imines.[26] These kinetic aspects resemble those of the Baeyer–Villiger oxidation which shows likewise the change of the order in HA together with the complexities of the apparent ρ values.[10] The most distinct difference between the C=N and the C=O additions lies in the relative susceptibilities to acid catalysis, reflecting the large difference in basicity between C=N and C=O ($\Delta pK_a \sim 12$–14).

Nitrone Formation. Nitrones are formed directly by the reaction of C=N with PBA, since the produced oxaziranes and nitrones are stable under the reaction conditions. The nitrone formation is favored by the electron-donating substituents in the imines and by aprotic solvents, the order being dioxane > benzene ≫ *t*-BuOH > EtOH. This solvent effect seems to show that the selectivity for the nitrone increases, when the addition of PBA to C=N is slowed down.

The approximate rate constants for the nitrone formation (k_{obsd} × nitrone selectivity) exhibit a large substituent effect, suggesting a negative ρ value. The effect of solvents on the rate is in the order: benzene ≫ dioxane ∼ alcohols. These kinetics resemble those for the peracid oxidation of olefins, amines, and sulfides, suggesting the similar mechanism. The details of this problem will be discussed in our next paper.[26]

Experimental Section

All melting and boiling points were not corrected. Uv spectra were measured by a Model 124 Hitachi spectrophotometer using 1.0-cm quartz cells. Nmr spectra were measured at room temperature with a JNM-C60-HL (Japan Electron Optics).

Materials. PBA was synthesized as previously noted.[10] Solvents were purified by fractional distillations. Substituted benzylidene-*tert*-butylamines were obtained from benzaldehydes and *tert*-butylamine.[17] Their substituents and boiling points (or melting points) are as follows: *p*-MeO, 141–143° (18 mm) [lit.[17] 110–113° (2.1 mm)]; H, 117–119° (36 mm) [lit.[17] 63–64° (1.0 mm)]; *p*-NO_2, mp 76.5–78.1° (lit.[17] 72–75°). Ethanol-d_1 was obtained by adding D_2O to dry EtONa in ether and distilled repeatedly.

Rates and Products Determinations. The rates of PBA oxidation of the imine were determined directly in an optical cell by following the decrease or increase of the absorbance at 300–340 nm. Usually excess PBA was used, and k_{obsd} was calculated by dividing the resulting pseudo-first-order rate constant by [PBA] according to eq 3.

The yield of oxazirane was determined by the following iodometry. The reaction mixture was added to EtOH (5 ml)–AcOH (5 ml)–dimethyl sulfoxide (2 ml) and allowed to stand for *ca.* 5 min to consume the remaining peracid. Then, aqueous KI (2 ml) and, after standing a few minutes, water (50 ml) were added, and the liberated iodine was titrated by aqueous $Na_2S_2O_3$.

The nitrones were determined by uv spectrophotometry; X in $XC_6H_4CH{=}N(O)$-*t*-Bu, λ_{max} (ϵ) in ethanol: *p*-MeO, 305 (20,400); H, 295 (16,700)[1]; *p*-Cl, 298 (22,650);[27] *p*-NO_2, 362 (15,800).[1]

α-(p-Methoxyphenyl)-N-*tert*-butylnitrone. To obtain pure oxazirane or nitrone, peracetic acid was used in place of PBA, since PBA was not appropriate because of the contamination of a trace of benzoic acid. Thus, *p*-methoxybenzylidene-*tert*-butylamine (2.0 g, 10.4 mmol) and peracetic acid (10.4 mmol) were allowed to react in toluene (40 ml)–EtOH (10 ml) at room temperature for 1 hr. After being washed twice with water and aqueous $NaHCO_3$ and dried over Na_2SO_4, the toluene solution of oxazirane was heated at 110° for 4 hr. The solvent was evaporated under reduced pressure. The resulting light yellow liquid was crystallized from ether–petroleum ether at −20° to afford 1.45 g (67%) of the titled nitrone, mp 96.2–97.3°; uv 305 nm (ϵ 20,400) in EtOH, 308 (19,400) in benzene; nmr (60 MHz, CCl_4 *vs.* TMS) δ 8.15 (2 H, d, J = 8.4 Hz, *o*-H), 7.29 (1 H, s, CH=N(O)), 6.79 (2 H, d, J = 8.4 Hz, *m*-H), 3.78 (3 H, s, CH_3O), 1.52 (9 H, s, *t*-Bu).

Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.5; H, 8.29; N, 6.76. Found: C, 67.0; H. 8.24; N, 7.0.

(26) Y. Ogata and Y. Sawaki, *J. Amer. Chem. Soc.*, **95**, 4692 (1973).

(27) The data of Me in place of *t*-Bu: T. Kubota, M. Yamakawa, and Y. Mori, *Bull. Chem. Soc. Jap.*, **36**, 1552 (1963).

Peracid Oxidation of Imines. Kinetics and Mechanism of Competitive Formation of Nitrones and Oxaziranes from Cyclic and Acyclic Imines

Yoshiro Ogata* and Yasuhiko Sawaki

Contribution No. 190 from the Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan.
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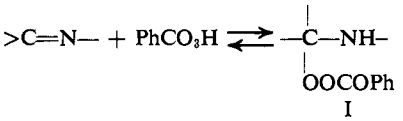
Abstract: The reaction of 3,4-dihydroisoquinoline (IIa) and 3,4-dihydro-1-methylisoquinoline (IIb) with perbenzoic acid (PBA) has been shown to give nitrones as well as reported oxaziranes, their selectivities changing with reaction conditions. The direct formation of nitrones is apparent irrespective of the imine structure, acyclic or cyclic. Generally, the oxazirane formation is predominant in the presence of alcohols or carboxylic acids, while the yield of nitrones increased in aprotic media. The kinetic study suggests that the oxazirane formation proceeds *via* a two-step mechanism similar to the Baeyer–Villiger reaction, and that a rate-determining step for PBA oxidation of the cyclic imines is generally a SNi reaction of the C=N adduct, contrary to the case of acyclic imines. On the other hand, the nitrone formation is a nucleophilic attack of N lone-pair electrons of C=N on peracid oxygen. The rate constants of nitrone formation in benzene at 25° are 0.52 M^{-1} sec^{-1} for IIa and 2.0 M^{-1} sec^{-1} for IIb, which are considerably smaller in comparison to that of an amine with the same pK_a value.

