acetone solution, retention times of the unconjugated and conjugated isomers being 10.9 and 15.4 min, respectively. Preparative columns employed were: 7 ft × 0.25 in. aluminum 10% FFAP, 70/80 Chromosorb W; 8 ft × $^3/_8$ in. aluminum, 10% FFAP, 70/80 Chromosorb W; and 20 ft × $^3/_8$ in. aluminum, 20% FFAP on 60/70 Chromosorb W. All samples were injected without dilution by solvent, but on all preparative columns isomerization was noted, presumably due to prolonged times at high temperatures; therefore, preparative chromatography could not be used to further purify the isomers.

Spectroscopic Techniques.—Infrared measurements were carried out on a Perkin-Elmer Model 257 spectrophotometer, using liquids on sodium chloride plates, or solutions of carbon tetrachloride and carbon disulfide. Raman spectra were obtained on a Perkin-Elmer LR-1 spectrophotometer equipped with a 70-mW Ne–He 6328-Å gas laser, using a liquid sample in borosilicate glass capillary cells. Ultraviolet spectra were obtained in cyclohexane solution on a Beckman DK-2 spectrophotometer, using 0.1-mm quartz cells. Nmr measurements were carried out at room temperature on 10% carbon tetrachloride solutions with tetramethylsilane as an internal standard, using a Varian A-60 Model spectrometer. Mass spectrometry was carried out on a Bendix Model 12 time-of-flight mass spectrometer (70 eV).

Registry No.—I (*cis*), 3047-65-2; II (*trans*), 21308-79-2.

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Linear Free-Energy Relationship between Alcohol pK_a and Solvolysis Rates of Esters Where Substituent Variation Is in the Alkyl Portion of the Ester

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It has previously been shown[1-3] that rates of solvolysis of some acetate esters can be linearly related to the pK_a of the leaving group. The purpose of the present report is to extend this correlation to other ester series, many of which have heretofore not followed a linear free energy relationship, to demonstrate that alcohol pK_a serves as a very effective model for ester solvolysis.

A number of attempts have been made in the past to correlate rates of solvolysis of aliphatic esters with model systems in order to generate linear free energy relationships.[4] The most successful of these, for variation in the acyl portion of aliphatic esters, has been the treatment by Taft.[5] Taft eliminates the variable steric requirement in these reactions by subtracting the rate of acid hydrolysis (mainly sterically controlled) from the rate of alkaline hydrolysis (polar and sterically controlled) to generate polar substituent constant (σ^*). Successful application of σ^*, for a wide variety of reactions, has been made with a Hammett-type expression[6]

$$\log \frac{k}{k_0} = \sigma^* \rho^* \qquad (1)$$

In reaction series that follow eq 1, the steric effect can be assumed to be constant or negligible.

For variation in the alkyl portion of aliphatic esters, correlation of hydrolytic rates with σ^* have been unsuccessful.[7] The reason for this failure was shown[7] to be a variable steric requirement in the alkyl portion of the ester; the steric effect was reported to be larger in the alkyl than in the acyl portion of these esters.

Since alcohol dissociation represents the only effective model for aliphatic esters, where substituent variation is in the alcohol portion of the ester, it seems worthwhile to extend this correlation to other series to demonstrate the generality of the procedure.

Table I demonstrates the linear relationship that exists between rates of solvolysis and pK_a of the alcohol for a variety of esters. The symbolism used in Table I has the following meaning: Q is the least-squares fitted slope of a log rate constant *vs.* pK_a plot, S is the standard deviation of points from the line, and R is the correlation coefficient for the line. Every oxygen ester series tested with this model gave excellent correlation, while thiol ester hydrolysis could not be correlated with alcohol pK_a. That thiol ester correlation failed is not surprising considering the difference in size, polarizability, and electron configuration of a mercaptan sulfur and an alcohol oxygen.

