3	≈1
	hν(254 nm)/5 h	38	13	10	≈11	≈3
	Δ(95 °C)/4 h	16	27	16	≈12	8

a) A solution of 0.02 M **9** was photolyzed at room temperature or thermolyzed under air unless noted otherwise.
b) Products were detemined by NMR, GLC, and GC-MS. The structure of diketone **14** was deduced from its GC-MS spectra although it could not be isolated.

product, was negligible in MeOH (Eq. 8). The product ratios were not changed largely by changing the decomposition conditions, *e.g.*, wavelength of irradiating light,[19] air, or temperature. Somewhat different ratio



(8)

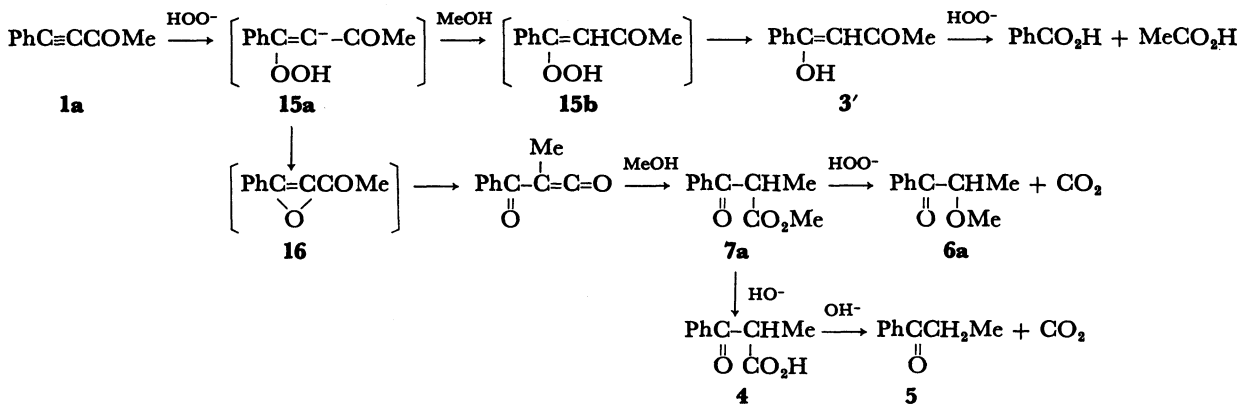
9 **10** **11** **12** **13** **14** **3**

of products has been reported for the photolysis of **9**.[21] The present values are more accurate since the reaction mixture was analyzed directly by NMR and GLC. At any rate, it is apparent that β-diketone **3** is not formed in MeOH and the Wolff rearrangement afforded two products **11** and **12** by methyl and phenyl migration.

Oxidation Mechanism. One of mechanistic points for the HOO⁻ oxidation of electron-deficient acetylenes lies in the intermediacy of oxirene and/or keto carbene. As noted above, acetylbenzoylcarbene **10** affords two products *via* the Wolff rearrangement (*i.e.*, **11** and **12** by Me and Ph migration), but benzoylacetone **3** is not formed in MeOH. In contrast, major primary products for the reaction of **1a** and HOO⁻ are β-diketone **3** and rearranged ester **7a**, which is converted to hydrolyzed acid **4**, propiophenone **5**, and α-methoxypropiophenone (**6a**) (Eq. 5). It is noteworthy that any products (*e.g.*, methyl phenylacetate or α-methoxybenzyl methyl ketone (**6c**)) were not detectable. Therefore, keto carbene (*e.g.*, **10**) is not involved in the HOO⁻ oxidation of **1a**, excluding an equilibrium reaction such as Eq. 7. This is consistent with our recent results not involving ketocarbene in the electrophilic oxidation of phenylacetylenes with peroxy acid.[5] According to calculation by MINDO/3 method oxirene is more stable than keto carbene,[22] but more rigorous ab initio methods leads to a reverse result.[23] Our previous[5] and present studies suggest a rearrangement *via* oxirene itself and a significant energy barrier in isomerization between oxirene and keto carbene.

A reasonable pathway for the nucleophilic oxidation of **1a** would then be formulated as Scheme 1. The addition of HOO⁻ to **1a** produces **15a**, which cyclizes to form α-keto oxirene **16** or is protonated to yield adduct **15b**.[24] For the case of olefinic ketones, the cyclization to epoxides is very facile.[7] But for acetylenic ketones the cyclization to oxirene **16** would be significantly retarded owing to its large strain energy.[25]

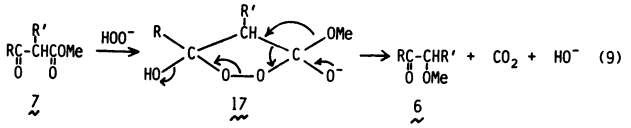
Recently we have reported that the migration aptitude in oxirene rearrangement (*i.e.*, H≫Me>Ph) is in line with that of the Wolff rearrangement of keto carbene.[5] In fact, the rearrangement of ketocarbene **10** afforded two products **11** and **12** by Me and Ph migration, respectively. In contrast, the present oxidation of **1a** with HOO⁻ yielded only **7a** as a rearranged product.



