Rate Measurements.—Benzil has an absorption maximum in methanol at 380 mμ (ε 73.3), where benzaldehyde, triphenylimidazole, and ammonium acetate have little absorption. The data with various imidazoles are shown in Table IV. All of the compounds satisfy the Lambert–Beer law and the concentration of the above compounds can be estimated by spectrophotometry.

A typical measurement was made in the following manner. An acetic acid solution of ammonium acetate and a mixture of benzil, benzaldehyde, and acetic acid were mixed in a flask fitted with a reflux condenser and thermometer after reaching thermal equilibrium (100 ± 0.5°). Aliquots (each 1 ml) were taken out at regular intervals of time and diluted with methanol, and the absorbances at 380 mμ for benzil and for imidazole were measured. The first-order rate coefficient with benzil was calculated from the ordinary integrated equation.

Acknowledgment.—The authors wish to thank the referees for their helpful suggestions.

Registry No.—Benzil, 134-81-6; ammonium acetate, 1066-32-6; benzaldehyde, 100-52-7.

Kinetics of the Baeyer–Villiger Reaction of Benzaldehydes with Perbenzoic Acid in Aquoorganic Solvents

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The Baeyer–Villiger reaction of benzaldehydes with perbenzoic acid to give ultimately phenols and/or benzoic acids has been studied kinetically in aquoorganic solvents at various pH's. The rate in acidic media increases with increasing pH and exhibits general base catalysis but not acid catalysis. The rate at pH > 10 is independent of pH with some kind of aldehydes, while the rate for others decreases with increasing pH. The effect of substituent in benzaldehydes on hydride shift affording benzoic acids gives a ρ value of 1.1–1.8. These results, together with solvent and temperature effects, are discussed in terms of a mechanism containing formation, ionization, and rearrangement of an addition intermediate between the carbonyl group and peracid.

Heterolytic 1,2 rearrangements of organic peroxides have been studied extensively and they are recognized as intramolecular nucleophilic substitution on peroxide oxygen.[1] For example, highly negative ρ values were observed with heterolysis of substituted cumene hydroperoxide esters ($\rho = -5.1$)[2] and with acid-catalyzed rearrangement of cumene hydroperoxides ($\rho = -4.6$ for σ^+).[3] A similar but smaller ρ value (-1.1 to -1.4) was obtained for the Baeyer-Villiger reaction of acetophenones with trifluoroperacetic acid,[4] although most others afforded smaller and less straightforward effects of substituents, which deviates from the Hammett equation.[5]

The Baeyer–Villiger reaction in alkaline media, especially in aqueous media, has been disclosed less than that in acidic media. A typical alkaline reaction is the Dakin reaction.[6] The oxidation of ketones with alkaline hydrogen peroxide[7a] or with alkaline *t*-butyl hydroperoxide[7b] has been reported to give fission products by way of an ionic mechanism, but a homolysis could not be included.[1] Kinetics of the alkaline oxidation of *o*-sulfobenzaldehyde with substituted perbenzoate ion has been reported.[8]

The present study is an attempt at the elucidation of the mechanism of the Baeyer–Villiger reaction of benzaldehydes on the basis of migratory aptitude together with the effects of substituents, pH, solvent, and temperature.

Results

Migratory Aptitude.—Migrating groups in the Baeyer–Villiger rearrangement of benzaldehydes are either hydride or aryl anion (eq 1).

$$\mathrm{ArCHO} \xrightarrow{\mathrm{PhCO_3H}} \mathrm{ArCO_2H} + \mathrm{ArOH} \tag{1}$$

Migrating ratios of Ar/H differ largely, not only by ring substituents in the aldehydes, but also by the acidity of media, as shown in Table I. The aryl shift occurs exclusively with *p*- and *o*-hydroxybenzaldehydes. On the other hand, unsubstituted benzaldehyde and those with electron-attracting groups (*p*-Cl, *m*- and *p*-NO_2) gave solely the corresponding acids by a hydride shift regardless of the acidity of media. The oxidation of anisaldehydes is in a border line; *i.e.*, the hydride

TABLE I

MIGRATORY APTITUDE FOR THE BAEYER–VILLIGER REACTION OF BENZALDEHYDES BY PERBENZOIC ACID IN 80% METHANOL AT 2–5° FOR 24 HR[a]

		Products, %[b]					
		Alkaline[c]		Neutral[d]		Acidic[e]	
Registry no.	Substituent	Ar-CO_2H	ArOH	Ar-CO_2H	ArOH	Ar-CO_2H	ArOH
123-08-0	*p*-OH	0	94	0	92	0	91
90-02-8	*o*-OH	0	99	0	95	0	98
100-83-4	*m*-OH	65	2.1				
123-11-5	*p*-OMe	69	4.7	17	40	19	73
135-02-4	*o*-OMe	39	37	1	68		
100-52-7	H	100	0	90	0	90	0
104-88-1	*p*-Cl	93	0	97	0		
555-16-8	*p*-NO_2	100	0	98	0		
99-61-6	*m*-NO_2	98	0				

[a] Initial concentration: [ArCHO] ~ 0.10 *M* and [$PhCO_3H$] ~ 0.13 *M*. Reaction in nitrogen atmosphere. [b] Per cent yield based on a charged aldehyde. Material balance is above 95%. [c] [NaOH] ~ 0.60 *M*. [d] Weakly acidic conditions caused by the presence of perbenzoic and produced benzoic acids. [e] [H_2SO_4] ~ 0.30 *M*.

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(1) A. G. Davies, "Organic Peroxides," Butterworth and Co. Ltd., London, 1961, p 143.

(2) K. Nelson, quoted by S. Winstein and G. C. Robinson, *J. Amer. Chem. Soc.*, **80**, 169 (1958).

(3) A. W. De R. Van Stevenick and E. C. Kooyman, *Rec. Trav. Chim. Pays-Bas*, **79**, 413 (1960).