It is not at all obvious that alcohol dissociation would serve as a model for ester hydrolysis since it is well known that a considerable steric influence exists in the alkyl portion of aliphatic esters, and steric influence in acid dissociation of alcohols is unexpected. Moreover, Taft,[5d] and Ballinger and Long[8] have reported that the pK_a of alcohols is linearly related to σ^* and one might have supposed, therefore, that correlation of rates of hydrolysis with pK_a would not be feasible, since nonlinearity is observed when rate constants of hydrolysis are plotted against σ^*. However, σ^*, as used by both Taft and by Ballinger and Long, refers to R in RCH_2OH. The interposition of a methylene group between R and OH effectively removes the steric influence. Figure 1 demonstrates the degree of scattering that occurs when σ^* is defined as R in ROH as compared with R in RCH_2OH. It is precisely this steric influence that is paralleled in ester hydrolysis, and for this reason alcohol dissociation is a good model for ester reactions (CPK models of the alcohols show significant shielding of the oxygen for any chain length above ethyl).

It would appear from the above discussion that successful correlation of rates of hydrolysis of aliphatic esters, where substituents are in the alkyl component of the ester, can be made using σ^* if we define σ^* as R in $RCH_2O(C{=}O)R'$. Treatment of the alkaline hydrolysis data for benzoates, in this manner, does show a marked

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[1] T. C. Bruice, T. H. Fife, J. T. Bruno, and N. E. Brandon, *Biochemistry*, **1**, 7 (1962).

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[5] (a) R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Chapman and Hall, London, 1956, p 556; (b) R. W. Taft, *J. Amer. Chem. Soc.*, **74**, 3120 (1952); (c) *ibid.*, **74**, 2729 (1952); (d) *ibid.*, **75**, 4231 (1953).

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TABLE I

CORRELATION OF REACTION RATES (LOG k/k_0, k_0 = METHYL ESTER) WITH DISSOCIATION CONSTANTS OF ALCOHOLS (LOG K/K_0, K_0 = METHANOL)[a]

Esters	Q	S	R	Substituents[b]
Lactates[c,d]	0.560	0.036	0.989	2, 7, 8, 9, 11[e]
Benzoates[f,g]	0.708	0.087	0.981	2, 3, 4, 7, 8, 9, 11, 16
Acetates[h,i]	0.701	0.104	0.972	2, 7, 8, 9, 11, 16
Propionates[h,i]	0.779	0.130	0.982	2, 7, 9, 16
3,5-Dinitrobenzoates[j,k]	0.647	0.056	0.990	2[e], 3, 4, 7[e], 8, 9, 11[e], 16[e]
Acetates[l,m]	0.674	0.140	0.973	2[e], 7[e], 11[e], 16[e]
Acetates (acid hydrolysis[l,m]	0.271	0.050	0.979	2, 7, 11, 16
Formates[n,o]	0.297	0.028	0.991	2, 7, 8, 9, 16
Acetates[n,o]	0.481	0.044	0.991	2, 3, 7, 8, 9, 16
Propionates[n,o]	0.538	0.063	0.986	2, 3, 7, 8, 9, 16
Butyrates[n,o]	0.549	0.059	0.988	2, 3, 7, 8, 9, 16
Isobutyrates[n,o]	0.757	0.063	0.993	2, 3, 7, 8, 9, 16
Trimethylacetates[n,p]	1.185	0.152	0.983	2, 3, 7, 8, 9, 16
Methoxyacetates[n,o]	0.554	0.039	0.995	2, 3, 7, 8, 9, 16
Glycolates[n,o]	0.548	0.066	0.985	2, 3, 7, 8, 9, 16
Lactates[n,o]	0.558	0.048	0.992	2, 3, 7, 8, 9, 16
α Hydroxyisobutyrates[n,o]	0.722	0.072	0.991	2, 3, 7, 8, 9, 16
Formates[q,r]	0.502	0.039	0.995	2, 7, 8, 9, 16
Acetates[q,r]	0.593	0.045	0.994	2, 7, 8, 9, 16