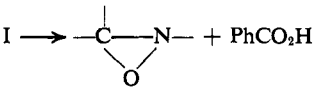
Although facile additions of various nucleophiles to C=N are well known,[1,2] reported nucleophilic reactions of C=N itself are rather limited to acyl and alkyl halides,[1] where a reaction site is the N lone-pair electrons of imine. One exception is the reaction of C=N with peracids to form oxaziranes; Emmons[3] postulated

(1) R. W. Layer, *Chem. Rev.*, **63**, 489 (1963).
(2) W. P. Jencks, *Progr. Phys. Org. Chem.*, **2**, 63 (1964).
(3) (a) W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5739 (1957); (b) W. D. Emmons, *Chem. Heterocycl. Compounds*, **19**, 630 (1964).

an epoxidation-type (one-step) mechanism *via* a nucleophilic reaction of π-bonding electrons, which has been supported, and their high reactivity was explained as "pseudo-α-effect" by Madan and Clapp.[4] However, we can confirm in the previous report[5] that oxaziranes are formed *via* a two-step (the Baeyer–Villiger type) mechanism, the first step (eq 1) being acid-catalyzed addition of peracid to C=N, followed by an internal nucleophilic (SNi) reaction of the adduct I to afford oxaziranes (eq 2).

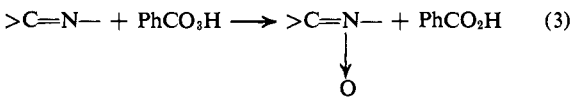


(1)



(2)

Since peracids are effective electrophiles as well as nucleophiles[6,7] and imines are fairly strong bases,[8] it was curious to us that the main reaction is not a nucleophilic attack of imines toward peracids. But we can find that such a nucleophilic reaction of C=N does occur to afford nitrones (eq 3), which is competitive with the

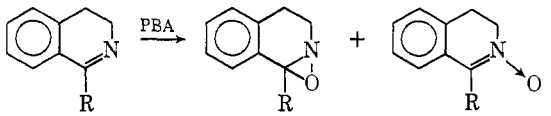


(3)

oxazirane formation. This is a nucleophilic reaction of N lone-pair electrons of C=N̈, but not π-bonding electrons. The present report summarizes and discusses some mechanistic aspects of the competitive formation of nitrones and oxaziranes from some cyclic and acyclic imines.

Results

Formation of Nitrones and Oxaziranes. The reaction of 3,4-dihydroisoquinoline (IIa) or 3,4-dihydro-1-methylisoquinoline (IIb) with perbenzoic acid (PBA) gave both nitrone and oxazirane (eq 4), their selectivities



(4)

IIa, R = H; b, R = Me — IIIa, R = H; b, R = Me — IVa, R = H; b, R = Me

depending on solvents (Table I). The yields of oxaziranes were determined by iodometry[5] and those of nitrones by uv spectrophotometry. Produced oxaziranes (IIIa,b) and nitrones (IVa,b) are stable under these conditions, although they are converted gradually to the corresponding isoquinolines on long standing at room temperature.

Table I shows that the product selectivity depends on the structure of imines and on the reaction conditions (solvents and acids). Thus, the oxazirane formation is a main reaction for IIa (R = H), while IIb (R = Me) affords predominantly nitrone IVb in aprotic solvents. The nitrone formation is reduced by protic solvents or carboxylic acids. Table I also lists the results for acyclic imines, benzylidenealkylimines. Although the yield of nitrone in these cases is lower (<8%), the solvent effect is similar to the above cyclic imines. The nitrone formation from acetophenonecyclohexylimine is also of low yield (<1%), suggesting that no significant increase in the nitrone selectivity resulted by changing aldimines to a ketimine.

Table I. Per Cent Yields of Nitrones and Oxaziranes by PBA Oxidation of Cyclic and Acyclic Imines at 25° [a]

	IIa		IIb		PhCH=NMe		PhCH=NC$_6$H$_{11}$	
Conditions	N	O	N	O	N	O	N	O
C_6H_6	80.6	4.8	24.0	75.0	100	3.2	96.0	3.0
C_6H_6, 1 *M* AcOH	79.0	5.3	52.5	38.3	94.8	2.3	97.0	2.6
50% dioxane[b]	69.3	17.3	23.0	81.0	91.0	7.8	90.0	5.7
5% EtOH[b]	80.9	4.5	62.1	37.1	104	1.5		
50% EtOH[b]	84.1	2.9	89.4	12.8	106	0.5	102	0.7

[a] The values listed are per cent yield (±5%) based on the charged imine. Initial concentrations: [PBA] = [imine] = 0.025 *M*; reaction time, 2–3 hr. Nitrones were determined by uv absorbance and oxaziranes by iodometry. N = nitrone; O = oxazirane. [b] Volume % in benzene.

The preference for the oxazirane formation in the presence of acids is apparent in Table I and more clearly in view of a marked increase in the nitrone yield for the oxidation in diluted solutions. Thus, the nitrone yield increased up to 64, 95, and 91% with IIa, IIb, and benzylidenecyclohexylimine, respectively, at the initial concentrations of [PBA] = [C=N] = 0.0010 *M* in benzene at 25°.

Kinetics in Benzene. The rates were measured by following the increase or the decrease of absorbance at 300–330 nm, k_{obsd} being calculated by eq 5. The

$$v = k_{obsd}[C{=}N][PBA] \quad (5)$$

k_{obsd} values were divided from product selectivities into two terms, *i.e.*, $k_{nitrone}$ for the nitrone formation and $k_{oxazirane}$ for the oxazirane formation (Table II).

The oxidation rate of IIa is nearly constant, *i.e.*, k_{obsd} = 1.0 M^{-1} sec^{-1} with various initial concentrations of PBA (Table IIA). The value of $k_{oxazirane}$ increases with increasing concentration of PBA, while $k_{nitrone}$ decreases only slightly. The addition of carboxylic acid reduces k_{obsd}, and the reaction is slowed down by ~1 *M* acetic acid or ~0.1 *M* monochloroacetic acid (Table IIB). Apparently, $k_{oxazirane}$ is not influenced by these acids so significantly as $k_{nitrone}$.

The solvent effect exhibits an interesting aspect (Table IIC). Although the effect on the k_{obsd} value is not so large, there is slight retardation by basic solvents including ethers and alcohols. The value of $k_{oxazirane}$ for IIa (R = H) is unaffected by solvents, while that for IIb (R = Me) increases in the order of basic aprotic < aprotic < protic solvents. In contrast, $k_{nitrone}$ increases in the order of protic < basic aprotic < aprotic solvents.