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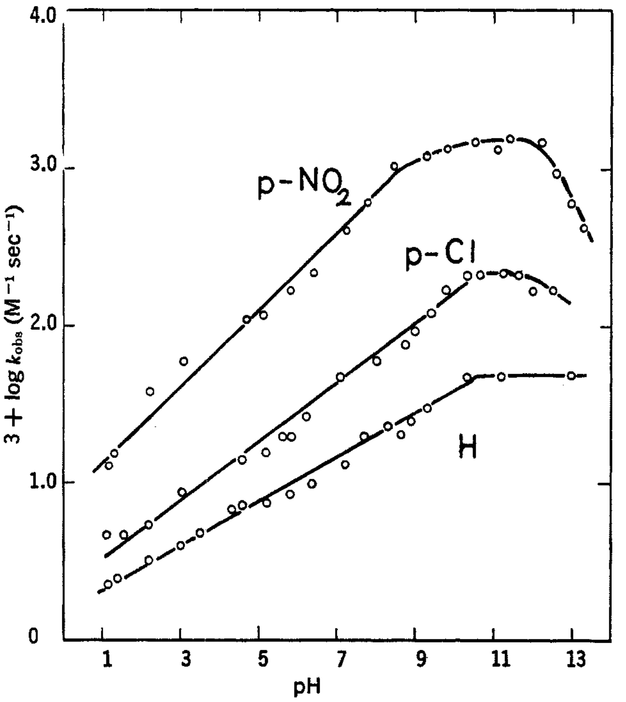

Figure 1.—Effect of pH on the reaction of substituted benzaldehydes with perbenzoic acid in 40% ethanol at 25 ± 0.1°. Initial concentrations are 0.05–0.020 *M*.

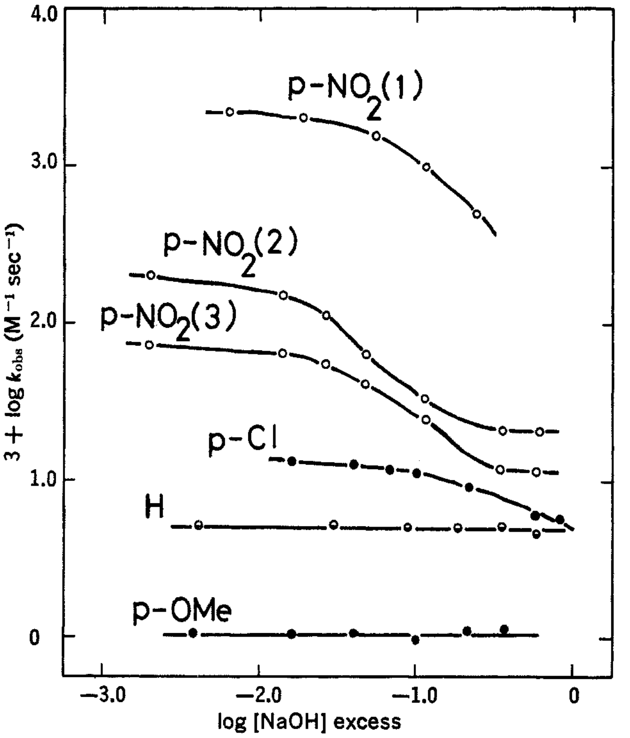

Figure 2.—Effect of excess [NaOH] on the reaction of substituted benzaldehydes with perbenzoate ion. Solvent and temperature: *p*-NO$_2$ (1) in 60% dioxane at 15°; *p*-NO$_2$ (2) in 40% methanol at 10°; *p*-NO$_2$ (3) in 80% methanol at 10°; *p*-Cl, H, and *p*-OMe at 5°. Initial concentrations are 0.01–0.02 *M*.

shift is predominant in alkaline media, while the aryl shift is preferred in acidic media.

Rate Law.—The oxidation rates of benzaldehydes by perbenzoic acid were measured by iodometry of remaining peroxide oxygen. Generally, second-order kinetics without an induction period were observed up to 20–80% conversion (eq 2). The subscripts in eq 2 mean stoichiometric concentration.

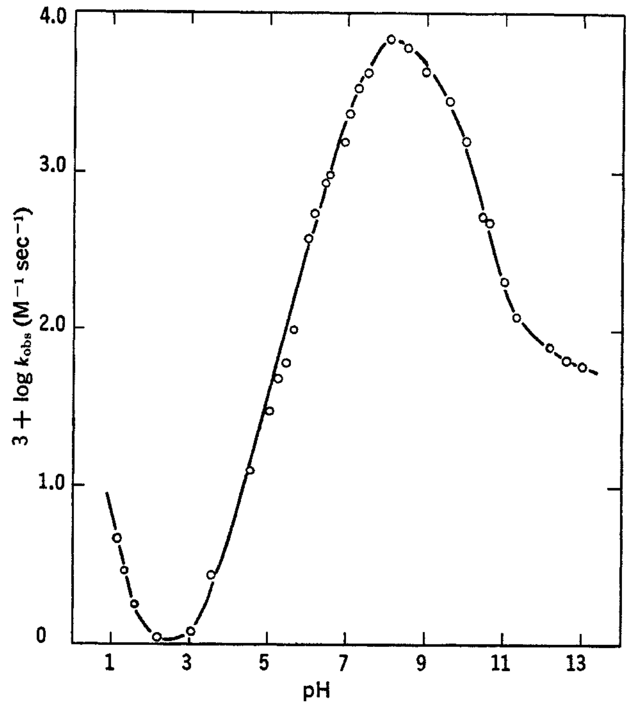

Figure 3.—Effect of pH on the reaction of *p*-hydroxybenzaldehyde with perbenzoic acid in 40% ethanol at 25 ± 0.1°. Initial concentrations are 0.040–0.020 *M*.

$$v = k_{obsd}[\mathrm{ArCHO}]_s[\mathrm{PhCO_3H}]_s \qquad (2)$$

Rate constants at various initial concentrations of reactants hold constant at constant pH. The dependence of rate on pH differs significantly with ring substituents, as is shown in the next section.

Effect of Acid and Base.—The oxidation rates of aldehydes reacting with a hydride shift increase with increasing pH up to *ca.* 10, the plots of log k_{obsd} *vs.* pH affording slopes of 0.15 for H, 0.19 for *p*-Cl, and 0.24 for *p*-NO$_2$ (Figure 1). The pK_a value of perbenzoic acid in 40% ethanol was titrated to be 8.55, which is *ca.* 0.5 greater than that in water. A further increase of alkali concentration resulted in either a decrease or no influence in the rate. That is, the oxidation rates of benzaldehyde and *p*-anisaldehyde are not affected by excess alkali, while the other aldehydes substituted with *p*-Cl and *m*- and *p*-NO$_2$ were significantly retarded by excess alkali (Figure 2).