[a] Dissociation constants used were averaged values from J. Hine and M. Hine, *J. Amer. Chem. Soc.*, **74** 5266 (1952), and H. Shigematsu, Y. Nishikawa, and Y. Ishii, *J. Ind. Chem.*, **65**, 945 (1962); these constants were determined in 2-propanol, but they are linearly related to those determined in water: P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, **82**, 795 (1960). [b] Refers to Table II. [c] K. H. Vogel and J. C. Warner, *J. Amer. Chem. Soc.*, **75**, 6072 (1953). [d] 0° in water. [e] Calculated from Arrhenius plots. [f] E. Tommila, *Ann. Acad. Sci. Fennicae Ser.*, A57, No. 13, 3 (1941), No. 3, 3 (1942); A59, No. 4, 3 (1942): *Chem. Abstr.*, **38**, 6174 (1944). [g] 25° in 56% acetone. [h] R. W. A. Jones and J. D. R. Thomas, *J. Chem. Soc., B*, 661 (1966). [i] 24.7° in 70% v/v acetone. [j] J. R. Robinson, *Anal. Chem.*, **39**, 1178 (1967). [k] 25° in 40% v/v acetonitrile. [l] P. N. Rylander and D. S. Tarbell, *J. Amer. Chem. Soc.*, **72**, 3032 (1950). [m] 25° in 62 wt % acetone. [n] E. J. Salmi and R. Leimu, *Suomen Kemistilehti*, **20B**, 43 (1947); *Chem. Abstr.*, **42**, 4031 (1948). [o] 25° in water. [p] 25° in 16.67 vol.% dioxane–water. [q] S. Sun and K. A. Connors, *J. Pharm. Sci.*, **58**, 1150 (1969). [r] 25° in 37% v/v acetone.

improvement in linearity, but what significance a plot such as this has is not quite clear.

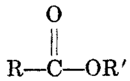
It would be most desirable to have an extensive compilation of alcohol pK_a's in order to encompass a wide variety of substituents. However, because of the small number of pK_a's of alcohols available, and because rate data would appear to be more accurate than these difficultly determinable quantities, we have chosen the alkaline hydrolysis of alkyl-substituted 3,5-dinitrobenzoates[9] as the standard process. This particular study was chosen as a standard since it probably represents the longest series available for hydrolysis of an ester with variation in the alkyl component. Rates of hydrolysis of this ester series and alcohol pK_a are related by a constant value. Equation 2 gives the definition of the substituent constants for variation in the alkyl portion of the ester, where k_0 in eq 2 equals the rate constant for the methyl ester. All of the substituent constants, with the exception of *t*-butyl and phenyl, were obtained from the study on the alkaline hydrolysis of 3,5-dinitrobenzoates and are shown in Table II.

$$\phi^{10} = \delta_R \Delta G^{\pm} = 2.303RT \log (k/k_0) \qquad (2)$$

The *t*-butyl value appeared to be inconsistent with other studies, and, since it consisted of only two determinations, an adjusted value was used. The phenyl derivative was not studied in the 3,5-dinitrobenzoates, but since it represented an electron sink, a value was determined based on the benzoate series (second reaction in Table I) and adjusted to the 3,5-dinitrobenzoate scale.

TABLE II

SUBSTITUENT CONSTANT FOR R′ IN



$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OR'$

Substituent	ϕ
Phenyl	+0.725
Methyl	0.000
Allyl	−0.157
Benzyl CH_2	−0.183
Cinnamyl	−0.297
β-Phenethyl	−0.481
Ethyl	−0.623
n-Propyl	−0.743
n-Butyl	−0.827
n-Amyl	−0.863
Isobutyl	−0.911
Isoamyl	−0.933
n-Hexyl	−0.978
n-Octyl	−1.033
Dodecyl	−1.101
Isopropyl	−1.567
Cyclopentyl	−1.611
Cyclohexyl	−1.762
sec-Butyl	−1.922
2-Pentyl	−2.039
2-Heptyl	−2.051
2-Octyl	−2.152
3-Methyl-2-butyl	−2.317
3-Pentyl	−2.414
3-Hexyl	−2.573
t-Butyl	−3.340
t-Amyl	−3.744

These substituent constants can be plotted against rate data, in a Hammett-type plot (eq 1), to yield

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(9) J. R. Robinson *Anal. Chem.*, **39**, 1178 (1967).

(10) (a) Since the polar and steric contributions to these substituent constants have not as yet been separated, we have refrained from using the conventional $\sigma\rho$ nomenclature. (b) Defined at 25° and solvent composition of 40% vol. %/vol. % acetonitrile–water containing 0.05 *M* phosphate.