Kinetics in Absolute Ethanol. The oxidation of the cyclic imines, IIa and IIb, in ethanol affords an almost quantitative yield of nitrones, where carboxylic acids exhibit both accelerating and retarding effects (Table

(4) V. Madan and L. B. Clapp, *J. Amer. Chem. Soc.*, **91**, 6078 (1969); **92**, 4902 (1970).
(5) Y. Ogata and Y. Sawaki, *J. Amer. Chem. Soc.*, **95**, 4687 (1973).
(6) R. Curci and J. O. Edwards, "Organic Peroxides," Vol. I, D. Swern, Ed., Wiley, New York, N. Y., 1970, p 236.
(7) A. G. Davies, "Organic Peroxides," Butterworths, London, 1961, p 137.
(8) The values of pK_a's of protonated imines are only 2–3 pK_a units lower than those of the corresponding amines.

Table II. Nitrone Selectivities and Rate Constants for the PBA Oxidation of Imines in Benzene at 25° [a]

Reaction conditions[b]	IIa N, %[c]	IIa k_{obsd}, M^{-1} sec^{-1}	IIa $k_{nitrone}$[d]	IIa $k_{oxazirane}$[d]	IIb N, %[c]	IIb k_{obsd}, M^{-1} sec^{-1}	IIb $k_{nitrone}$[d]	IIb $k_{oxazirane}$[d]	PhCH=NC$_6$H$_{11}$ N, %[c]
A. Effect of Initial Concentration of PBA									
0.5 m*M* PBA	68.1	0.86	0.58	0.12					
1.0 m*M* PBA	64.3	0.87	0.56	0.31					90.6[e]
2.0 m*M* PBA	51.2	1.02	0.52	0.50					65.8
4.0 m*M* PBA	33.8	1.03	0.35	0.68					
8.0 m*M* PBA	25.6	1.12	0.29	0.84					19.7[f]
B. Effect of Added Carboxylic Acid									
None	51.2	1.02	0.52	0.50	93.5	2.09	1.95	0.14	65.8
5 *m*M AcOH	50.0	0.96	0.48	0.48	86.5	1.74	1.51	0.25	52.7
10 m*M* AcOH	44.4	1.05	0.47	0.58	84.0	1.56	1.28	0.28	45.1
50 m*M* AcOH	32.4	0.72	0.23	0.49	77.4	0.94	0.73	0.21	27.2
100 m*M* AcOH	25.0	0.76	0.19	0.57	69.0	0.57	0.40	0.18	22.3
1000 m*M* AcOH	~0	<0.01			~0	<0.001			
1 m*M* ClAcOH	42.6	0.68	0.29	0.39	79.2	0.62	0.49	0.13	
10 m*M* ClAcOH	~0	<0.001			~0	<0.001			
100 m*M* ClAcOH	~0	<0.001			~0	<0.001			
C. Effect of Solvent									
100% benzene	51.2	1.02	0.52	0.50	93.5	2.09	1.95	0.14	65.8
20% $CHCl_3$	52.0	1.20	0.62	0.57	93.5	2.20	2.05	0.14	
20% CCl_4	47.8	0.84	0.40	0.42	93.0	1.96	1.82	0.14	
20% MeCN	53.1	1.00	0.53	0.47	95.5	2.18	2.08	0.10	
20% AcOEt	37.8	1.14	0.43	0.71	94.2	1.89	1.78	0.11	
20% DMF	15.3	0.61	0.09	0.51	70.2	0.42	0.29	0.13	
20% Et_2O	70.0	0.42	0.29	0.13	~100	1.35	1.30	<0.01	85.1
2% dioxane					93.5	2.10	1.96	0.14	
20% dioxane	44.0	0.52	0.22	0.33	~100	1.13	1.13	<0.01	94.8
2% EtOH					72.2	2.01	1.45	0.56	
20% EtOH	3.8	~0.73	0.03	0.70	23.1	0.60	0.14	0.46	3.4
20% MeOH	3.3	~0.73	0.02	0.71	16.3	0.51	0.08	0.43	
20% *i*-PrOH	6.2	~0.58	0.04	0.55	35.0	0.47	0.16	0.31	4.9
20% *t*-BuOH	6.6	~0.72	0.05	0.67	51.2	0.47	0.24	0.23	7.9
20% *n*-BuOH	5.0	~0.85	0.04	0.81	30.0	0.66	0.20	0.46	

[a] Initial concentrations are [PBA] = 2.0 m*M* and [imine] = 0.10 m*M* for IIa and IIb, [PBA] = [imine] = 2.0 m*M* for PhCH=NC$_6$H$_{11}$ unless otherwise noted. [b] AcOH and ClAcOH are acetic acid and monochloroacetic acid, and % solvent is shown as vol % in benzene. [c] Yield of nitrone (N) was determined from uv absorbance, which corresponds to the apparent selectivity of nitrone, since the total yield of nitrone and oxazirane is 100 ± 5%. [d] Observed second-order rate constants (k_{obsd}) are divided into $k_{nitrone}$ and $k_{oxazirane}$ from product selectivities. [e,f] Initial concentrations are [PBA] = [imine] = 1 m*M* and [PBA] = 8 m*M*, respectively.

IIIA). In contrast, such a retarding effect by acids is not observable for the case of acyclic imines (ref 5 and Table IIIA).

Interestingly, the oxazirane formation is base catalyzed by imines themselves and sodium acetate (Table IIIB and C). Plots of k_{obsd} *vs.* [base] are linear and afford catalytic constants of 8 and 1.5 M^{-2} sec^{-1} for IIB and sodium acetate, respectively.

Kinetics in 40% Aqueous Ethanol. The oxidation in 40% aqueous ethanol affords mostly oxaziranes, and the rate is dependent on pH (Table IIID). The plots of log k_{obsd} *vs.* pH give lines of unit slope at pH <6, while the rate is independent of pH at pH 6–8 and then slowed down at higher pH. The rate constant for IIa at pH <6 is *ca.* 30-fold higher than that of IIb, although IIb is a stronger base by 1.1 pK_a units.[9]

The formation of nitrone becomes significant at high pH, where k_{obsd} is decreased. For example, the oxidation of IIb at pH ~9 (carbonate buffer) affords nitrone in *ca.* 40% yield, and the oxidation at pH 11.3 gives predominantly nitrone (>90%), where k_{obsd} is as low as 0.0041 M^{-1} sec^{-1}. But, if this slow reaction is between a free imine and PBA (not peracid anion),[10] the corresponding second-order rate constant is 2.6 M^{-1} sec^{-1} which is of the same magnitude as that in benzene (k_{obsd} = 2.1 M^{-1} sec^{-1}).