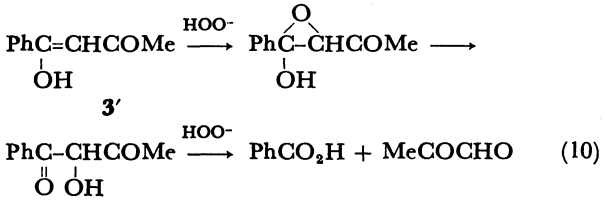
Scheme 1.

This is comprehensible because oxirene **16** is unsymmetrically substituted and the two groups are attacked to different migration origins, *i.e.*, methyl group to carbonyl and phenyl group to oxirene. Methyl migration in oxirene **16** affords β-benzoyl ester **7a** *via* ketene. Subsequent decarboxylation of β-keto acids is well known.[26]

The novel reaction of β-keto esters with HOO^- to afford α-alkoxy ketones is interesting mechanistically. An appropriate scheme for this oxidative substitution is outlined in Eq. 9, which is somewhat similar to the ring contruction of β-diketones with H_2O_2 (*e.g.*, the synthesis of cyclopentanecarboxylic acid from α-acylcyclohexanone).[27]

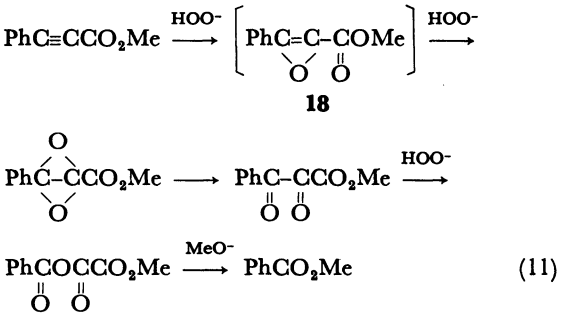


As a major pathway for the HOO^- oxidation of **1a**, carbanion **15a** is protonated to form olefinic hydroperoxide **15b**, which would be promptly decomposed into β-diketone **3** (or its enol **3'**).[28] The diketone **3** could be isolated in *ca.* 30% yield from the reaction mixture at an earlier stage. A possible scheme for the cleavage of **3** is probably *via* an epoxidation of enol **3'** (Eq. 10).[29]



The facile cleavage of α-hydroxy ketones with HOO^- is reported previously.[30a] The involvement of pyruvaldehyde is in agreement with a fact that CO_2 yields from the aldehyde were in the same range (40—50%) with those from diketone **3'** when treated with a mixture of 1.2 M H_2O_2 and 0.2 M NaOH in 50% EtOH.[30b]

The HOO^- oxidation of **1b** would proceed similarly as Scheme 1. The formation of methyl benzoate seems to suggest a diepoxide pathway (Eq. 11). Since methoxyl group in **18** is probably of very low migratory aptitude, oxirene **18** is further oxidized to diepoxide and then to α-diketone. Ester formation from α-diketone and HOO^-/MeO^- is established.[31]



In conclusion, acetylenic ketone **1a** is cleaved efficiently by HOO^-, β-diketone **3** being a predominant intermediate. α-Keto oxirene is probably formed even as a minor pathway and affords rearranged products in a different way from the corresponding diazo ketone. β-Keto esters are found to be oxidized by HOO^- to α-alkoxy ketones *via* a novel oxidative substitution of ester group.

Experimental

IR and NMR spectra were recorded on a Parkin-Elmer 337 and a Hitachi R-24 spectrometer, respectively. GLC analysis was carried out by a Yanagimoto G-180 gas chromatograph using biphenyl as an internal standard and three columns: PEG 20M, 10% on Chromosorb WAW, 1 m; Silicon OV-17, 5% on Shimalite W, 1 m; Apiezone GE 15% and 5% H_3PO_4 on Celite 545, 1.5 m. GC-MS spectra were recorded on a JEOL JMS D300 mass spectrometer.

Materials. 4-Phenyl-3-butyn-2-one (**1a**),[32] methyl phenylpropiolate (**1b**),[33] and methyl α-benzoylpropionate (**7a**)[34] were prepared by the literature methods. Methyl α-acetylphenylacetate (**7c**) was prepared from α-phenylacetoacetonitrile.[35] α-Methoxypropiophenone (**6a**) and α-methoxy-α-phenylacetone (**8c**) were obtained by BF_3-catalyzed decomposition[36] of α-diazopropiophenone[37] and 1-diazo-1-phenyl-2-propanone.[38] 2-Diazo-1-phenyl-1,3-butanedione (**9**) was synthesized from benzoylacetone and tosyl azide.[39] Purities of these materials were checked by NMR and/or GLC analysis.

