ringe through the septum to give the characteristic deep red color of the anion. THF (50 mL) was distilled into another side-arm flask containing a carefully weighed amount of halide (1.0 to 10.0 mmol) also under an argon atmosphere.

The rapid-mixing stopped flow apparatus, thermostated at 20 °C, was flushed with several aliquots of dry THF and then with the anion solution until the effluent in the stop syringe maintained the anion color. Solutions of anion and halide were transferred to the apparatus by gas-tight syringes in a manner that excluded air or moisture. After several flushes of the respective chambers by the anion and halide solutions, oscilloscope traces of multiple runs were photographed. Each photograph was analyzed by measuring the intensities at various times and obtaining the pseudo-first-order slope by computer analysis.

9,10-Dihydroanthracene. To a solution of anthracene (36 g, 20 mmol) in THF (300 mL) and an excess of sodium (20 g) was added methanol (75 mL) over a period of 3 h. The product was isolated and recrystallized twice from ethanol to give 27 g, mp 107–108 °C (lit.[10b] mp 108 °C).

Alkylation of 9-Alkyl-9,10-dihydroanthracene. All the reactions were conducted in the following way. To the 9-alkyl (5 mmol) dissolved in 100 mL of THF and maintained under an atmosphere of argon at −40 °C was added over 30 min *n*-butyl lithium (5 mmol, 2.3 M in hexane). The solution turned red immediately. After 30 min of stirring, the alkyl halide (2 mL in 40 mL of THF) was added drop by drop. After decolorization and extraction with ether, the reaction products were analyzed by gas chromatography (3 m, 10% silicon QF, on Varaport 100–120, at 130 °C). The products were separated by chromatography on an activated aluminum column. The isomers were first collected together and the purity was checked by mass spectroscopy. A second chromatography using petroleum ether eluted first the trans isomer, next the cis isomer, and finally 9-alkyl-9,10-dihydroanthracene.

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Registry No.—9,10-Dihydroanthracene, 613-31-0; anthracene, 120-12-7.

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Oxidative Cleavage of α-Ketols and Related Ketones with Alkaline Hydrogen Peroxide[1]

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The oxidative C–C cleavage of α-ketols $R_1COC(OH)R_2R_3$ (**1**) has been found to proceed smoothly with alkaline hydrogen peroxide in aqueous methanol affording high yields of ketones $R_2R_3C{=}O$ and carboxylic acids R_1CO_2H. The reaction obeys second-order kinetics: $v = k_2[R'OO^-][\text{ketol}]$, where $R'OO^-$ may be t-$BuOO^-$ or $PhCO_3^-$ in place of HOO^-. The cleavage of aromatic ketones (R_1 = Ph) is much faster than that of aliphatic ketones (R_1 = Me). The relative rate with $PhCO_3^-$ (a stronger oxidant) vs. HOO^- varies from 0.14 to 2.8 with changing ketols. These results are explained by the rate-determining concerted fragmentation of the C=O adduct **6** (Scheme I). Acyloins (**1**, R_2 = H) were cleaved to carboxylic acids and aldehydes R_3CHO, which were further oxidized to acids. α-Amino ketones **3** were cleaved to ketimine or ketone. α-Methoxy-α,α-diphenylacetophenone (**2**) is also cleaved, the rate being only $^1/_{2000}$ that of the corresponding α-ketol **1a** ($R_1 = R_2 = R_3$ = Ph), to benzophenone dimethyl acetal and α-hydroperoxy-α-methoxydiphenylmethane, suggesting an intermediacy of α-alkoxy carbonium ion. Alkaline hydrogen peroxide is advantageous in the selective cleavage of α-ketols in comparison with the other ordinary oxidants.

Ordinary reagents for the oxidative cleavage of α-hydroxy ketones (α-ketols) are periodic acid in aqueous solution and lead tetraacetate in organic solvents.[2] The other known reagents are bromine,[3] peracids,[4] and nickel peroxide.[5] We wish to report here that alkaline hydrogen peroxide is a mild and effective oxidant for the cleavage of α-ketols and related ketones. This reagent is inactive to 1,2-glycols, contrary to the case with periodic acid or lead tetraacetate, and hence may cleave α-ketols selectively even in the presence of a 1,2-dihydroxy group.

Results and Discussion

Oxidative Cleavage of α-Phenylbenzoins. α-Phenylbenzoin **1a** ($R_1 = R_2 = R_3$ = Ph) can be easily oxidized by al-

Table I. Rates of Oxidative Cleavage of α-Phenylbenzoin 1a by Alkaline Hydrogen Peroxide in 80% Aqueous MeOH at 25.0 °C[a]

Initial concentrations, M [α-ketol]	[H_2O_2]	[NaOH][a]	HOO^-, %[b]	$10^2 k_{obsd}$,[c] $M^{-1} s^{-1}$
(A) Effect of [α-ketol] and [H_2O_2]				
0.05	0.10	0.30	79	6.65
0.05	0.05	0.30	79	6.71
0.05	0.025	0.30	79	6.31
0.07	0.04	0.30	79	6.89
(B) Effect of [NaOH]				
0.05	0.05	0.025	24	~1.53
		0.05	39	2.38
		0.10	56	4.14
		0.20	72	6.05
		0.30	79	6.71
		0.50	86	7.20
(C) Oxidation with *t*-BuOOH in place of H_2O_2				
0.05	0.05	0.1	10[d]	0.49
		0.2	18[d]	1.03
		0.4	31[d]	2.12