Discussion

Oxazirane Formation. Our previous report[5] on the PBA oxidation of benzylidene-*tert*-butylamines revealed that the rate of oxazirane formation is determined by an acid-catalyzed addition of PBA to C=N (eq 1). Likewise, the oxazirane formation from cyclic imines, IIa and IIb, is catalyzed by weak acids such as PBA and alcohols in benzene (Table IIA and C) and also by dilute carboxylic acids in ethanol (Table IIIA), while the retarding effect appears with more concentrated carboxylic acids (Table IIB and Table IIIA). These effects of acids are due to the acid–base interaction of the imine nitrogen with acid.[12] These effects of acids and bases are in contrast to the peracid oxidation of

(9) The pK_a values of protonated IIa and IIb were measured by uv spectrophotometry to be 6.4 for IIa and 7.5 for IIb in 40% aqueous ethanol at 25°.

(10) Imine IIb (pK^s = 7.5)[9] exists as a free imine at higher pH; [PBA] at pH 11.3 may be estimated from its pK_a value of 8.5 in 40% aqueous ethanol.[11] The alternative mechanism of the nitrone formation *via* the reaction of PBA$^-$ and free imine is unlikely on the basis of the slope of −1 for the pH–log k_{obsd} profile at pH > 9, since the slope, contrary to the observation, should be zero at these high pH's where the dissociation of PBA to PBA$^-$ is nearly complete, and the main reaction is the nitrone formation. Moreover, any electrophilic reaction of peracid anion is unknown.

(11) Y. Ogata and Y. Sawaki, *J. Org. Chem.*, **34**, 3985 (1969).

(12) Equilibrium constants for protonation of the imine may be estimated from uv spectra; K = 25 M^{-1} for monochloroacetic acid and 10 M^{-1} for acetic acid in benzene (K = [C=NH$^+$]/[HA][C=N]).

Table III. Acid and Base Catalyses for the PBA Oxidation of Imines in Ethanol and 40% Aqueous Ethanol at 25.0°

Reaction conditions	k_{obsd},[a] M^{-1} sec^{-1} IIa[b]	IIb[c]	ArCH=NC$_6$H$_{11}$[b]	ArCH=NC$_{12}$H$_{25}$[b]
	A. Effect of Added Acid in EtOH			
None	0.164	0.0025	1.09	0.58
0.001 *M* ClAcOH	0.173	~0.011		
0.010 *M* ClAcOH	0.236	~0.012 (0.023)[d]	1.83	0.59
0.050 *M* ClAcOH	0.235	0.011 (0.022)[d]		
0.10 *M* ClAcOH	0.178	0.0073 (0.0188)[d]		
0.50 *M* ClAcOH	0.065	0.0016 (0.0120)[d]		
1.0 *M* ClAcOH	0.032	0.0006 (0.0143)[d]	~1.24	~0.62
2.0 *M* ClAcOH	0.006	0.0002 (0.0078)[d]		
	B. Effect of Initial Concentration of Imine in EtOH[e]			
0.0004 *M* C=N		0.0123		
0.0008 *M* C=N		0.0194		
0.0012 *M* C=N		0.0217		
0.0016 *M* C=N		0.0232		
	C. Effect of Sodium Acetate in EtOH[e]			
0.0004 *M* AcONa		0.0175		
0.0040 *M* AcONa		0.0245		
0.010 *M* AcONa		0.0292		
0.020 *M* AcONa		0.0468		
	D. Effect of pH in 40% Aqueous EtOH[f]			
pH 2	0.001	<0.001		
pH 4.6	0.35	0.0077		
pH 5.2	1.11	0.0347		
pH 5.7	3.23	0.121		
pH 6.4	Fast	3.78		
pH 7.2	Fast	~2.7		
pH 7.8	Fast	~3.1		
pH 9.0		~1.5[g]		
pH 11.3	Slow	~0.0041[g]		

[a] The PBA oxidation afforded an almost quantitative yield of oxazirane under these conditions, *i.e.*, in the presence of excess carboxylic acids, PBA, and hydroxylic solvents. [b] Initial concentrations: [PBA] = 0.020 *M*, [C=N] = 0.001 *M*. Ar is *p*-ClC$_6$H$_4$. [c] Initial concentrations: [PBA] = 0.040 *M*, [C=N] = 0.0008 *M*. [d] The values in parentheses are k_{obsd} for the reaction with added AcOH in place of ClAcOH. [e] The reaction in the presence of 1 *M* AcOH. [f] Initial concentrations: [PBA] = 0.01–0.02 *M*, [C=N] = 0.001–0.0004 *M*. The pH's of the media were maintained by 0.01 *M* HClO$_4$(pH 2), 0.1 *M* acetate buffer (pH 4.6, 5.2, and 5.7), 0.1 *M* phosphate buffer (pH 6.4, 7.2, and 7.8), and 0.1 *M* carbonate buffer (pH 8.5 and 11.3). [g] Nitrone is formed.

amines[5,13] and olefins,[13,14] where no catalysis by these acids is observed and alcohols only reduced the rate as an oxygenated base.

The kinetic results for the oxazirane formation suggest the Baeyer–Villiger-type (two-step) mechanism (eq 1 and 2) as shown below. Sometimes, a slow step is the acid-catalyzed addition of PBA to C=N (eq 1), when the catalysis is not so effective as with very dilute PBA (Table IIA) or in basic solvents (Table IIIA). But the subsequent SNi reaction of the adduct I (eq 2) is rate determining under most conditions in these nonaqueous solvents. Since an amine loses its nucleophilicity on protonation,[15] it is well understood that the reaction is retarded by protonation with carboxylic acids and assisted by deprotonation by bases such as sodium acetate or imine itself. The rate-determining SNi reaction of I may also explain the rather small effect of solvents in contrast to the case of acyclic imines, where significant catalysis by alcohols was observed.[5] On the other hand, an epoxidation-type (one-step) mechanism for the oxazirane formation cannot explain the results, especially the accelerating and the retarding effects by the same acids and the solvent effect.[16a]

Why is the addition equilibrium of PBA to C=N (eq 1) for the cyclic imines established much more facile than that for acyclic imines? This is probably due to their large difference in the equilibrium constants between cyclic and acyclic imines. This difference seems to be apparent in view of the facts that the cyclic imines are stable against hydrolysis in contrast to the facile hydrolysis of acyclic imines and that the equilibrium constant for the addition of hydrogen peroxide to IIa is too small to be observable ($K < 10^{-3}$ M^{-1}).[16b]

Reaction in 40% Aqueous Ethanol. The cyclic imines, IIa and IIb, are stable against hydrolysis and are mostly protonated at pH <6 in view of pK_a = 6.4 for IIa and 7.5 for IIb.[9] The addition of PBA anion (PBA$^-$) may be shown to be rate determining from the following reasonings for the oxazirane formation at pH <6.

(i) Assuming a nucleophilic attack of π-bonding electrons of free C=N on PBA, the unit slope of the pH–rate profile should be due to protonation preequilibrium of imine. Then, the relative reactivity of free imines toward PBA may be calculated as IIa:IIb

(13) Y. Sawaki and Y. Ogata, unpublished results.