The pH–rate profile for *p*-hydroxybenzaldehyde, which favors the aryl shift, is quite different from those which favor the hydride shift (Figure 3). Acid catalysis is apparent at pH below 2, while the reaction at pH 3–8 is hydroxide ion catalyzed, the plot of log k_{obsd} *vs.* pH giving a line of unit slope. A further increase of pH from 8 decreases the rate and the slope is between 0 and −1.

General base catalysis was observed with acidic oxidation of all these aldehydes (Table II). Plots of k_{obsd} *vs.* base concentration gave a set of parallel lines corresponding to pairs of aldehyde and base. There is no evidence for general acid catalysis.

On the other hand, general base catalysis was not observed for alkaline oxidation; *i.e.*, no increase of rate was observed when sodium acetate (0.4 *M*) or *p*-cresol (0.05 *M*) was added or when sodium hydroxide was re-

TABLE II

GENERAL BASE CATALYSIS FOR PERBENZOIC ACID OXIDATION OF BENZALDEHYDES IN 40% ETHANOL AT 25 ± 0.1° (μ = 0.20)

Substituent	Buffer, molar ratio[a]	pH[b]	Intercept,[c] 10^{-3} M^{-1} sec^{-1}	Slope,[d] 10^{-3} M^{-2} sec^{-1}
p-OH[e]	$ClCH_2COOH$–Na, 2:1	3.0	1.2	20
	$ClCH_2COOH$–Na, 1:2	3.5	2.7	20
	CH_3COOH–Na, 4:1	4.6	12.5	570
	CH_3COOH–Na, 1:1	5.2	29.3	660
	CH_3COOH–Na, 1:2	5.5	48.0	720
H[e]	$ClCH_2COOH$–Na, 2:1	3.0	4.1	25
	$ClCH_2COOH$–Na, 1:2	3.5	4.8	25
	CH_3COOH–Na, 4:1	4.6	7.2	48
	CH_3COOH–Na, 1:1	5.2	7.5	42
p-Cl[e]	$ClCH_2COOH$–Na, 2:1	3.0	8.7	59
	CH_3COOH–Na, 4:1	4.6	13.7	56
	CH_3COOH–Na, 1:1	5.2	15.6	54
	CH_3COOH–Na, 1:4	5.8	19.8	63
p-NO_2[e]	$ClCH_2COOH$–Na, 2:1	3.0	61.0	320
	CH_3COOH–Na, 1:1	5.2	76.5	960

[a] Buffer concentration 0.03–0.20 *M*. [b] Measured by glass electrode. [c] Second-order rate constant at zero buffer concentration. [d] Slope obtained from the plot of k_{obsd} *vs.* [RCO_2Na]. [e] Initial concentrations ([ArCHO] = [$PhCO_3H$]): 0.010 *M* for *p*-OH; 0.020 *M* for H; 0.010 *M* for *p*-Cl and *p*-NO_2.

TABLE III

SUBSTITUENT EFFECT FOR REACTION OF SUBSTITUTED BENZALDEHYDES WITH PERBENZOIC ACID

	$k_{obsd} \times 10^3$, M^{-1} sec^{-1}					
	Reaction in 40% EtOH (25°)			Reaction at pH *ca.* 12.1 (10°)[a]		
Substituent	pH 1.2[b]	pH 3.0[c]	pH 5.2[d]	40% EtOH	80% EtOH	80% MeOH
p-OH	3.0	1.2	29.3	1420[e]	330[e]	2060[e]
m-OH						1.0
p-OMe	2.1		20.4[f]	8.2	3.1	2.0
H	2.4	4.1	7.5	28.5	13.6	8.4
p-Cl	4.4	8.7	15.6	81.3	47.2	22.4
m-NO_2				442	223	65.6
p-NO_2	15.4	61.0	76.5	446	246	70.8
ρ[g]	1.03	1.51	1.29	1.67	1.79	1.55
r[h]				0.995	0.989	0.977

[a] *Ca.* 0.014 *M* of excess NaOH over peracid was added. [b] Perchloric acid was added. [c] Chloroacetate buffer (2:1) was used and rate constant was extrapolated to zero buffer concentration. [d] Acetate buffer (1:1) was used and rate constant was extrapolated to zero buffer concentration. [e] *Ca.* 0.0003 *M* of excess NaOH was used. [f] Buffer concentration 0.10 *M*. [g] Hammett's ρ value *vs.* σ calculated for aldehydes of hydride shift: H, *p*-Cl, and *p*-NO_2 for the acidic oxidation and *p*-OMe, H, *p*-Cl, *m*-NO_2, and *p*-NO_2 for the alkaline oxidation. [h] Correlation coefficient.

placed by carbonate or bicarbonate. This means that anions such as OH^-, AcO^-, CO_3^{-2}, HCO_3^-, and *p*-$CH_3C_6H_4O^-$, and also weak acids such as *p*-cresol, HCO_3^-, and HPO_4^{-2}, cannot be catalysts in alkaline conditions.

Substituent Effect.—As is apparent in Figures 1, 2, and 3, the substituent effect varies with pH and is tabulated in Table III. Hammett's relationship is satisfied at a constant pH for aldehydes which are oxidized with a hydride shift, *i.e.*, benzaldehydes with *p*- and *m*-NO_2, *p*-Cl, H, and *p*-MeO (in alkaline condition), affording positive ρ values of 1.1–1.8. The plots for those with an aryl shift, *i.e.*, *p*-HO and *p*-MeO (in acidic conditions), deviate largely from the correlation. Apparently, the effect of ring substituents for aldehydes with a migrating hydride is reversed for those with a migrating aryl group.