[a] [NaOH] indicates total alkali concentration added as aqueous NaOH containing 0.05 mol % EDTA based on [NaOH]. Since MeOH is more acidic than water, most of the added base exists as MeO^- rather than HO^-. [b] Percent dissociation of R'OOH was obtained from the K_6 values of 12.7 and 1.13 M^{-1} for R' = H and *t*-Bu, respectively, in 80% MeOH at 25 °C. [c] Second-order plots vs. time were linear up to 80% conversion; probable error ±5%. [d] *t*-$BuOO^-$.

kaline hydrogen peroxide to give high yields of benzophenone and benzoic acid in aqueous MeOH at 25 °C (eq 1). The re-

$$\underset{\text{1}}{R_1\overset{\overset{O}{\|}}{C}-\overset{OH}{\overset{|}{C}}R_2R_3} + H_2O_2 \xrightarrow[\text{aq MeOH}]{\text{NaOH}} R_1CO_2H + R_2R_3C{=}O \quad (1)$$

action is complete within 1 h with a 1:1 stoichiometry of **1a** and H_2O_2. The rate was followed iodometrically and expressed as eq 2 as obvious from Table I(A).

$$v = k_{obsd}[H_2O_2][\text{ketol}] \quad (2)$$

The k_{obsd} value increases with increasing [NaOH] and approaches a constant at high base concentrations [Table I(B)]. All the reactions were started by adding aqueous NaOH containing 0.05 mol % EDTA to avoid a possible redox reaction, although the presence or absence of EDTA was not essential under our conditions. The oxidation with alkaline *t*-BuOOH is considerably slow at low base concentrations but has a comparable rate at high alkalinity [Table I(C)]. The reaction does not occur in neutral solution or in the presence of sodium acetate.

The cleavage reaction of substituted α-phenylbenzoins proceeds similarly to give benzophenone in 80–95% yields. The rates are faster for the ketols with electron-attracting groups, affording a Hammett's ρ value of 1.96 (vs. σ) with a correlation coefficient $r = 0.995$ (Table II). The positive ρ value is comprehensible in view of the substituent effect for a nucleophilic addition to C=O, which is of the similar magnitude with other additions to C=O (i.e., ρ = 2–3).[6]

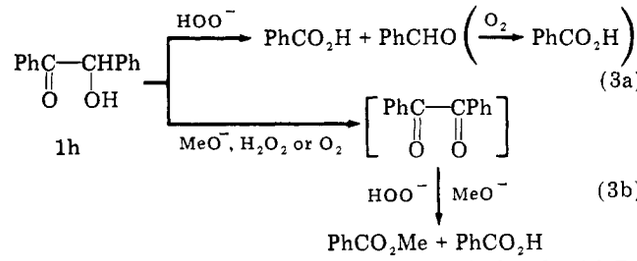
Cleavage of Other α-Ketols and Related Compounds. Various α-ketols are likewise cleaved by alkaline hydrogen peroxide to give carboxylic acids and ketones or aldehydes (Table III). When R_2 = H (**1i,j**), produced aldehydes are further oxidized to acids. The base-catalyzed oxidation or autoxidation (eq 3b) also occurs competitively for the case of benzoin **1h**, affording benzoic acid, benzaldehyde, and methyl benzoate. The formation of the ester occurs probably via

Table II. Oxidative Cleavage of Substituted α-Phenylbenzoins by Alkaline Hydrogen Peroxide[a]

Ketol	Registry no.	R_1 in $R_1\overset{\overset{O}{\|}}{C}-\overset{OH}{\overset{|}{C}}Ph_2$	$10^2 k_{obsd}$,[b] $M^{-1} s^{-1}$
1b	4338-69-6	*p*-MeOPh	1.16
1c	4625-47-2	*p*-MePh	1.43
1a	4237-46-1	Ph	4.14
1d	63704-18-7	*p*-ClPh	11.0
1e	63704-19-8	*m*-ClPh	18.2

[a] Reaction with [ketol] = [H_2O_2] = 0.05 M, [NaOH] = 0.10 M, and [EDTA] = 10^{-4} M in 80% MeOH at 25.0 °C. Ph = C_6H_5 or C_6H_4. Substituted phenylbenzoins afforded benzophenone in 80–95% yields and the corresponding benzoic acids which were identified as methyl esters. [b] Average of two or three determinations. Plot of log k_{obsd} vs. σ gives ρ = 1.96 (r = 0.995).

benzil as shown in eq 3b.[7] While the autoxidation of benzoin is a slow reaction with base alone,[8] the present oxidation with alkaline H_2O_2 is complete within several minutes under N_2 and hence the oxidation may proceed also via the reaction of H_2O_2 with the enolate ion of **1h** to afford benzil.