(14) R. Curci, R. A. DiPrete, J. O. Edwards, and G. Modena, *J. Org. Chem.*, **35**, 740 (1970).

(15) (a) K. M. Ibne-Rasa and J. O. Edwards, *J. Amer. Chem. Soc.*, **84**, 763 (1962); (b) J. O. Edwards, "Peroxide Reaction Mechanism," J. O. Edwards, Ed., Interscience, New York, N. Y., 1962, p 98.

(16) (a) No acceleration by these weak acids has been reported for the one-step oxidation of amines, olefins, and sulfides.[5] Hence, it is unreasonable exceptionally to explain the effect by a special interaction of PBA with acids (*i.e.*, dimer[4]). The oxazirane formation from imine II is rather insensitive to the nature (*i.e.*, aprotic or protic or basic property) of solvents, which is likewise different from the PBA oxidation of other nucleophiles.[5] (b) The uv spectra of IIa and IIb were not affected by the addition of 1 *M* H_2O_2 in 40% aqueous ethanol, which shows that the equilibrium constants for addition of H_2O_2 are less than 10^{-3} M^{-1}. There is no reason that the *K* value for PBA, a weaker nucleophile, is higher than that of H_2O_2.

= 2.6:1 from k_{obsd} (30:1) and $\Delta pK_a = 1.1$. The reaction of weaker base IIa should be faster than IIb, which is abnormal as a SN reaction of nucleophiles with peracids, since there is no reason for the reversal of their nucleophilicities.[17] Moreover, it is difficult to explain the change of products from oxazirane to nitrone at higher pH.[10] Hence, this assumption is not tenable.

(ii) Assuming the establishment of the following two equilibria and a rate-determining SNi reaction of I or I′ (eq 6), the rate constant for OH^- catalyzed deprotonation (step 2, eq 6), k_{OH}, may be calculated as $k_{OH} >$

$$>C{=}NH^+- + PBA \underset{}{\overset{K_1}{\rightleftharpoons}} \underset{OOCOPh}{\overset{|}{-C-}}NH_2^+- \overset{k_{OH}[OH^-]}{\rightleftharpoons} \quad (6)$$

I′

$$\underset{OOCOPh}{\overset{|}{-C-}}NH- \longrightarrow \underset{O}{\overset{|}{-C-}}N-$$

I

10^{12} M^{-1} sec^{-1} for IIa.[18] This value is too fast to be real,[19] denying the second assumption.

(iii) The observed unit slope for the plots of log k_{obsd} *vs.* pH at pH <6 might be due to a reaction between free imines and PBA^-. But this cannot explain the slowing down of the oxidation at higher pH,[20] where [PBA^-] and [free imine] are increased.

(iv) The most probable explanation is the rate-determining addition of PBA^- to protonated imine (eq 7). The pH–rate profile affords the k_7 values of 3000

$$>C{=}NH^+- + PBA^- \underset{slow}{\overset{k_7}{\longrightarrow}} I \longrightarrow \underset{O}{\overset{|}{-C-}}N- \quad (7)$$

M^{-1} sec^{-1} for IIa and 75 M^{-1} sec^{-1} for IIb. These values are not unreasonable in view of the kinetic data of other nucleophilic additions. For example, the corresponding rate constant for the addition of PBA^- to ArCHO is 10^3 M^{-1} sec^{-1} [21] and the relative rates for ArCHO:ArCOMe are 100:1;[22] the addition of OH^- to protonated acyclic imines is in the order of 10^5–10^6 M^{-1} sec^{-1} in water.[23,24] It is natural to assume that the same mechanism for the oxazirane formation is operative in 40% aqueous ethanol or in organic solvents. Hence, assumption iv is the most probable and can explain the rate for the oxazirane formation decrease at high pH on the basis of the decrease of [$C{=}NH^+$] in spite of an increase of [PBA^-].

The oxidation rate of IIb levels off at pH 6–8 and then decreases above the pH region, where the oxazirane formation changes to the nitrone formation. The reaction rate between IIb and PBA (but not PBA^-) to give nitrone[10] is estimated to be 2.6 M^{-1} sec^{-1} at pH 11.3 and 2.4 M^{-1} sec^{-1} at pH 9 using the pK_a value of 8.5 for PBA.[11] These results are understood by two pathways, *i.e.*, the oxazirane formation *via* the protonated imine and the nitrone formation *via* the free imine.

Nitrone Formation. Solvents affect the rate of the nitrone formation in the decreasing order: $CHCl_3 > C_6H_6 > CCl_4 >$ AcOEt $> Et_2O >$ dioxane $>$ DMF (Table IIC), alcohols exhibiting a retarding effect as an oxygen base. This is the same order as the epoxidation of olefins[6,14] and the PBA oxidation of amines.[5,13] The rate constant for the PBA oxidation of free imine IIb in 40% aqueous ethanol is 2.6 M^{-1} sec^{-1}, which is close to that in benzene (2.0 M^{-1} sec^{-1}). The similar magnitude of solvent effect is observed for the olefin epoxidation.[25] These effects of solvents are due to the formation of hydrogen bonding between solvents and PBA[14] and to the solvent polarity,[25] suggesting a mechanism similar to the peracid oxidation of olefins and amines.

The values of $k_{nitrone}$ for IIa (pK_a = 6.4) and IIb (pK_a = 7.5) are 0.52 and 2.0 M^{-1} sec^{-1}, respectively, in benzene. Substituent effect for the nitrone formation from benzylidene-*tert*-butylamine showed a trend of the nucleophilic reaction of the imines.[5] The nucleophilic nature of the nitrone formation is apparent in view of these relative reactivities together with the effects of solvents and pH. The direct formation of nitrones suggests that the nucleophilic site is the N lone-paired electrons of C=N. This is natural, since the protonation or hydrogen bonding occurs at the N atom.[26]

Nucleophilicity of C=N. The apparent higher reactivity of C=N compared to C=C was explained in terms of the "pseudo-α-effect" by Madan and Clapp.[4] However, our study suggests that oxaziranes are formed *via* the adduct between peracid and C=N (eq 1 and 2) and that the nucleophilic attack of C=N to peracid affords nitrones.

Generally, pK_a values of protonated imines are less than those of parent amines only by 2–3 pK_a units,[27] but the nucleophilicity of C=N in the present PBA oxidation is much lower than that expected from their pK_a's (Table IV). That is, the rate constants for amines with the same pK_a's as those of IIa and IIb are expected to be 400 and 1700 M^{-1} sec^{-1}, respectively, from the data of PBA oxidation of *N*,*N*-dimethylanilines (k_{obsd} = 15 M^{-1} sec^{-1} and ρ −2.4).[13] The oxidation rate ($k_{nitrone}$) is only *ca.* $^1/_{1000}$th of the expected value, k_{estd}. In contrast, the expected value for azobenzene (5.3×10^{-4} M^{-1} sec^{-1}) is of the same order of magnitude as the observed one (2.2×10^{-4} M^{-1} sec^{-1}).