TABLE III

CORRELATION OF REACTION RATES (log k/k_0) WITH ϕ

Reaction[a]	Esters	m	S	R	Substituents[b]
1	Lactates	0.680	0.073	0.996	2, 7, 8, 9, 11,[c] 19,[c] 26[c]
2	Benzoates	0.852	0.047	0.999	1, 2, 3, 4, 6, 7, 8, 9, 11, 12, 13, 14, 16, 17, 18, 19, 26, 27
3	Acetates	0.787	0.055	0.998	2, 7, 8, 9, 11, 16, 18, 19, 26
4	Propionates	0.867	0.089	0.992	2, 7, 9, 16
5	3,5-Dinitrobenzoates	1.000		1.000	All except phenyl
6	Acetates	0.744	0.083	0.997	2,[c] 7,[c] 11,[c] 16,[c] 26[c]
7	Acetates (acid hydrolysis)	0.277	0.047	0.993	2,[c] 7,[c] 11,[c] 16,[c] 26[c]
8	Formates	0.328	0.028	0.992	2, 7, 8, 9, 16
9	Acetates	0.525	0.050	0.988	2, 3, 7, 8, 9, 16
10	Propionates	0.591	0.060	0.987	2, 3, 7, 8, 9, 16
11	Butyrates	0.602	0.056	0.989	2, 3, 7, 8, 9, 16
12	Isobutyrates	0.827	0.077	0.989	2, 3, 7, 8, 9, 16
13	Trimethylacetates	1.312	0.096	0.993	2, 3, 7, 8, 9, 16
14	Methoxyacetates	0.608	0.034	0.996	2, 3, 7, 8, 9, 16
15	Glycolates	0.599	0.069	0.983	2, 3, 7, 8, 9, 16
16	Lactates	0.612	0.043	0.993	2, 3, 7, 8, 9, 16
17	α-Hydroxyisobutyrates	0.851	0.041	0.997	2, 3, 7, 8, 9, 16
18	Formates	0.578	0.031	0.997	2, 7, 8, 9, 11, 12, 16, 19
19	Acetates	0.714	0.058	0.996	2, 7, 8, 9, 11, 12, 13, 16, 19
20	Bromination of monoalkylbenzenes, C_6H_5–R[d,e]	0.222	0.028	0.997	2, 7, 16, 26
21	Bromination of monobenzenes, C_6H_5–CH_2–R[d,e]	0.158	0.019	0.998	2, 7, 16, 26

[a] Refer to Table I for reference and reaction conditions. [b] Refers to Table II. [c] Calculated from Arrhenius plots. [d] E. Berliner and F. Berliner, *J. Amer. Chem. Soc.*, **72**, 272 (190). [e] 25°, 85% HAC.

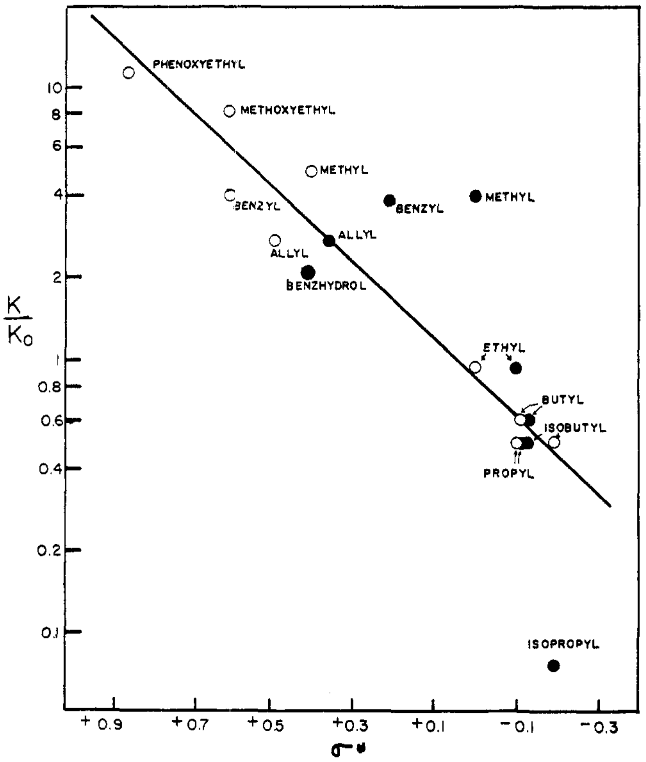

Figure 1.—Relationship of relative dissociation constants of alcohols to polar substituent constants: ●, ROH; ○, RCH_2OH.