The rates of cleavage are much faster for the ketols with R_1 = Ph than that with R_1 = Me (**1g**); when R_2 = H, the order of reactivities is **1h** > **1i** ≫ **1j**. Mandelic acid (**1k**) is also cleaved slowly with excess H_2O_2. This reaction is probably homolytic in view of the low (<30%) selectivity vs. consumed H_2O_2, the poor reproducibility of the yield, and the tendency of alkaline H_2O_2 to radical decomposition.[9a] Presumably, the reaction proceeds via the abstraction of α-hydrogen by HO· or HOO· produced from the spontaneous decomposition of alkaline H_2O_2. Similar oxidative cleavage was recently reported for ketols and α-hydroxy acids having α-hydrogen using excess superoxide ion in nonaqueous solvents.[9b]

Table IV lists the reactions of HOO^- with α-methoxy and α-amino ketones. The reaction of α-methoxy-α,α-diphenylacetophenone **2** is 2000 times slower than that of **1a**, and the major product is not benzophenone but its dimethyl acetal **4**. Excess H_2O_2 gives a significant yield of α-hydroperoxy-α-methyldiphenylmethane (**5**) (Table IV).

$$\underset{\text{2}}{Ph\overset{\overset{O}{\|}}{C}-\overset{OMe}{\overset{|}{C}}Ph_2} \xrightarrow[\text{80\% MeOH}]{H_2O_2,\ \text{NaOH}} \underset{\text{4}}{Ph_2C(OMe)_2} + \underset{\text{5}}{Ph_2C\overset{OMe}{\underset{OOH}{<}}} + Ph_2C{=}O + PhCO_2H \quad (4)$$

The cleavage of α-amino ketones is also observed; the oxidation of **3a** (X = NH_2) is fast to give high yield of benzophenonimine ($Ph_2C{=}NH$). The reaction of α-methylamino ketone **3b** (X = NHMe) is considerably slower (ca. 0.1), affording benzophenone, a hydrolysis product of imide. The reaction of α-dimethylamino ketone **3c** (X = NMe_2) is too slow probably because of the steric retardation by dimethyl group on the C=O addition.

The oxidative cleavage with alkaline H_2O_2 is thus shown to be effective for α-hydroxy, α-methoxy, α-amino, and α-methylamino ketones. Since 1,2-glycols are easily cleaved by periodate or lead tetraacetate[2] and C=C is attacked by bromine or peracid, this cleavage of α-ketols with HOO^- is an effective reagent especially when the substrates, α-ketols,

Table III. Rates and Products from the Oxidative Cleavage of Various α-Ketols by Alkaline Hydrogen Peroxide in 80% MeOH at 25 °C[a]

	Registry no.	$R_1COC(OH)R_2R_3$ R_1	R_2	R_3	$10^2 k_{obsd}$,[b] $M^{-1} s^{-1}$	Products (%)[c] R_1CO_2H	$R_2R_3C{=}O$
1a	7473-98-5	Ph	Ph	Ph	6.52	86	97
1f	3155-01-9	Ph	Me	Me	2.62	89	69[d]
1g	119-53-9	Me	Me	Ph	0.338	*e*	88
1h	513-86-0	Ph	H	Ph	~22[f]	110–130[f]	30–50[f]
1i	4444-11-5	Me	H	Me	~4.47[g]	*e*	18[d,g]
1j	90-64-2	n-C_7H_{15}	H	n-C_7H_{15}	0.06	~180	Trace
1k[h]	5457-37-4	HO	H	Ph[h]	<0.01	$PhCO_2H$, 10–48%[h]	

[a] Reaction with 0.20 M NaOH, 0.05 M α-ketol, 0.06 or 0.05 M H_2O_2, and 0.1 mM EDTA. [b] Second-order rate constant with $[H_2O_2]$ = 0.05 M. [c] Reaction with 0.06 M H_2O_2 and reaction time of 2 h for **1a, 1f, 1h, 1i,** and 30 h for the other substrates. Products were determined by GLC analysis, benzoic acid being down after methylation with diazomethane. [d] Determined as 2,4-dinitrophenylhydrazone. [e] Not determined. [f] Base-catalyzed autoxidation of benzoin and benzaldehyde occurred simultaneously. Hence, k_{obsd} value was not determined accurately. Approximately 20% of methyl benzoate was also produced. [g] The rate constant was obtained from the initial reaction up to 40% conversion, since the consumption of H_2O_2 increased gradually owing to the further reaction with acetaldehyde produced. [h] Mandelic acid with 0.10 M H_2O_2 and 0.20 M NaOH afforded 10–49% of benzoic acid; 90–49% of the starting material was recovered. This oxidation is probably homolytic, since the consumption of H_2O_2 was fast in the absence of EDTA and the reproducibility of the conversion was low.

Table IV. Oxidative Cleavage of α-Methoxy and α-Amino Ketones with Alkaline H_2O_2[a]

	Registry no.	$R_1COCXR_2R_3$ R_1	X	R_2	R_3	$10^2 k_{obsd}$,[b] $M^{-1} s^{-1}$	Products (%)[c]
1a	5457-37-4	Ph	OH	Ph	Ph	6.52 (47.1)	$Ph_2C{=}O$, 95%
2		Ph	OMe	Ph	Ph[d]	0.0035	$Ph_2C(OMe)_2$, 43%; $Ph_2C{=}O$, 8%
2		Ph	OMe	Ph	Ph[e]		$Ph_2C(OMe)_2$, 50%; $Ph_2C(OMe)OOH$, 45%; $Ph_2C{=}O$, 3%
3a	56140-60-4	Ph	NH_2	Ph	Ph	(26.2)	$Ph_2C{=}NH$, 93%
3b	63704-20-1	Ph	NHMe	Ph	Ph	0.32 (3.0)	$Ph_2C{=}O$,[g] 90%
3c	63704-21-2	Ph	NMe_2	Ph	Ph	<0.1[h] (<0.5)	$Ph_2C{=}O$, <2%[h]