TABLE IV

SOLVENT EFFECT FOR THE REACTION OF SUBSTITUTED BENZALDEHYDES WITH PERBENZOIC ACID

		$k_{obsd} \times 10^3$, M^{-1} sec^{-1}			
Substituent	Solvent	80%[g]	60%	40%	20%
		A. Alkaline Oxidation at 10 ± 0.1°			
p-OH	MeOH[a]	2060	2230	3340	5150
p-OH	EtOH[a]	329	535	1440	4460
H	MeOH[b]	9.2	14.4	24.8	33.0
p-Cl	MeOH[c]	22.2	32.6	39.1	45.3
p-Cl	EtOH[c]	47.3	58.6	66.7	78.5
p-Cl	Dioxane[d]	110	162	144	
p-NO_2	MeOH[c]	70.2	118	145	170
p-NO_2	Dioxane[d]	1800	2000	2200	1750
		B. Acidic Oxidation at 25 ± 0.1°			
p-OH	EtOH[e]		22.4	46.0	137
p-Cl	EtOH[f]		14.3	18.2	23.2

[a] Initial concentrations: [ArCHO] = [$PhCO_3Na$] = 0.00133 *M* and excess [NaOH] = 0.00035 *M*. [b] Initial concentrations: [ArCHO] = [$PhCO_3Na$] = 0.020 *M* and excess [NaOH] = 0.040 *M*. [c] Initial concentrations: [ArCHO] = [$PhCO_3Na$] = 0.010 *M* and excess [NaOH] = 0.014 *M*. [d] Initial concentrations: [ArCHO] = [$PhCO_3Na$] = 0.0050 *M* and excess [NaOH] = 0.019 *M*. [e] Acetate buffer (1:1, 0.05 *M*) was used. [f] Acetate buffer (1:1, 0.10 *M*) was used. [g] Volume per cent of solvent.

Solvent Effect.—The data in Table IV indicate two different features of solvent effect between hydride and aryl shifts. The rate of aryl shift for *p*-hydroxybenzaldehyde increases with increasing content of water and the rate in aqueous methanol is considerably faster than that in aqueous ethanol. On the contrary, the rate for hydride is in the order aqueous methanol < aqueous ethanol < aqueous dioxane. A maximum is observed in a plot of k_{obsd} *vs.* water content in the dioxane–water system.

Temperature Effects.—Temperature dependence of the rate was studied at 5–35° and the activation parameters obtained from the Arrhenius plots are listed in Table V. Enthalpies of activation are in the range 6–16 kcal mol^{-1} and entropies of activation are in the range −11 to −41 eu. As for alkaline oxidation, the aryl shift seems to be entropy controlled more than the hydride shift.

Discussion

Reaction Scheme.—The addition of hydrogen peroxide to benzaldehydes has recently been reported to be subject to general acid and base catalysis.[9] The oxidation of aldehydes[8] and sulfoxides[10] with perbenzoate ion is much faster than that with the free peracid, showing a sigmoid curve for the rate–pH profile. In contrast, the present oxidation, proceeding with hydride shift, shows a rather small dependence on the change of pH and the rate–pH profile gives no sigmoid curve. This oxidation, however, is heterolytic in nature, since the reaction gives almost quantitative yields of acids and/or phenols and there is no effect on addition of oxygen or other radical scavengers, *e.g.*, ethylenediaminetetraacetate or phenols.

There are three conceivable mechanisms: (A) a rate-determining addition of peracid or its anion to carbonyl, (B) a rapid equilibrium of carbonyl addition followed by a slow rearrangement, and (C) a borderline case, where a steady-state theory should be applied to the steps involving the addition and rearrangement.

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(9) E. G. Sander and W. P. Jencks, *J. Amer. Chem. Soc.*, **90**, 4377, 6154 (1968).

(10) R. Curci and G. Modena, *Tetrahedron Lett.*, 1749 (1963); 863 (1965); *Tetrahedron*, **22**, 1227, 1235 (1966).

TABLE V

TEMPERATURE DEPENDENCE FOR THE REACTION OF BENZALDEHYDES WITH PERBENZOIC ACID[a]

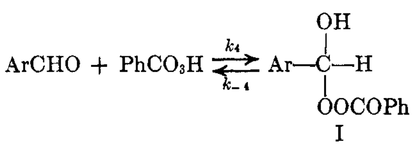
Substituent	Solvent, vol. %	Excess [NaOH], M	$k_{obsd} \times 10^3$, M^{-1} sec^{-1} 15°	25°	ΔH^*, kcal mole^{-1}	ΔS^*, eu
		A. Alkaline Oxidation				
p-OH	MeOH, 80	0.00036	2470	3920	6.18	−35
p-OH	MeOH, 40	0.00036	4270	6300	6.13	−34
p-OH	MeOH, 40	0.10	78.8	162	8.65	−33
p-OH	EtOH, 80	0.00036	437	752	6.36	−30
p-OH	EtOH, 40	0.00036	1740	2670	8.83	−35
H	MeOH, 40	0.014	33.9	63.2	11.0	−27
p-Cl	MeOH, 80	0.014	34.2	74.2	13.2	−15
p-Cl	MeOH, 40	0.014	68.7	150	12.7	−20
p-Cl	EtOH, 80	0.014	72.2	157	12.9	−19
p-Cl	EtOH, 40	0.014	116	247	11.4	−23
p-Cl	Dioxane, 60	0.014	275	489	10.7	−24
p-NO$_2$	MeOH, 80	0.014	121	313	16.2	−11
		B. Acidic Oxidation				
p-OH	EtOH, 40	pH 5.2[b]	24.6	42.2	9.1	−34
H	EtOH, 40	pH 5.2[b]	5.18	8.46	7.9	−41
p-Cl	EtOH, 40	pH 5.2[b]	10.95	17.9	8.1	−39
p-NO$_2$	EtOH, 40	pH 5.2[b]	62.9	101	8.0	−36

[a] Temperature range studied is 10–35° and two values at 15 and 25° are listed here. Sufficiently straight Arrhenius plots were obtained in each case. [b] Acetate buffer 0.05 M.

The following results cannot be explained by a rate-determining addition of peracid (mechanism A). Proton catalysis and hydroxide ion catalysis are rather weak, which is in contrast to the stronger catalysis for the addition of a stronger nucleophile, hydrogen peroxide.[9] The rate for p-hydroxybenzaldehyde is much faster than that for aldehydes having a stronger electron-attracting group. The oxidation is generally accelerated by increasing the content of water in the solvent. The oxidation of p-nitrobenzaldehyde exhibited a break in the rate–pH profile at high alkalinity.