Oxidation of 4-Phenyl-3-butyn-2-one (1a) with HOO⁻. In a 50-ml flask were added EtOH (6 ml), 4 M H_2O_2 (12 ml), **1a** in EtOH (1 M×2 ml), water (10 ml), 10^{-2} M EDTA (2 ml), and 1 M NaOH (8 ml). After 10 h at 25 °C, 1 M HCl (10 ml) was added and evolved CO_2 gas was determined by titration with aqueous $Ba(OH)_2$. Then the reaction mixture was

diluted with saturated NaCl and extracted three times with ether. Benzoic and acetic acids were determined by GLC after methylation with diazomethane.

In another run, benzoylacetone **3** could be isolated from 15 min reaction of 0.08 M **1a**, 0.17 M H_2O_2, and 0.17 M NaOH in 50% EtOH at 25 °C. After acidification with HCl, dilution with water, and extraction with ether, 30% of **3** was isolated by column chromatography using Mallinckrodt silica gel (100 mesh, pH 4) and petroleum ether–chloroform (2 : 1). Its NMR and IR spectra were identical with those of authentic sample.

The addition rate of HOO^- was followed by UV absorbance of **1a** at 277 nm in water. The reaction was conducted with 5×10^{-5} M **1a** and 2—10 mM H_2O_2 in buffered aqueous solution. The results are listed in Table 1.

Decomposition of 2-Diazo-1-phenyl-1,3-butanedione (9). Photolysis of **9** was conducted with a low pressure (254 nm) or medium pressure Hg lamp (>290 nm through Pyrex filter). Typically, a solution of 0.02 M **9** in alcohol was photolyzed for 4—8 h at room temperature. Thermolysis was carried out at 80 °C in MeOH or 90 °C in EtOH. The products were identified and determined by NMR, GLC and/or GC-MS analyses.

NMR and GC-MS Data. NMR data for products and authentic sample are as follows (δ, $CDCl_3$). Benzoylacetone (**3**): 2.17 (s, 3H), 6.15 (s, 1H), 7.4—8.0 (m, 5H); minor keto isomer: 2.27 (s, 3H), 4.07 (s, 2H). Methyl α-benzoylpropionate (**7a**): 1.50 (d, J=5.6 Hz, 3H), 3.68 (s, 3H), 4.41 (q, J=5.6 Hz, 1H), 7.4—7.6 (m, 3H), 7.9—8.1 (m, 2H). α-Methoxypropiophenone (**6a**): 1.43 (d, J=6.7 Hz, 3H), 3.29 (s, 3H), 4.42 (q, J=6.7 Hz, 1H), 7.4—7.6 (m, 3H), 7.9—8.2 (m, 2H). Methyl α-benzoylacetate (**7b**); keto isomer: 3.64 (s, 3H), 3.86 (s, 2H); enol isomer: 3.73 (s, 3H), 5.62 (s, 1H), 12.66 (s, 1H); 7.3—8.0 (m, 5H). Methyl α-acetylphenylacetate (**7c**): 2.06 (s, 3H), 3.65 (s, 3H), 4.52 (s, 1H), 7.23 (s, 5H). α-Methoxyacetophenone (**6b**): 3.40 (s, 3H), 4.50 (s, 2H), 7.4—7.6 (m, 3H), 7.85—8.04 (m, 2H). α-Methoxy-α-phenylacetone (**6c**): 2.11 (s, 3H), 3.89 (s, 3H), 4.67 (s, 1H), 7.39 (s, 5H); GC-MS, *m/e* (relative intensity), 43, 121 (100%), 164 (<1%).

2-Methoxy-1-phenyl-1,3-butanedione (**13**, R=Me): 2.24 (s, 3H), 3.30 (s, 3H), 7.2—7.6 (m, 5H), 14.95 (s, 1H); GC-MS, *m/e* (rel intensity), 105 (100), 118 (25), 150 (35), 160 (11), and 192 (3). 1-Methoxy-2-phenyl-1,3-butanedione (**14**, R=Me): 2.36 (s, 3H), 3.54 (s, 3H), 5.10 (s, 1H); GC-MS, *m/e* (rel intensity), 105 (18), 118 (60), 150 (100), 160 (27), and 192 (9). 2-Ethoxy-1-phenyl-1,3-butanedione (**13**, R=Et): 1.18 (t, J=5 Hz, 3H), 2.34 (s, 3H), 3.58 (q, J=5 Hz, 2H), 15.2 (s, 1H); GC-MS, *m/e* (rel intensity), 91 (4), 105 (100), 118 (21), 136 (11), 160 (14), 164 (36), and 206 (4). 1-Ethoxy-2-phenyl-1,3-butanedione (**14**, R=Et): 1.21 (t, J=5 Hz, 3H), 2.29 (s, 3H), 3.70 (q, J=5 Hz, 2H), 5.13 (s, 1H); GC-MS, *m/e* (rel intensity), 91 (9), 105 (17), 118 (49), 136 (30), 160 (34), 164 (100), 165 (11), and 206 (8).

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