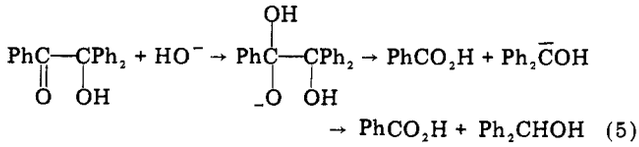
[a] Reaction with [substrate] = $[H_2O_2]$ = 0.025 M, [NaOH] = 0.20 M, and [EDTA] = 0.1 mM in 80% MeOH at 25 °C if not noted otherwise. [b] The values in parentheses are those in 30% MeOH–20% H_2O–50% DMF (vol %). [c] Reaction with 0.05 M H_2O_2. Products were determined by GLC and/or NMR analysis. Benzoic acid was not determined. [d] Reaction with 0.10 M H_2O_2 for 65 h; 45% of the starting ketone was recovered. [e] Reaction with 13 M H_2O_2 for 42 h resulted in 99% conversion. [g] Product was not an imine but benzophenone produced by its hydrolysis. [h] The reaction was very slow, while the presence of the amine accelerated considerably the base-catalyzed decomposition of H_2O_2.

contain such a group as *gem*-diol or C=C. The solvents may be water, aqueous alcohol, or aqueous DMF.

Effect of Solvent. The solvent effect was examined for α-ketol **1f** in order to distinguish (a) rate ∝ $[R'OO^-]$ from (b) rate ∝ $[R'OOH][HO^-]$. The rate in 50% MeOH is faster by a factor of 2 than that in 80% MeOH (Table V). This factor is always the same when 0.1 or 0.2 M NaOH is used or when *t*-BuOOH is used in place of H_2O_2. The same is true for the case of **1g.**

Table V also lists the molar ratio of $R'OO^-$:R'OOH together with the K_6 value determined from UV absorbance at 280 nm. Apparently, k_{obsd} values are parallel with $[R'OO^-]$ and not with $[R'OOH][HO^-]$; the change from 80% MeOH to 50% MeOH decreases both [R'OOH] and $[HO^-]$ and hence it is difficult to explain the duplicate increase in k_{obsd} by means of the relation: rate ∝ $[R'OOH][HO^-]$.

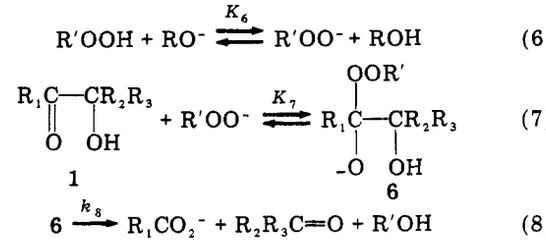
Mechanism. A similar type of reaction is the base-catalyzed α-fission of α-ketols:[10]



$$\rightarrow PhCO_2H + Ph_2CHOH \quad (5)$$

However, this reaction is only possible by heating above 60 °C. The present oxidative cleavage proceeds smoothly at room temperature and may be written as Scheme I containing a rate-determining fragmentation of C=O adduct **6** (eq 8). This scheme leads to a rate equation

Scheme I[a]



(6) (7) (8)

[a] R' = H, *t*-Bu, or PhCO; R = H or Me.

$$v = k_{obsd}[R'OOH][ketol] = k_2[R'OO^-][ketol] \quad (9)$$
$$= k_8K_7[R'OO^-][ketol]$$

For the case of **1a** in 80% MeOH, the relation of k_{obsd} vs. [NaOH] can well be reproduced by assuming k_2 = 0.079 $M^{-1} s^{-1}$ for HOO^- and 0.057 $M^{-1} s^{-1}$ for *t*-$BuOO^-$ (see Figure 1). The positive ρ value of 1.96 is consistent with Scheme I, reflecting the substituent effect in the nucleophilic addition to C=O.[6] The rate equation (eq 9) satisfies the solvent effect in Table V.

Rate-Determining Step. The following consideration leads to a conclusion that the rate-determining step is not the addition to C=O (eq 7) but the fragmentation of the adduct **6** (eq 8). (i) The reactivity order, **1a** > **1f** ≫ **1g** (i.e., benzoyl ≫ acetyl), is abnormal since nucleophilic additions to acetyl are generally much faster than those to benzoyl.[11] The observed order is comprehensible only if the addition is not rate

Table V. Solvent Effect on the Reaction of $PhCOC(OH)Me_2$ 1f with Alkaline H_2O_2 or *t*-BuOOH in Aqueous MeOH[a]

R'OOH	[NaOH],[b] M	Solvent,[c] % M	K_6[d]	R'OO⁻:R'OOH[e]	$10^2 k_{obsd}$,[f] $M^{-1} s^{-1}$
HOOH	0.10	80	12.7	56:44	1.76
		50	30.2	75:25	3.68
	0.20	80	12.7	72:28	2.62
		50	30.2	86:14	4.47
t-BuOOH	0.20	80	1.13	18:82	0.331
		50	3.24	39:61	0.696

[a] Reaction with [1f] = [R'OOH] = 0.050 M at 25.0 °C. [b] See footnote *a* in Table I. [c] Vol % of aqueous methanol. [d] Determined from UV absorbance at 280 nm at 25 °C. [e] Molar ratio of R'OO⁻:R'OOH was calculated from K_6 values listed. [f] Average of two to six determinations.