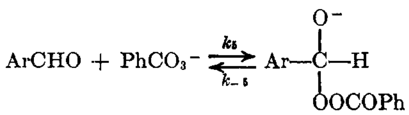
Mechanism B involves mobile preequilibriums 3–6. However in this case, the rate–pH profile should give a sigmoid curve and does not agree with the observed break at high alkalinity and the absence of base catalysis for the alkaline oxidation. Further, it was proved that there are no mobile preequilibriums 4 and 5, or, if there were, the concentration of adducts I and II would be very low, since the carbonyl absorption is virtually unchanged at the initial stage of the reaction. Also, the rate of decrease of C═O absorbance of aldehyde determined spectrophotometrically was close to that of peracid as determined iodometrically.[11]

$$PhCO_3H \overset{K_3}{\rightleftharpoons} PhCO_3^- + H^+ \tag{3}$$



$$ArCHO + PhCO_3H \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Ar\text{—}C(OH)(OOCOPh)\text{—}H \tag{4}$$

I



$$ArCHO + PhCO_3^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Ar\text{—}C(O^-)(OOCOPh)\text{—}H \tag{5}$$

II

$$I \overset{K_6}{\rightleftharpoons} II + H^+ \tag{6}$$

$$I \xrightarrow{k_7} \text{products} \tag{7}$$

$$II \xrightarrow{k_8} \text{products} \tag{8}$$

Mechanism C assumes the existence of two forms of addition intermediate, I and II, in a steady state.

$$d[I + II]/dt = k_4[ArCHO][PhCO_3H] + k_5[ArCHO][PhCO_3^-] - (k_{-4} + k_7)[I] - (k_{-5} + k_8)[II] = 0$$

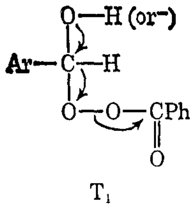
Since the proton transfer should be much faster than the other steps, *i.e.*, $K_3[PhCO_3H] = [PhCO_3^-][H^+]$ and $K_6[I] = [II][H^+]$, the rate of formation of products is written as in eq 9.

$$v = k_7[I] + k_8[II] = [ArCHO]_s[PhCO_3H]_s \left\{\frac{k_4[H^+]}{K_3 + [H^+]} + \frac{k_5K_3}{K_3 + [H^+]}\right\} \times \left[\frac{k_7}{k_{-4} + k_7 + \{(k_{-5} + k_8)K_6/[H^+]\}} + \frac{k_8}{\{(k_{-4} + k_7)[H^+]/K_6\} + k_{-5} + k_8}\right] \tag{9}$$

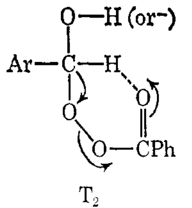
If proton transfer between I and II is not as fast as other steps, separate steps 4 and/or 5 should be considered, but this assumption cannot explain the pH–rate profile with its nonsigmoid curve and its low slope of less than unity. Hence, the steady-state assumption of the total concentration of adducts, I + II, is thought to fit to the data as outlined in eq 3–8.[12]

(11) The decrease of carbonyl absorbance was determined for p-chlorobenzaldehyde at 275 mμ directly in a 2-mm silica cell at 20–22°. With the initial concentration of 0.0005 M aldehyde, 0.005 M perbenzoic acid, and 0.10 M buffer in 40% ethanol, the carbonyl absorbance of the aldehyde at 275 mμ decreased gradually and the second-order rate constants, k_{obsd}, were 7.3 (10), 11 (15), and 15 (18) M^{-1} sec^{-1} with [AcOH]/[AcONa] = 4:1, 1:4, and 1:8, respectively. (The figures in parentheses are rate constants from the titer of peracid). Hence, the rate constant determined from the decrease of carbonyl absorbance of aldehyde was comparable with those from the decrease of peracid.

(12) The transition state for reactions 7 and 8 may be written as T_1 or T_2 (cyclic) together with the corresponding base-catalyzed ones. We prefer T_1



T_1



T_2

for the present reaction in these aqueous media, where the internal hydrogen bonding is less important, but the choice requires a further detailed study involving kinetic isotope effect and solvent effect.

Hydride Shift in Alkaline Conditions.—The hydride shift is generally catalyzed by base and accelerated by formation of α-oxy anion, *e.g.*, in Cannizzaro reaction,[13a] permanganate oxidation of fluoral,[13b] and the base-catalyzed reaction of some hydroperoxide ethers to form carbonyls[13c] analogous with the ionic decomposition of nitrate or chromate esters.

However, the present reaction at pH > 10 was not catalyzed by bases, *e.g.*, hydroxide, acetate, *p*-cresoxide, and carbonate ions. Moreover, in the case of *p*-chloro- and *m*- and *p*-nitrobenzaldehydes, the rate decreased with increasing concentration of alkali. These facts might be explained by several assumptions: the presence of II alone as an intermediate followed by an uncatalyzed shift, *i.e.*, $v = k[\mathrm{II}]$; the operation of specific hydroxide ion catalysis for I, *i.e.*, $v = k[\mathrm{I}][\mathrm{OH}^-]$; or the presence of mobile dissociation equilibrium between I and II, both of which rearrange to products. The second assumption does not easily explain the observed decrease of the rate with increasing pH, since the derived rate equation has no terms of $[\mathrm{OH}^-]$ in these alkaline conditions. Moreover, the $\mathrm{p}K_6$ value should be below 8 to explain the observed rate–pH profile, because the rate, if $\mathrm{p}K_6 > 8$, would increase with pH, but this is not the case. It is more reasonable to assume that $\mathrm{p}K_6 \geq 13$ in view of the $\mathrm{p}K_a$ values of aldehyde hydrates.[14] The first assumption contains the anion II as a sole intermediate, which cannot explain the rate decrease at high pH.

In conclusion, the third assumption is convincing, which is outlined in eq 3–8. This assumes that the sum of [I] and [II] is in a steady state and the $\mathrm{p}K_6$ value should be above 13. A similar assumption of two forms of adducts has been reported.[15] The assumption of $\mathrm{p}K_6 \geq 13$ is reasonable, as stated above.[14] Hence, eq 9 may be rewritten for the alkaline oxidation as follows.

$$k_{\mathrm{obsd}} = k_5\left[\frac{k_7}{k_{-4} + k_7 + \{(k_{-5} + k_8)K_6/[\mathrm{H}^+]\}} + \frac{k_8}{\{(k_{-4} + k_7)[\mathrm{H}^+]/K_6\} + k_{-5} + k_8}\right] \tag{10a}$$

When $[\mathrm{H}^+] \gg K_6$

$$k_{\mathrm{obsd}} \simeq k_5k_7/(k_{-4} + k_7) \tag{10b}$$

and when $[\mathrm{H}^+] \ll K_6$

$$k_{\mathrm{obsd}} \simeq k_5k_8/(k_{-5} + k_8) \tag{10c}$$

The situation of $[\mathrm{H}^+] \gg K_6$, where the reaction proceeds *via* I, is applied for *p*-anisaldehyde and benzaldehyde, whereas the latter situation of $[\mathrm{H}^+] \ll K_6$, *i.e.*, the reaction *via* II, is applied to the oxidation of nitrobenzaldehydes at higher concentration of alkali. The rate–pH profile for nitrobenzaldehydes exhibited an S-shaped curve at high pH, which suggests a $\mathrm{p}K_6$ value of *ca.* 13.2 for the *meta* isomer in 80% methanol at 10°, and for the *para* isomer *ca.* 13.0 in 40% ethanol at 25°, *ca.* 12.8 in 40% methanol, and 13.0 in 80% methanol at 10°. The value of $\mathrm{p}K_6$ for *p*-chlorobenzaldehyde is too large to estimate under these conditions.