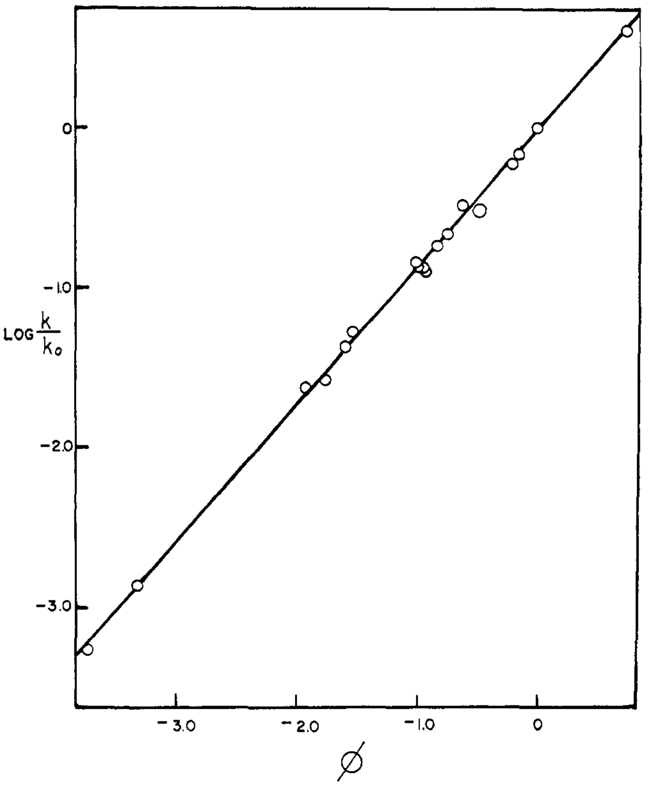

Figure 2.—Plot of log k/k_0 against ϕ for the alkaline hydrolysis of benzoates (reaction 2, Table III) in 56 wt % acetone at 25°.

linear plots with slopes of m. Interpretation of m is based on the meaning of ϕ and at present only qualitative inferences can be made. ϕ contains a steric factor as well as a polar factor, and in the absence of entropy and enthalpy data on the dissociation constants of alcohols, it is impossible to assign separated polar and steric effects. Therefore, the sign and magnitude of ϕ cannot be described in terms of resonance or inductive effects alone, but must include a steric factor as well. However, for reactions that give linear correlations between rates and ϕ, it can be said that the steric and polar factors are proportional to the steric and polar factors involved in the dissociation of alcohols. For convenience, it is useful to consider substituents with positive values of ϕ as electron sinks and negative values as electron sources, since it can be assumed that for small molecules the polar effects would be more important than the steric effects. Similarly, we can tentatively assign the same meaning to m as Hammett's ρ, namely that a positive m would indicate that low electron density favors the reaction, while a negative m would imply that the reaction is favored by high electron density. However, it should be recognized that if steric factors predominate in a reaction, the above is not necessarily true.

Discussion

Figure 2 demonstrates the excellent correlations that are obtained using the substituent constants given in Table II, and Table III lists reaction series that were tested, together with their results. The standard deviation and correlation coefficients are excellent and bear out the validity of the model.[11] Reactions 20 and 21 are included in Table III to show that reactions other than ester hydrolysis would appear to follow this model.

Inspection of the slopes for the various reactions reported in Table III leads to some interesting speculations. For example, reactions 3, 6, 9, and 19 are for the alkaline hydrolysis of acetate esters in a variety of acetone–water mixtures. The change in slope that is observed for these reactions would appear to be related to the polarity of the solvent, the largest slope being in 70% acetone–water and the smallest slope in pure water. That this is quantitatively due to a polar effect rather than a special solvent effect in these reactions was established by plotting the slopes against Kosower's Z values[12] and obtaining a linear relationship, the equation for the line being[13] $m = -0.0258Z + 2.935$.