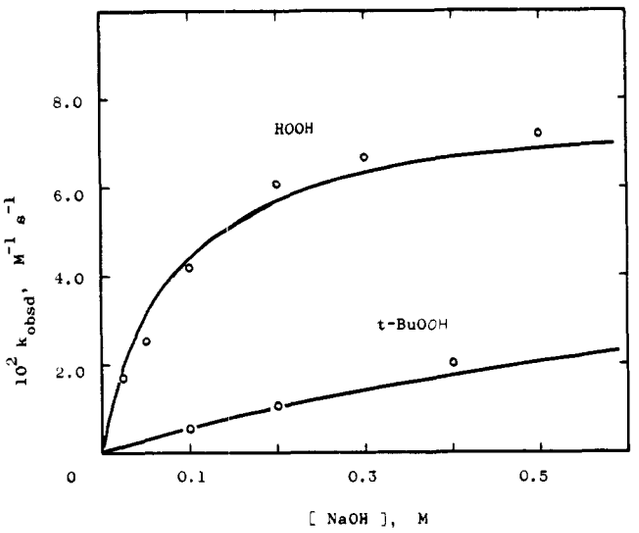


Figure 1. Plots of k_{obsd} vs. [NaOH] for the oxidative cleavage of 1a in 80% MeOH at 25 °C (see Table I for data). Solid lines were calculated from $k_2 = 0.079\ M^{-1} s^{-1}$ and $K_6 = 12.7\ M^{-1}$ for H_2O_2 and $k_2 = 0.057\ M^{-1} s^{-1}$ and $K_6 = 1.13\ M^{-1}$ for *t*-BuOOH.

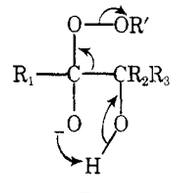
Table VI. Comparison of the Rates between HOO^- and $PhCO_3^-$ in 80% MeOH at 0 °C[a]

α-Ketol (R_1, R_2, R_3)	$10^2 k_2$,[b] $M^{-1} s^{-1}$ HOO⁻	$PhCO_3^-$
1a (Ph, Ph, Ph)	1.10	0.152
1f (Ph, Me, Me)	0.585	1.65
1g (Me, Me, Ph)	0.103	0.098
1h (Ph, H, Ph)[c]	~1.55	~1.34
$PhCOC(OOH)Ph_2$[d]	10.0[e]	

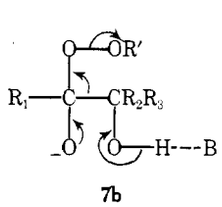
[a] Reaction with [ketol] = [oxidant] = 0.025 M, [NaOH] = 0.20 M, and [EDTA] = 0.1 mM. Perbenzoate ion afforded similar yields of the products as in the case of H_2O_2, except that methyl benzoate was formed in 10–20% yields via the reaction of the peracid with MeO⁻. [b] Second-order rate constant calculated from $v = k_2[R'OO^-][ketol]$; the dissociation of H_2O_2 into HOO^- is 72%. [c] Reaction in 90% MeOH gave 35–50% yields of PhCHO together with 10–40% of $PhCO_2Me$. [d] Alkaline decomposition of α-hydroperoxy ketone with 0.20 M NaOH in 80% MeOH in the absence of oxidant. [e] Second-order rate constant for the reaction with HO^- from $v = k_2[\alpha\text{-HOO-ketone}][HO^-]$. $[HO^-]$ was estimated from the acidity difference between H_2O and MeOH (see ref 14 and 21).

determining. (ii) The reaction of $PhCO_3^-$, an oxidant much stronger than HOO^-, is faster for **1f** but slower for the cases of **1a** and **1h** than that of HOO^- (Table VI). If the C=O addition were slow, the order should be $HOO^- > PhCO_3^-$,[12a] which is not the case. The rate-determining fragmentation of **6** may explain the observed variable order in reactivity; that is, the overall rate is governed by the product K_7k_8 and compensated with each other. This is because the relative order of K_7 is probably $HOO^- > PhCO_3^-$ but k_8 for $PhCO_3^-$ is much faster than that for HOO^- because the pK_a of the departing $PhCO_2^-$ is 12 units higher than that of HO^- in the fragmentation step. (iii) The base-catalyzed decomposition of $PhCOC(OOH)Ph_2$ with HO^- gave $k_{obsd} = 0.10\ M^{-1} s^{-1}$ in 80% MeOH at 0 °C (Table VI).[13] This value is much higher than that ($0.011\ M^{-1} s^{-1}$) of **1a** and HOO^- (Table VI). Since the α-effect for C=O addition is large, i.e., $HOO^- \gg HO^-$,[12] the rate-determining fragmentation of **6** can only explain why the reaction of HO^- with the α-hydroperoxy ketone is much faster than that of HOO^- with **1a**, a less hindered ketone. Thus, it is concluded that the fragmentation of the C=O adduct (eq 8) is rate determining.