It is rather surprising that the apparent rate through the anion II is slower than the rate through I. Probably, k_8 is larger than k_7 because of the pushing effect of α-oxy anion, analogous with other hydride shifts.[13] The slower apparent rate through II may arise from $k_{-5} > k_{-4}$, resulting in a decrease of the apparent rate when $[\mathrm{H}^+] < K_6$ (*cf.* eq 10b and 10c).

In spite of the operation of base catalysis for carbonyl formation from $\mathrm{ArCH_2OOR}$,[13c] no base catalysis was observed for the present reaction at pH above 10, which may be due to the easier hydride shift of I. This is probably caused by a large difference between the acidities of the departing group (above 10 in $\mathrm{p}K_a$ unit) and by an anchimeric assistance of α oxygen.

Hydride Shift in Acidic Conditions.—The Baeyer–Villiger reaction is known to be acid-catalyzed;[1,4] hence, it is surprising to note that the present hydride shift is not catalyzed by acid. The reaction at pH below 6 is slowed down with increasing acidity and the plots of log k_{obsd} *vs.* pH gives a line of positive slope of *ca.* 0.2, suggesting general base catalysis at constant pH. Interestingly, the reaction is subject to base catalysis only in acidic conditions. Assuming $\mathrm{p}K_6 \geq 13$, *i.e.*, $K_6/[\mathrm{H}^+] \ll 10^{-7}$, eq 9 may be rewritten in an acidic condition as in eq 10d. Here, reactions 5 and 7 are not catalyzed by base, since acid and base catalysis was not observed in alkaline conditions. In analogy with the addition of hydrogen peroxide to carbonyl,[9] reaction 4 is probably catalyzed by hydroxide ion. This seems to constitute one reason for the low value of the slope of the rate–pH plot, but eq 10d cannot cover all the pH region below 6. Base catalysis may be operative also for other steps. A similar low slope is reported for the peracid oxidation of sulfoxides, without explanation.[10]

$$k_{\mathrm{obsd}} \simeq \left\{\frac{k_4[\mathrm{H}^+]}{K_3 + [\mathrm{H}^+]} + \frac{k_5K_3}{K_3 + [\mathrm{H}^+]}\right\}\frac{k_7}{k_{-4} + k_7} \tag{10d}$$

Acid and Base Catalysis in Aryl Shifts.—The rate–pH profile for the *p*-hydroxybenzaldehyde conversion with aryl shift is different from those for the other aldehyde conversions with hydride shift. A plot of log k_{obsd} *vs.* pH gives slopes of −1.0 at pH below 2, +1.0 at pH 3–7. The same oxidation with peracetic acid also exhibits first-order dependence on proton at high acidity.[16] These results may be explained by alternative mechanisms, as follows.

The first mechanism involves a rate constant of aryl shift, k_7, in the observed rate constant. The slope of +1.0 at pH 3–7 in the plot of log k_{obsd} *vs.* pH is explicable if $k_4 \ll k_5$, where eq 10d may be simplified to eq 10e.

$$k_{\mathrm{obsd}} \simeq \frac{K_3k_5k_7}{k_{-4} + k_7} \times \frac{1}{[\mathrm{H}^+]} \tag{10e}$$

Acid catalysis at pH below 2 is comprehensible only if steps 4 and 7 are catalyzed by proton and $k_4 \gg k_5K_3/(K_3 + [\mathrm{H}^+])$, resulting in first-order dependence on proton. The rate decrease at high pH is consistent with the assumption that the main reaction for the accumulation of I is between perbenzoate ion and un-ionized *p*-hydroxybenzaldehyde whose titrated $\mathrm{p}K_a$ is 8.30 in 40% ethanol. Another explanation, which assumes

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[13] (a) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Company, Inc., New York, N. Y., 1959, p 547; (b) R. Stewart and M. M. Mocek, *Can. J. Chem.*, **41**, 1160 (1963); (c) P. A. S. Smith, "Molecular Rearrangements," Part I, P. D. Mayo, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963, p 573.

[14] For example, $\mathrm{p}K_a$'s for $\mathrm{CH_3CH(OH)_2}$, $\mathrm{CCl_3CH(OH)_2}$, and $\mathrm{C_6H_5C(OH)_2CF_3}$ in water are 13.6, 10.0, and 10.0, respectively: R. P. Bell, "Advances in Physical Organic Chemistry," Vol. 4, V. Gold, Ed., Academic Press, London, 1966, p 15.

[15] (a) S. L. Johnson, "Advances in Physical Organic Chemistry," Vol. 5, V. Gold, Ed., Academic Press, Inc., London, 1967, p 238; (b) G. L. Schmir and B. A. Cunningham, *J. Amer. Chem. Soc.*, **87**, 5692 (1965); G. L. Schmir, *ibid.*, **90**, 3478 (1968).

[16] Y. Ogata and I. Tabushi, *Bull. Chem. Soc. Jap.*, **32**, 108 (1959).

the hydroxide ion catalyzed rearrangement of I, is ruled out by the fact of very low concentrations of I and OH^-, and by the absence of maximum rate at pH *ca.* 10 (phenolic proton of I may have pK_a of *ca.* 10).