The signs for the slopes for acid- and base-catalyzed hydrolysis of acetate esters (reactions 6 and 7) are both positive, but their absolute values are different, the acid reaction m being a smaller positive number. This qualitatively accords with the expectation that alkaline hydrolysis is hindered by high electron density, while acid hydrolysis is aided. The involvement of steric effects in ϕ probably accounts for the failure of m to be negative for acid-catalyzed reactions.

It is apparent that alcohol dissociation serves as an excellent model for solvolysis of aliphatic esters where substitution is in the alkyl portion of the molecule.

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[11] Note that since dissociation constants of alcohols quantitatively parallel rates of reaction, we now have a fairly reliable estimate of dissociation constants for a number of alcohols which have not been experimentally studied, simply by interpolation from a plot of pK_a *vs.* ϕ.

[12] E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958).

[13] Z values for 37% and 62% acetone–water mixtures were found by interpolation to be 88.5 and 84.8, respectively.

Aralkyl Hydrodisulfides.[1] X. Reactions with Iron Salts

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Redox reactions of hydroperoxides with ferrous or cuprous ion already have been elucidated.[2,3] Hydrodisulfides, thio analogs of hydroperoxides, however, may be expected to behave differently toward redox reagents in view of the information presented so far. For instance, aralkyl hydrodisulfides are oxidized to the corresponding diaralkyl tetrasulfides almost quantitatively with iodine,[4] 2,2-diphenyl-1-picrylhydrazyl, or benzoquinone,[5] and in the case of mercaptans which are considered the lower homologs of hydrodisulfides, they are oxidized with ferric ion in the presence of oxygen[6] or with ferric caprilate.[7] In the present Note we will report the reaction of aralkyl hydrodisulfides with iron salts.

Benzyl or benzhydryl hydrodisulfide in dioxane was added dropwise to an aqueous or a dioxane solution of ferric chloride hexahydrate at room temperature under a nitrogen gas stream. In both cases the color of ferric ion disappeared completely after the addition of an equimolar amount of the hydrodisulfide. The corresponding tetrasulfide was produced in good yields, as shown in experiments 1–3, Table I. A nearly equivalent amount of ferrous ion was formed in experiments 1–3, and an appreciable amount of proton was detected in experiments 1 and 2, where the determinations were successfully carried out by utilizing the aqueous layer. In Table I all the data were adjusted in per mole bases. Although each separated amount of tetrasulfide shown in experiments 1–3 was not quantitative, the reaction appeared to be a good one, because nmr spectra of the filtrate after the first recrystallization of the tetrasulfide indicated that the filtrate contained minor amounts of the disulfide and trisulfide along with the major component, the tetrasulfide. From the results shown in experiments 1–3, the main reaction path will be formulated as

$$2\text{RSSH} + 2\text{Fe}^{3+} \longrightarrow \text{RSSSSR} + 2\text{Fe}^{2+} + 2\text{H}^{+} \qquad (1)$$

Two possible side reactions were checked. The first possibility is a participation of a trace amount of oxygen which might have been present in the solution. Under atmospheric oxygen, the reaction was completed instantaneously by the addition of the first drop of aqueous ferric chloride solution, giving the result shown in experiment 4, Table I. This result, as compared with those in experiments 1–3, clearly indicates that ferric ion in the presence of a sufficient amount

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[1] Part IX: J. Tsurugi, T. Horii, T. Nakabayashi, and S. Kawamura, *J. Org. Chem.*, **33**, 4133 (1968).

[2] M. Kharasch, A. Fono, W. Nudenberg, and B. Bishof, *J. Org. Chem.*, **17**, 207 (1952).

[3] J. Kochi, *J. Amer. Chem. Soc.*, **84**, 3271 (1962).

[4] J. Tsurugi and T. Nakabayashi, *J. Org. Chem.*, **24**, 807 (1959).

[5] T. Nakabayashi and J. Tsurugi, *ibid.*, **28**, 813 (1963).

[6] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 1, Chemical Publishing Co., New York, N. Y., 1958, p 118.

[7] T. Wallace, *J. Org. Chem.*, **31**, 3071 (1966).