Fragmentation of C=O Adduct 6. The transition state for the fragmentation of **6** may be written as **7a** or **7b** (B = base or solvent).[15] Apparently, the hydroxyl group plays an important role in the transition state, since the reaction of α-methoxy ketone **2** is quite slow. The choice of **7a** or **7b** is not straightforward, but the following examinations suggest **7a** is more probable. The addition of 50% DMF, an aprotic basic solvent, accelerated the reaction by factors of 4–10 (Table IV), while the effect of 10–20% DMF is rather small (within a factor of 1.5);[16a] this nonlinearity between k_{obsd} and [DMF] seems to deny the reaction via **7b** of general base catalysis by DMF. No observation of a general base catalysis by HO^- at a high concentration (0.5 M) is also consistent with **7a** rather than **7b.** The nonlinear acceleration by DMF is explicable by solvation of DMF by the hydroxylic solvent, resulting in a decrease of intermolecular hydrogen bonding by MeOH or H_2O to the adduct anion **7** and then in an increase of naked [**7a**].[16b]

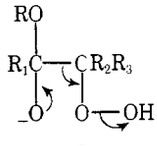


7a

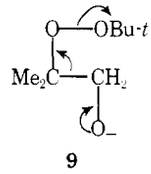


7b

The facile fragmentation of **6** is probably caused by the concerted C–C and O–O fission, which is contrary to the α-fission of α-ketol with HO^- (eq 5). A preference of Ph ≫ Me in the substituent effect of R_1 suggests a conjugation of phenyl with the developing carbonyl group in **7a.** The effect of an R_2 or R_3 group is much smaller, which indicates a less important resonance with the developing C=O of the right-hand carbon in **7a.** A related transition state **8** was reported for the base-catalyzed decomposition of α-hydroperoxy ketones,[14] where

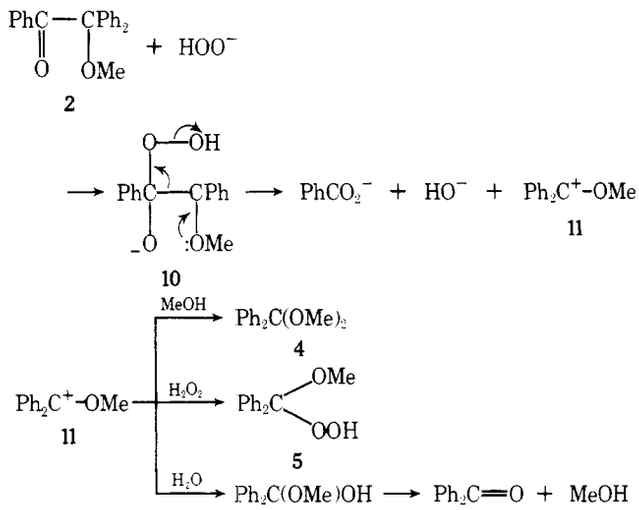


8



9

Scheme II



a phenyl group always accelerated the fragmentation by any substitution in R_1, R_2, and R_3. The cause of this difference is not obvious at present. A related case of peroxide reaction is the fragmentation of **9** to acetone, formaldehyde, and t-BuO^-, the rate of which was assumed to be 0.5 s^{-1} (40% MeOH, 30 °C).[17] The common driving force for the facile decomposition of **7**, **8**, and **9** is surely the concerted carbonyl-forming fragmentation together with the pushing effect by the α-oxy anion. The latter effect is well known in other peroxide reactions[18] and in benzilic acid rearrangement.[19]

Mechanism of Cleavage of α-Methoxy Ketone (2). The reaction of HOO^- with α-methoxy ketone **2** gave acetal **4** and in the presence of excess H_2O_2 hydroperoxide **5** (eq 4). The results are explicable by Scheme II. One of the driving forces for the concerted fragmentation of **10** is the high stability of the α-alkoxy carbonium ion **11**. Cation **11** is then trapped by neutral solvents but not by anions. This is based on the following examination between reactions of **2** with 0.1 and 13 M H_2O_2 in the presence of 0.20 M NaOH. There is no large difference between the concentrations of anions; i.e., $[HOO^-]$ = 0.085 and 0.108 M, $[MeO^-]$ = 0.094 and 0.075 M, and $[HO^-]$ = 0.021 and 0.017 M for the reactions with 0.1 and 13 M H_2O_2, respectively.[20] Thus, the only one large difference between the two conditions is the concentration of neutral H_2O_2, i.e., $[H_2O_2]$ = 0.15 and 12.9 M, which should be reflected on the product distribution (see Table IV).

An analogous mechanism as Scheme II will be written for the reaction of α-amino ketone **3**, since amines are much less weak acids[22] and have lower ionization potentials than alcohols or ethers.[23] The large difference of the acidity between NH_2 and OH makes it difficult to explain the observed comparable rates between **1a** and **3a** by the same mechanism as Scheme I.

Experimental Section

Melting and boiling points were not corrected. IR and NMR spectra were recorded on a Perkin-Elmer 337 spectrophotometer and a Hitachi R-24B NMR spectrometer using Me_4Si as an internal standard. The GLC analysis was performed with a Yanagimoto 550-F gas chromatograph.

Materials. α-Phenylbenzoin **1a** was obtained by the reaction of benzil with PhMgBr,[24] mp 87–88 °C (lit.[24] 87–88 °C). Substituted phenylbenzoins **1b–e** were synthesized via the α-bromination of the corresponding α,α-diphenylacetophenones[14] followed by its hydrolysis. Thus, α,α-diphenyl-*p*-methoxyacetophenone (2.0 g, 6.6 mmol) in 20 mL of dioxane was brominated with 0.5 mL (10 mmol) of bromine at 40 °C for 2 h. After the addition of 10 mL of water, the mixture was refluxed for 30 min, poured into water, and extracted with benzene (30 mL). After drying (Na_2SO_4) and condensation, *n*-hexane was added to precipitate the crude α-ketol **1b**. Recrystallization from benzene–*n*-hexane gave 1.5 g (71%) of α-phenyl-*p*-methoxybenzoin **1b**: mp 132–133.5 °C; IR (Nujol) 3340 (OH), 1650 cm^{-1} (C=O). Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 79.02; H, 5.79.