The other mechanism involving a rate-determining carbonyl addition, *i.e.*, k_7 or $k_8 \gg k_{-4}$ or k_{-5}, seems to explain the data more concisely. That is, the slope of -1 at pH < 2 corresponds to the proton-catalyzed addition step, 4, as rate-determining, and the slope of $+1$ at pH 3–7 coincides with the slow addition of peracid anion (step 5), since the pK_a value of the peracid is 8.5 in 40% ethanol. The bell-shaped curve at pH above 7 is also consistent with the assumption that the addition of peracid anion is much faster for benzaldehyde with p-OH than that with p-O^- because of the unfavorable anion–anion reaction 5. Since the migratory aptitude is surely in the order of p-$O^- \gg p$-OH,[17] the data seem to suggest the rate-determining addition to carbonyl.

Substituent Effect. A. Hydride Shift.—Substituent effects of benzaldehydes on hydride shift gave a positive ρ value of 1.1–1.8. The ρ value of 1.6–1.8 for the alkaline reaction is close to the value for the alkaline permanganate oxidation ($\rho = 1.83$),[18a] cyanohydrin formation ($\rho = 2.33$),[18b] and semicarbazone formation ($\rho = 1.81$),[19] which suggests a similarity in mechanism. That is, the apparent substituent effect reflects mainly the effect on concentration of I, although the ρ value for k_7 or k_8 (migrating step) is probably negative.

Hammett's relationship is well correlated with σ but poorly with σ^+, suggesting less importance of resonance in a transition state. Although the carbonium character of benzyl carbon atom is significant in the transition of peroxide rearrangements,[20] the effect of ring substituent would be small compared with the large stabilizing power of α-hydroxyl group in I.[21] Large anchimeric assistance by α oxygen has been reported for the ionic decomposition of peresters.[22] Indeed, the substituent effect is small ($\rho = ca.\ +0.14$) for the alkaline oxidation of o-sulfobenzaldehyde by substituted perbenzoate ions.[9] Here, a larger ρ value would be expected if the effect on hydride shift were significant.[23]

Similar but slightly small ρ values were obtained from the acidic oxidation, revealing that the effect is mainly on formation of I. Our kinetic data cannot discriminate between the substituent effect of two steps.

B. Aryl Shift.—Our data cannot afford a definite effect of the substituent on the aryl shift. For example, if it is roughly estimated from p-methoxy- and p-hydroxybenzaldehydes, ρ value is *ca.* -1.6 at pH 5.2 and -23 at pH 7.8. Moreover, the rate for p-O^- is much slower than that for p-HO, which may reflect the less favorable formation of I because of the electrostatic repulsion between two anions. At any rate, it is apparent that the aryl migration is facilitated by an electron-releasing *para* substituent, while the acceleration is poor with m-HO.

These results are natural in view of the highly negative ρ value (~ -5) for the ionic rearrangements of peroxides[3] and the importance of its bridged transition state.[20] The peracid oxidation of acetophenones ($\rho = -1.1$ to -1.5) possesses a different transition state, a protonated addition intermediate,[4] but it seems to be rather obscure as to whether the substituent effect corresponds to the migration step or to the protonation equilibrium of the intermediate. The present oxidation, however, does not have such a protonated intermediate at pH > 3.

Solvent Effect.—The reaction rate increases with increasing content of water in the solvent. The order for hydride shift is aqueous methanol < aqueous ethanol < aqueous dioxane, while the reverse is true for aryl shift. These solvent effects cannot be correlated by any solvent parameters, *e.g.*, Grunwald–Winstein's Y value. A maximum in the rate was observed in dioxane–water. These results suggests that the solvent polarity influences the rate differently for aryl and hydride shifts. That is, the solvent effect on aryl migration reflects its importance on the migration step more than the addition step, whereas the reverse effect for hydride shift shows that the rate is mainly governed by the concentration of I.

Temperature Effect.—The temperature effect shows low enthalpies of activation (6–7 kcal mol^{-1}) and entropies of activation ranging from -11 to -41 eu. These activation parameters satisfy the isokinetic relationship $\delta\Delta H^* = \beta\delta\Delta S^*$, where β and correlation coefficient (r) are 305°K and 0.946, respectively. A more satisfactory correlation ($r = 0.971$) was obtained for the alkaline oxidation alone, β value being 375°K. However, the relation may be spurious, since log k *vs.* ΔS^* is not correlated.

Experimental Section

Materials.—Perbenzoic acid was prepared from benzoyl peroxide and alkaline hydrogen peroxide[24] and recrystallized from n-hexane. Benzaldehydes were purified by distillation or by recrystallization. Substituents and melting point or boiling point are as follows: m-NO_2, mp 57–58°; p-NO_2, mp 105–106°; p-Cl, mp 47.0–47.5°; H, bp 77° (25 mm); p-MeO, mp 45–46° (25 mm); p-HO, mp 115–116°. Solvents were carefully redistilled.

Reaction Products.—A mixture of aldehyde and perbenzoic acid in a molar ratio of *ca.* 1.3:1 was kept standing at 2–5° for 24 hr in 80 vol. % methanol under nitrogen atmosphere. In general, over 90% of the charged peracid was consumed.

The acids and/or phenols produced were determined by uv spectrophotometry[25] at their characteristic absorption after dilution or extraction with chloroform. When this method was unsuccessful, glpc was used. For example, in the case of p-anisaldehyde the carboxylic products were determined by the uv method after extraction of aldehyde and phenol from a weakly alkaline reaction mixture. The extracted aldehyde was estimated by the uv method and p-methoxyphenol was estimated by glpc after its etherification by dimethyl sulfate using p-cresol as an internal standard. The glpc analysis was carried out by a Yanagimoto Model 550F gas chromatograph using a 1-m length of 30% silicon DC550 on Celite 545 at 120°. This method was of sufficient accuracy (±6%) to be used to check the data obtained

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[17] For example, R. Baird and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 567 (1963).

[18] (a) K. B. Wiberg and R. Stewart, *ibid.*, **77**, 1786 (1955); (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, p 181.

[19] R. Wolfenden and W. P. Jencks, *J. Amer. Chem. Soc.*, **83**, 2763 (1961).

[20] E. Hedaya and S. Winstein, *ibid.*, **89**, 1661 (1967).

[21] Similar explanation has been done for α-hydrogen abstraction of benzyl ethers: G. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1964).

[22] E. Hedaya and S. Winstein, *Tetrahedron Lett.*, 563 (1962).

[23] The situation is very similar to the case of semicarbazone formation, *i.e.*, $\rho = 1.81$ for the formation equilibrium of tetrahedral intermediate and $\rho = -0.17$ for the following dehydration step.[19]

[24] Y. Ogata and Y. Sawaki, *Tetrahedron*, **23**, 3327 (1967).