The low nucleophilicity of C=N is exemplified in the peracid oxidation of hydrazones, where the reaction

(17) The acceleration of a methyl group is large for the epoxidation of olefins: D. Swern, *J. Amer. Chem. Soc.*, **69**, 1692 (1947); *Chem. Rev.*, **45**, 1 (1949). Highly negative ρ values have been observed for the peracid oxidation of amines, *e.g.*, ρ −1.86 for anilines[15a] and ρ −2.40 for *N*,*N*-dimethylanilines,[13] the reactivity of which is about twofold higher than that of aniline. These seem to reflect the unimportance of the steric factor of a methyl group in these PBA oxidations.

(18) Since $k_{OH}[OH^-][I'] = k_{OH}[OH^-]K_1 = k_{obsd} = 1$ M^{-1} sec^{-1} at pH 5.0 and $K_1 < 10^{-3}$ M^{-1} in comparison with that of H_2O_2,[16b] $k_{OH} = k_{obsd}/K_1[OH^-] > 10^{12}$ M^{-1} sec^{-1}.

(19) The corresponding k_{OH} value for the deprotonation of protonated amines by OH^- is *ca.* 10^{10} M^{-1} sec^{-1} in water: M. Eigen, *Angew. Chem.*, **75**, 489 (1963).

(20) Generally, a nucleophilic attack to free C=N is slow. For example, ref 2; J. Archila, H. Bull, C. Lagenaur, and E. H. Cordes, *J. Org. Chem.*, **36**, 1345 (1971).

(21) Y. Ogata and Y. Sawaki, *J. Amer. Chem. Soc.*, **94**, 4189 (1972).

(22) Y. Ogata and Y. Sawaki, *J. Org. Chem.*, **37**, 2953 (1972).

(23) E. H. Cordes and W. P. Jencks, *J. Amer. Chem. Soc.*, **85**, 2843 (1963).

(24) J. Hine, *ibid.*, **93**, 3701 (1971).

(25) The rate of PBA oxidation of olefins in aqueous ethanol is shown to increase with solvent polarity, affording a *m* value of *ca.* 0.30.[13]

(26) For example, M. A. El-Bayoumi, M. El-Asser, and F. Abdel-Halim, *J. Amer. Chem. Soc.*, **93**, 585, 590 (1971); J. Weinstein and E. McImrich, *ibid.*, **82**, 6065 (1960); J. W. Smith, "The Chemistry of the Carbon-Nitrogen Double Bond," S. Patai, Ed., Interscience, London, 1970, p 235.

(27) For example, ref 23; I. R. Bellobono and G. Favini, *Tetrahedron*, **25**, 57 (1969).

Table IV. Rates for the PBA Oxidation of Some Nitrogen Bases and Olefins in Benzene at 25.0°

Nucleophile[a]	pK_a[b]	k_{obsd}, M^{-1} sec^{-1}	k_{estd},[c] M^{-1} sec^{-1}
IIa (R = H)	6.4[d]	0.5[e]	400
IIb (R = Me)	7.5[d]	2.0[e]	1700
p-MeOC$_6$H$_4$CH=N-*t*-Bu	7.70[f]	0.2[e,g]	2200
C$_6$H$_5$NMe$_2$	4.85	15	15
C$_6$H$_5$N=NC$_6$H$_5$	−2.90[h]	0.00022	0.00053
C$_6$H$_5$CH=CH$_2$		0.00094	
C$_6$H$_5$CH=CHC$_6$H$_5$	~−6[h]	0.000425[i]	

[a] Products are N oxides for N bases and epoxides for olefins. [b] Values in water at 25°, if not otherwise noted. [c] Estimated values for an amine with the same pK_a from k_{obsd} of *N*,*N*-dimethylaniline and ρ −2.40.[13] [d] Values in 40% aqueous EtOH. [e] The rate of nitrone formation. [f] Reference 23. [g] Approximate value at 20° because the main reaction is the oxazirane formation. [h] E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 277 (1963). [i] B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

site is not the imino group but the amino group.[28] Similarly, the nucleophilic attack of ozone on imines[29] seems to show the low nucleophilicity of C=N in view of the fact that ozone is a potent electrophile for olefins, amines, and sulfides.[30] Consequently, the low nucleophilicity of imines seems to be general. Although the reason is not clear at this time, one reason for the low nucleophilicity might be that the proton affinity of C=N (*i.e.*, pK_a of its conjugate acid) is unexpectedly high because of the high stability of C=NH$^+$. This is conceivable in view of the fact that the basicity of the imine, RCH=NR′, is lower than the parent amine, R′NH$_2$, only by 2–3 pK_a units, while the nitrile, RC≡N, is a very weak base ($pK_a \sim -10$).[31] An explicit fact is that the "pseudo-α-effect"[4] is not accelerating but retarding if any, and this low nucleophilicity of C=N results in the convenient synthesis of oxaziranes by the peracid oxidation of imines.[32]

Conclusions

There are two pathways for the peracid oxidation of imines to give oxaziranes and nitrones, and their selectivities change with the structure of imines and the reaction conditions, especially acidity.

Oxaziranes are produced *via* a two-step mechanism (eq 1 and 2). The addition of peracid to C=N is catalyzed by various acids including alcohols as effective as carboxylic acids.[5] A rate-determining step is dependent both on the imine structure and on the extent of acid catalysis. The rate for the oxidation of acyclic imines under the usual kinetic conditions is governed by the acid-catalyzed addition of peracid to C=N (eq 1), but the slow step shifts to the subsequent SNi reaction of the adduct (eq 2) in the presence of a sufficient amount of acid. Whereas for the case of cyclic imines, the SNi reaction of the second step is usually rate determining, and excess carboxylic acid reduces the rate considerably.

The nitrone formation is a nucleophilic attack of the N atom of imines on the peracid *via* a mechanism similar to the peracid oxidation of olefins and amines. The nucleophilic site of C=N is N lone-paired electrons and the rate is slowed down by a factor of 1000 in comparison with the amine of the same pK_a value, which denies the "pseudo-α-effect" on the nucleophilicity of C=N.