Other α-phenylbenzoins **1c–e** were obtained by a similar method, as in the case of **1b**, and crystallized from *n*-hexane. α-Phenyl-*p*-methylbenzoin (**1c**) was synthesized in 76% yield; mp 57–59 °C (lit.[25] 57–59.5 °C). α-Phenyl-*p*-chlorobenzoin (**1d**) (92% yield): mp 87–88 °C; IR (nujol) 3400 (OOH), 1650 cm^{-1} (C=O). Anal. Calcd for $C_{20}H_{15}O_2Cl$; C, 74.42; H, 4.99. Found: C, 73.96; H, 4.85. α-Phenyl-*m*-chlorobenzoin (**1e**): mp 58–60 °C; IR (nujol) 3450 (OH), 1670 cm^{-1} (C=O). Anal. Calcd for $C_{20}H_{15}O_2Cl$: C, 74.42; H, 4.99. Found: C, 73.88; H, 4.90.

α-Hydroxyisobutyrophenone (**1f**) was prepared similarly from ketone. Thus, bromine (19.2 g, 0.12 mol) was added dropwise to isobutyrophenone (14.8 g, 0.1 mol) in 40 mL of dioxane and stirred for 1 h at room temperature. Ethanol (10 mL), water (50 mL), and NaOH (8 g, 0.2 mol) were then added and refluxed for 3 h. Extraction and distillation gave the ketol **1f** (80% yield): bp 118–120 °C (10 mmHg) [lit.[26] bp 125 °C (12 mmHg)]; IR (film) 3450 (OH), 1670 cm^{-1} (C=O); NMR (CCl_4) δ 1.52 (s, 6 H, CH_3), 3.80 (s, 1 H, OH), 7.2–7.5 (m, 3 H, *m*- and *p*-H), 7.8–8.0 (m, 2 H, *o*-H).

2-Phenylacetoin (**1g**),[27] capryloin (**1j**),[28] and α-methoxy-α,α-diphenylacetophenone (**2**)[29] were prepared by the literature methods. **1g**: bp 108–110 °C (3 mmHg); IR (film) 3450 (OH), 1710 cm^{-1} (C=O); NMR (CCl_4) δ 1.66 (s, 3 H, α-CH_3), 2.00 (s, 3 H, CH_3C=O), 4.12 (s, 1 H, OH), 7.1–7.4 (m, 5 H, ArH). **2**: mp 91–92 °C (benzene–*n*-hexane); NMR (CCl_4) δ 3.03 (s, 3 H, OCH_3), 7.0–7.5 (m, 13 H, ArH), 7.8–8.0 (m, 2 H, *o*-H). Acetoin (**1i**) was commercial grade.

α-Amino-α,α-diphenylacetophenone (**3a**) was easily obtained by refluxing α-bromo ketone in dioxane–28% aqueous ammonia (2:1) for 1 h. The reaction mixture was poured into water to precipitate the amino ketone; recrystallization from MeOH gave 53% of **3a**: mp 133–134 °C (lit.[30] 132 °C).

The same method with aqueous methylamine gave crude α-methylamino-α,α-diphenylacetophenone (**3b**); the crude amino ketone was extracted with 1 N aqueous HCl and then, after addition of excess NaOH, with CH_2Cl_2. Evaporation of the solvent and 3 days' standing led to crystallization of **3b**, which was recrystallized from MeOH to give 40% yield of **3b**: mp 90–92 °C; IR (film) 3350 (NH), 1675 cm^{-1} (C=O); NMR (CCl_4) δ ~2.0 (br s, 1 H, NH), 2.05 (s, 3 H, NCH_3), 7.0–7.6 (m, 15 H, ArH). Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 82.94; H, 6.50; N, 4.76.

α-Dimethylamino-α,α-diphenylacetophenone (**3c**) was obtained by the same method using aqueous dimethylamine. Prolonged standing of the neat sample led to crystallization of **3c**: mp 82–84 °C; IR (film) 1670 cm^{-1} (C=O); NMR (CCl_4) δ 2.08 [s, 6 H, $N(CH_3)_2$], 7.0–7.3 (m, 13 H, ArH), 8.1–8.3 (m, 2 H, *o*-H). Anal. Calcd for $C_{22}H_{21}NO$: C, 83.77; H, 6.71; N, 4.44. Found: C, 80.86; H, 6,78; N, 4.67.

Rates. To a mixture of α-ketol 1 (5 mL of a 0.10 M solution in MeOH), H_2O_2 (1 mL of a 0.5 M solution in water), and MeOH (3 mL) was added 1 mL of 2.0 M aqueous MeOH containing 1 mL of EDTA at 25.0 °C. Aliquots (1 mL) were taken out at appropriate time intervals, and the remaining hydrogen peroxide was titrated iodometrically using sodium molybdate catalyst in MeOH–H_2O–AcOH (2:1:1). The second-order rate constant, k_{obsd}, was calculated according to eq 2, and the reproducibility was within ± 5% for most runs.