[25] The molar absorbances of aldehydes and benzoic acids are reported previously: Y. Ogata, Y. Sawaki, F. Matsunaga, and H. Tezuka, *Tetrahedron*, **22**, 2655 (1966); L. Doub and J. M. Vandenbelt, *J. Amer. Chem. Soc.*, **71**, 2414 (1947).

by the uv method. The recovery of benzoic acid from the peracid was over 95% by means of uv analysis. The results are listed in Table I.

Rate Measurements.—The oxidation was started by adding a peracid solution to a thermostated solution containing aldehyde and buffer. Aliquots were taken out at appropriate intervals of time and the remaining peracid was determined by iodometry. No apparent difference in rates was observed for the reactions in air and under nitrogen atmosphere. The spontaneous decomposition of perbenzoic acid was negligible in most runs, but when it became significant in comparison with its reaction with aldehyde, the rate constants were corrected.

Registry No.—Perbenzoic acid, 93-59-4.

The Synthesis of Episulfides from Olefins and Sulfur Monochloride

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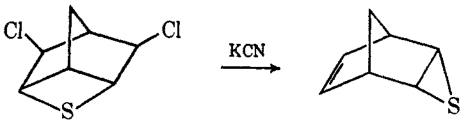
The addition of sulfur monochloride to an excess of many alkenes gives practical yields of β-chloroalkyl disulfides, which are readily reduced and dehydrohalogenated by sodium sulfide to give stereochemically pure episulfides.

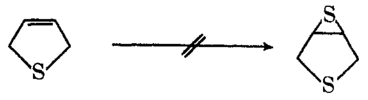
The principal synthetic approaches to episulfides have been reviewed recently.[1] Since the publication of these reviews, several new approaches have been disclosed: the reaction of ketohydrazones with sulfur,[2] the synthesis of *trans*-3,4-diphenyl-1,2-epithiocyclobutane in a yield of 34% by short irradiation of *cis*,-*trans*-β-phenylvinyl sulfide[3] as the first synthesis of a cyclobutene episulfide, the pyrolysis of aryl- or alkyl-2-hydroxyethyl thiolcarbonates,[4] the reduction of 2-hydroxyethyl disulfide with phosphines and secondary phosphine oxides,[5] and the reduction of the sulfide **1** to the unsaturated episulfide **2**.[6]

The most significant approaches may be classified into two groups. First, olefins can be oxidized with sulfur, leading to episulfides directly.[7] Second, olefinic compounds can be raised to the desired oxidation state and the resulting epoxides, dihalides, or chlorohydrins can be converted to episulfides by a variety of sulfur-containing reagents, such as potassium thiocyanate or thiourea in the case of epoxides. Related to the first group would be the reaction of the hypothetical thiohypochlorous acid, HSCl, with olefins. Although hypochlorous acid is readily prepared and effectively used in the synthesis of epoxides, the sulfur analogs HSBr and HSCl were only suggested as intermediates in the reaction of hydrogen sulfide with bromine or chlorine.[8] It can be doubted, however, that these sulfur analogs could be used effectively in view of their anticipated behavior as oxidizing agents and the ease of oxidation of the resulting halomercaptans to bis(β-haloalkyl) disulfides.

Whereas the first synthetic approach, the addition of sulfur to olefins, is still only of theoretical interest, the second path represents the almost exclusively used route for laboratory synthesis. This latter approach has several limitations. The conversion of cyclopentene oxide to the corresponding episulfide with thiourea or potassium thiocyanate is unsatisfactory [9] Furthermore, the formation of episulfides from sulfur-containing olefins such as 2,5-dihydrothiophene (**3**) *via* oxidative routes would necessarily involve oxidation of the sulfur atom; and as a consequence, a direct route to an episulfide such as **4** has not been available.



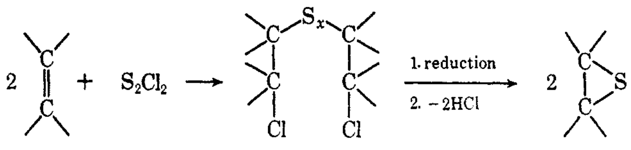
1 **2**



3 **4**

We now report a novel, two-step synthesis of episulfides from the corresponding olefins. Sulfur monochloride is added to the olefin in the first step to form mixtures of β-chloroalkyl mono-, di-, and trisulfides (**5–7**). The adducts **6** and **7** are then converted to the episulfide by means of sodium sulfide or aluminum amalgam (Scheme I).

SCHEME I



5, $x = 1$

6, $x = 2$

7, $x = 3$

Results and Discussion

Addition of Sulfur Monochloride to Olefins.—Although the addition of sulfur monochloride to olefins was reported as early as 1860,[10] the synthetic value of

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(1) D. D. Reynolds and D. L. Fields in "Heterocyclic Compounds with Three- and Four-Membered Rings," Interscience Publishers, New York, N. Y., 1964, p 576; M. Sander, *Chem. Rev.*, **66**, 297 (1966); L. Goodman and E. J. Reist in "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, New York, N. Y., 1966.

(2) N. Latif, I. Fathy, N. Mishriky, and B. Haggag, *Can. J. Chem.*, **44**, 629 (1966).

(3) E. Block, Ph.D. Thesis, Harvard University, 1967.

(4) D. L. Fields and D. D. Reynolds, U. S. Patent 3,247,225 (1966).

(5) M. Grayson and C. F. Farley, *Chem. Commun.*, **16**, 831 (1967).

(6) F. Lautenschlaeger in "The Chemistry of Sulfides," A. Tobolsky, Ed., Interscience Publishers, New York, N. Y., 1968, pp 73–81; *J. Org. Chem.*, **34**, 3998 (1969).

(7) P. Fowles, M. de Sorgo, A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **89**, 1352 (1967). For a review, see H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **4**, 143 (1966).

(8) M. Schmidt in "Inorganic Polymers," F. G. Stone and W. A. Graham, Ed., Academic Press, New York, N. Y., 1962, Chapter 3.

(9) See, *e.g.*, (a) E. E. van Tamelen, *J. Amer. Chem. Soc.*, **73**, 3444 (1951); (b) L. Goodman and B. R. Baker, *ibid.*, **81**, 4924 (1959).

(10) A. Niemann, *Ann.*, **113**, 288 (1860).