Experimental Section

Materials. PBA and solvents were purified as reported previously.[5] Benzylidenealkylimines, C$_6$H$_5$CH=NR, were obtained from benzaldehyde and amines in benzene; R, boiling point, and uv (EtOH): Me, bp 89.5–90.0° (30 mm) [lit.[33] 68–69° (20 mm)], uv 244 nm (ε 13,200), 277 sh (1220), 284 sh (880); cyclohexyl, bp 166–167° (30 mm) [lit.[34] 136–137° (15 mm)], uv 247 nm (ε 15,800), 278 sh (1440), 285 sh (920); *t*-Bu, bp 117–119° (36 mm) [lit.[23] 63–64° (1.0 mm)], uv 244 nm (ε 15,400), 277 sh (1210), 284 sh (800). Acetophenonecyclohexylimine had bp 127–129° (5 mm) [lit.[34] 185° (51 mm)]. The cyclic imines, IIa and IIb, were prepared by the condensation of *N*-β-phenylethylformamide and acetamide in polyphosphoric acid, respectively: IIa (R = H) bp 75–78° (4 mm) [lit.[35] 75–77° (1 mm)]; uv (EtOH) 254 nm (ε 7300), 280 sh (1120); uv (40% aqueous EtOH, pH 1), 282 nm (ε 9140), ~310 (1500); IIb (R = Me) bp 108–110° (9 mm) [lit.[35] 70–76° (1 mm)]; uv (EtOH), 250 nm (ε 7800), ~285 sh (1340); uv (40% aqueous EtOH, pH 1) 274 nm (10,600), ~310 sh (1800). Ir spectra of these imines showed the characteristic absorption at 1630 cm^{-1} (C=N).

Rates and Products Determinations. The rate was determined as reported previously.[5] Since the pseudo-first-order plots with respect to imines resulted in a curvature for the reaction in ethanol or in the presence of carboxylic acids in aprotic solvents, the rate constant was calculated with the reaction up to ~20% conversion. The curvature is due to the gradual change of the conditions, *i.e.*, acidity and basicity.

Oxaziranes were titrated iodometrically[1] and nitrones were determined by uv spectrophotometry. Nitrones and uv max in EtOH (ε) are as follows: C$_6$H$_5$CH=N(O)Me, 292 nm (21,150);[36] C$_6$H$_5$CH=N(O)-*t*-Bu, 295 nm (16,700);[3a] C$_6$H$_5$CH=N(O)C$_6$H$_{11}$, 291 nm in MeOH (17,600);[37] C$_6$H$_5$CMe=N(O)C$_6$H$_{11}$, 261 nm (11,690);[38] IVa, 305 nm (16,000); IVb, 296 nm (13,500).

3,4-Dihydroisoquinoline 1,2-Oxide (IIIa). The reaction of IIa (0.55 g, 4.0 mmol) with peracetic acid[39] (4.1 mmol) was conducted in benzene (18 ml)–EtOH (2 ml) for 2 hr at room temperature; the iodometry shows the formation of 97.1% of the oxazirane. The reaction mixture was washed twice with water and then with 5% aqueous NaHCO$_3$. After the mixture was dried over Na$_2$SO$_4$, benzene was evaporated under reduced pressure, affording the crude oxazirane, IIIa (86% purity by iodometry). Since the further purification was unsuccessful because of its low stability, the characterization of IIIa was done with the crude oxazirane as follows: (i) iodometry;[3a,5] (*ii*) the absence of the ir absorbance of C=N at 1630 cm^{-1}; (iii) the ir absorbance at 1260–1270 and ~750 cm^{-1} characteristic to the oxazirane ring;[40] (iv) the formation of IIa by the reduction with KI;[3a] (v) the chemical shift in nmr (CCl$_4$ *vs.* TMS) δ 6.9–7.7 (4 H, m, aromatic proton), 4.70 (1 H, s, oxazirane CH), 2.69 (2 H, t, J = 10.8 Hz, 3 -CH$_2$-), 2.40 (2 H, t, J = 10.8 Hz, 4 -CH$_2$-); (vi) the H$_2$SO$_4$ catalyzed isomerization to IVa.

Oxazirane IIIa was converted to isoquinoline on standing for about 2 weeks or by heating at 110–120° for several hours in a sealed tube under reduced pressure. Isoquinoline was obtained in an almost quantitative yield and identified by means of the characteristic uv spectra, tlc (silicic acid, AcOEt, R_f 0.51), and melting point of the picrate, 221–223°. The oxazirane IIIa was more stable in EtOH in comparison to aprotic solvents, but the neat sample was unstable.

3,4-Dihydroisoquinoline 2-Oxide (IVa). Oxazirane IIIa was

(28) B. T. Gillis and K. F. Schimmel, *J. Org. Chem.*, **27**, 413 (1962); **32**, 2865 (1967).
(29) A. H. Riebel, R. E. Erickson, C. J. Abshire, and P. S. Bailey, *J. Amer. Chem. Soc.*, **82**, 1801 (1960).
(30) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).
(31) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 277 (1963).
(32) Reference 3; R. G. Pews, *J. Org. Chem.*, **32**, 1628 (1967); L. A. Paquette, "Principles of Modern Heterocyclic Chemistry," W. A. Benjamin, New York, N. Y., 1968, p 63.
(33) K. N. Campbell, C. H. Helbing, M. P. Florkowski, and B K. Campbell, *J. Amer. Chem. Soc.*, 70, 3868 (1948).
(34) E. D. Bergmann and S. Pinchas, *Recl. Trav. Chim. Pays-Bas*, **71**, 161 (1952).
(35) J. G. Cannon and G. L. Webster, *J. Amer. Pharm. Ass.*, **47**, 353 (1958); *Chem. Abstr.*, **52**, 17273a (1958).
(36) T. Kubota, M. Yamakawa, and Y. Mori, *Bull. Chem. Soc. Jap.*, **36**, 1552 (1963).
(37) T. Thesing and W. Sirrenberg, *Chem. Ber.*, **91**, 1978 (1958).
(38) Uv data of C$_6$H$_5$CMe=N(O)Me.[36]
(39) PBA is not appropriate to obtain a pure oxazirane or nitrone because of its contamination with a trace of benzoic acid.
(40) K. Shingawa and I. Tanaka, *J. Phys. Chem.*, **68**, 1205 (1964).

isomerized to nitrone IVa in 40% H_2SO_4 in aqueous MeOH by standing overnight at room temperature: uv (EtOH) 305 nm (ε 16,000) [lit.[37] 304 nm (15,900) in MeOH); picrate, mp 138–141° (lit.[41] 141–142°).