Products. Products were identified and determined by GLC analysis, and by IR, NMR, and UV spectra in comparison with an authentic samples. GLC analyses were conducted at 80–250 °C using three different columns (1 m): PEG 20M, 2% on Chamelite CK; Silicone SE30, 10% on Chromosorb; Apiezone grease L, 15% on Celite 545. Carboxylic acids were determined after methylation with diazomethane.

For the case of ketols **1a–e**, a simple extraction with CH_2Cl_2 from water afforded benzophenone (over 90% yield). In the oxidative cleavage of benzoin **1h**, yields of PhCHO ranged from 30 to 50%, which were not altered by the reaction under N_2 or at 0 °C. The formation of methyl benzoate (~20%) indicates a competitive oxidation via benzil (eq 3b).

The oxidation of mandelic acid (**1k**) did not occur with equimolar H_2O_2 and the results in Table III are those with 4 equiv of H_2O_2.

Reaction of α-Methoxy Ketone 2 with Excess H_2O_2. The reaction of **2** with 0.1 M H_2O_2 in the presence of 0.2 M NaOH gave predominantly benzophenone dimethyl acetal **4**, but the reaction with a large excess of (13 M) H_2O_2 resulted in a new hydroperoxide **5**. Thus, **2** (88 mg) in 9 mL of MeOH was oxidized with 1 mL of 50% H_2O_2 and 2 M NaOH at 25 °C for 25 h. The reaction mixture was poured into cold 5% aqueous NaOH and neutral products were extracted with CH_2Cl_2 (10, 5, and 5 mL). Evaporation of the solvent yielded 25 mg (35%) of **4**; GLC retention time and IR and NMR spectra were iden-

tical with those of an authentic sample. The aqueous alkaline solution was neutralized with acetic acid, extracted with CH_2Cl_2, washed with aqueous Na_2HPO_4, and dried with Na_2SO_4. Evaporation of the solvent yielded a crude product, mp 58–60 °C; recrystallization from CCl_4–petroleum ether gave pure α-hydroperoxy-α-methoxydiphenylmethane (**5**) in 30% yield: mp 62–64 °C; IR (film) 3400 (OOH), 1205, 1085 cm^{-1} (C–O); NMR (CCl_4) δ 3.22 (s, 3 H, OCH_3), 7.0–7.5 (m, 11 H, ArH + OOH). The hydroperoxidic proton in NMR spectra is probably overlapped in the aromatic region, since the treatment with D_2O decreased the peak area at 7.0–7.5 by 1 H. The reduction of **5** with KI gave solely benzophenone. The pyrolysis GLC (injection temperature 250 °C) yielded benzophenone and methyl benzoate (2:3 ratio); the formation of the ester suggests the thermal 1,2 shift of the phenyl group in the hydroperoxide.

Reaction of α-Amino Ketone. The reaction of α-amino ketone **3a** with alkaline H_2O_2 was conducted in aqueous MeOH–50% DMF; DMF was added because of the low solubility of **3a.** The reaction mixture was diluted with water and extracted with CH_2Cl_2 to give pure benzophenonimine, $Ph_2C{=}NH$: IR (film) 3430, 3240 (NH), 1670 cm^{-1} (C=N); UV λ_{max} 242 nm in MeOH, 274 nm in 1 N HCl (lit.[31] 275.5 nm). The imine was converted to benzophenone by hot aqueous HCl.

The corresponding methylimine was not obtained for the case of **3b,** but solely benzophenone, a hydrolysis product, resulted. α-Dimethylamino ketone **3c** gave only a trace amount of benzophenone after 3 days of reaction.

Registry No.—5, 63704-22-3; $MeOC_6H_4$-*p*-$C(=O)CHPh_2$, 1889-74-3; MeC_6H_4-*p*-$COCHPh_2$, 41993-27-5; ClC_6H_4-*p*-$COCHPh_2$, 63704-23-4; ClC_6H_4-*m*-$COCHPh_2$, 63704-24-5; $Ph_2C{=}NH$, 1013-88-3; HOOH, 7722-84-1; *t*-BuOOH, 75-91-2; HOO^-, 14691-59-9; $PhCO_3^-$, 33451-32-0; isobutyrophenone, 611-70-1; α-bromo-α,α-diphenylacetophenone, 6905-43-7; ammonia, 7664-41-7; methylamine, 74-89-5; dimethylamine, 124-40-3.

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$$\mathbf{7} \xrightarrow{-R'O^-} R_1CO_2C(OH)R_2R_3 \rightarrow R_1CO_2H + R_2R_3C{=}O$$

We feel that the transition states **7a** and **7b** are the same for the fragmentation or the Baeyer–Villiger reaction. The difference lies only in whether the hemiacetal intermediate $R_1CO_2C(OH)R_2R_3$ is involved or not. Since the base-catalyzed decomposition of hemiacetals is very fast, the choice is difficult. But the relatively smaller difference in the rate between $R'OO^-$ and $PhCO_3^-$ (Table VI) seems to favor the fragmentation mechanism, since the Baeyer–Villiger reaction depends on the nature of peroxides (i.e., stretching of the O–O bond is important in the transition state);[15b] (b) Y. Ogata and Y. Sawaki, *J. Am. Chem. Soc.,* **94,** 4189 (1972).
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