3,4-Dihydro-1-methylisoquinoline 1,2-Oxide (IIIb). Imine IIb (3.75 mmol) was oxidized by peracetic acid (3.85 mmol) in benzene (27 ml)–EtOH (3 ml) at 25° for 4 hr. A treatment similar to that of IIIa gave crude oxazirane IIIb (86.9% purity by iodometry). This oxazirane was also difficult to purify and identified similarly to the case of IIIa: uv (EtOH) 207 nm (ε ~7000); nmr (CCl_4 *vs.* TMS) δ 6.9–7.7 (4 H, m, aromatic proton), 2.70 (2 H, t, J = 10.5 Hz, 3 $-CH_2-$), 2.40 (2 H, t, J = 10.5 Hz, 4 $-CH_2-$), 1.78 (3 H, s, 1 $-CH_3$).

On standing, IIIb was gradually converted to 1-methylisoquinoline, which was identified by the characteristic uv spectra, tlc, and nmr in comparison with the authentic sample.

3,4-Dihydro-1-methylisoquinoline 2-Oxide (IVb). Crude IIIb (0.835 g) was converted to nitrone IVb by H_2SO_4 catalyzed isomerization (40% H_2SO_4 in aqueous MeOH for 7 hr at room temperature). The reaction mixture was neutralized with aqueous Na_2CO_3, extracted with ether, washed with aqueous KH_2PO_4, and dried over Na_2SO_4; after evaporation of solvent, crystallization from petroleum ether gave crystals of IVb: mp below 0°; uv (EtOH) 218 nm (ε 11,200), 296 (13,500);[42] nmr (CCl_4 *vs.* TMS) δ 8.2–6.9 (m, aromatic proton), 3.82 (t, J = 8.5 Hz, 3 $-CH_2-$), 2.93 (t, J = 8.5 Hz, 4 $-CH_2-$), 2.40 (s, 1 CH_3). Nitrone IVb may be isolated as picrate: 1.2 (60% yield); mp 176–178° (from EtOH); nmr (DMSO-d_6 *vs.* TMS) δ 8.43 (2 H, s, aromatic proton of picric acid), 7.75–7.30 (4 H, m, aromatic proton), 4.15 (2 H, t, J = 8.5 Hz, 3 $-CH_2-$), 3.15 (2 H, t, J = 8.5 Hz, 4 $-CH_2-$), 2.55 (3 H, 2, 1 CH_3).

Anal. Calcd for $C_{16}H_{14}N_4O_8$: C, 49.23; H, 3.62; N, 14.4. Found: C, 48.5; H, 3.77; N, 14.8.

2-Cyclohexyl-3-phenyl-3-methyloxazirane. Acetophenonecyclohexylimine (3.24 mmol) was oxidized by peracetic acid in 30 ml of benzene at 25° for 3 hr. The benzene solution was washed twice with aqueous Na_2CO_3 and aqueous KH_2PO_4 and the solvent was evaporated. Crystallization from petroleum ether afforded the titled oxazirane: mp 45.3–46.5° (96.0% pure by iodometry); uv (EtOH) 208 nm (ε 4400), 252 (130), 257 (160), 263 (130); nmr (CCl_4 *vs.* TMS) δ 8.1–7.8 (4 H, m, aromatic proton), 2.44 (1 H, q, J = 14 Hz, N–CH), 1.67 (3 H, s, 3 CH_3), 1.9–1.1 (10 H, m, pentamethylene).

(41) J. Thesing and H. Mayer, *Justus Liebigs Ann. Chem.*, **609**, 46 (1957).

(42) The molar absorptivity of IVb was estimated from the uv spectra of the picrate (10^{-4} *M*) in EtOH. The uv spectra of picric acid was unaffected by addition of IVb or triethylamine, suggesting no acid–base interaction at these concentrations.

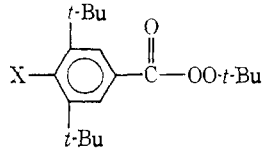
Phenolic Peresters. I. Radical and Base-Induced Decomposition

A. M. Hučeк, J. T. Barbas, and J. E. Leffler*

Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306. *Received October 2, 1972*

Abstract: The phenolic perester **1a** is prevented from giving the usual bimolecular reaction between phenols and acyl peroxides by its hindering *tert*-butyl groups. Although the spontaneous decomposition of **1a** shows only the normal substituent effect, removal of the phenolic hydrogen to give either the oxygen radical *or the anion* induces a rapid *radical* decomposition reaction. This perester is sensitive to base even at room temperature and below. The evidence suggests that the expected α-lactone intermediate **2** exists as a diradical **2a** and gives typical radical reactions. CIDNP signals are observed from the ring protons of the carboxylic acid produced in the base-initiated reaction in ethers and from the vinyl protons of unsaturated ethers corresponding to the solvent.

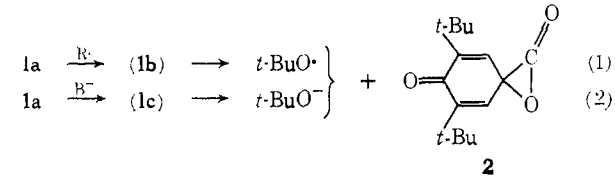
The synthesis of the perester **1a** was motivated by an interest in the interactions of the perester functional group with oxygen radical or anionic substituents.



1a, X = OH
b, X = O·
c, X = O^-
d, X = OD

Generation of a radical substituent in an aliphatic peroxide gives α- or γ-lactones[1] or alkenes[2] depending on the structure of the peroxide. Similar experiments with aromatic acyl peroxides, in which an atom was removed from a carbon atom of the ring or of a benzylic substituent, had only negative results.[3] The radicals reacted without any decomposition of the peroxide function.

Removal of the phenolic hydrogen from **1a** either as an atom or as a proton was expected to give the lactone **2**, a process that would provide a driving



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force for the decomposition of the perester. A further reason for interest in the reactions of **1a** is the re-

(1) (a) P. D. Bartlett and L. B. Gortler, *J. Amer. Chem. Soc.*, **85**, 1864 (1963); (b) L. B. Gortler and M. D. Saltzman, *J. Org. Chem.*, **31**, 3821 (1966); (c) H. Hart and F. J. Chloupek, *J. Amer. Chem. Soc.*, **85**, 1155 (1963); (d) C. Rüchardt and H. Schwarzer, *Chem. Ber.*, **99**, 1861 (1966).

(2) (a) L. M. Bobroff, L. B. Gortler, D. J. Sahn, and H. Wiland, *J. Org. Chem.*, **31**, 2678 (1966); (b) E. N. Cain, R. Vukov, and S. Masamune, *Chem. Commun.*, 243 (1969).

(3) (a) M. M. Schwartz and J. E. Leffler, *J. Amer. Chem. Soc.*, **90**, 1368 (1968); (b) *ibid.*, **93**, 919 (1971); (c) A. I. Dalton and T. T. Tidwell, *J. Org. Chem.*, **37**, 1504 (1972).