Linear Correlation of the Solvolysis Rates of Xanthates with the Grunwald–Winstein Y Values

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O-Cinnamyl and *O*-(2-methylthioethyl) *S*-methyl dithiocarbonates (xanthates) underwent thione–thiol rearrangement to the dithiol esters in various solvents. The reactions followed first-order kinetics and the rates were affected by change of the solvent polarity. Plots of the rate constants against the Y values showed good linear relationships. The rate constants may be used as a new empirical parameter of solvent polarity in place of Y values. Modified intermediate neglect of differential overlap (MINDO/3) calculations indicate that allylic xanthates undergo [3,3]-sigmatropic rearrangement *via* a polarizable transition state.

Keywords xanthate; thione–thiol rearrangement; solvent effect; allylic rearrangement; solvent polarity parameter; Y value; MINDO/3

In the previous paper,^{1a)} it was reported that solvolysis of *O*-(1-cyclopropylethyl) *S*-methyl dithiocarbonate (xanthate) (Ia) in various solvents results in thione–thiol rearrangement to give the corresponding dithiol ester, *S*-(1-cyclopropylethyl) *S*-methyl dithiocarbonate (IIa), and plots of the rate constants in protic solvents vs. Grunwald–Winstein Y values^{2a)} showed linear relationships, suggesting that the solvolysis rate constants of xanthates may be used as an empirical solvent polarity

parameter for correlating the solvent ionizing power and the rate of reactions.

However, *O*-(1-cyclopropylethyl) *S*-methyl xanthate (Ia) has some disadvantages as a substrate; it is a garlicky oil; it shows a large dependence of the reaction rate on solvent polarity, being inert in nonpolar solvents; it is not isolable in the pure state. So, we looked for better substrates.

In this paper, we present an excellent linear correlation between the rates of [3,3]-sigmatropic rearrangement³⁾ of *O*-cinnamyl *S*-methyl xanthate (Ib) and the Y values, and we also compare the data with those for *O*-(2-methylthioethyl) *S*-methyl xanthate (Ic),⁴⁾ which undergoes thione–thiol rearrangement *via* an episulfonium intermediate.

Chart 1

TABLE I. First-Order Rate Constants for Solvolyses of Ib, c in Various Solvents at 60 °C

Solvent	$k \times 10^5 \text{ (s}^{-1}\text{)}$		E_T value (kcal/mol)	Y value
	Ib	Ic		
Glycol	—	13.6	56.3	
MeOH	64.2	1.98	55.5	−1.090
80% EtOH	132.0	4.52	53.6	0.000
EtOH	29.8	0.792	51.9	−2.033
AcOH	42.8	1.01	51.9	−1.639
<i>n</i> -PrOH	20.6	0.320	50.7	
<i>n</i> -BuOH	23.2	0.603	50.2	
iso-PrOH	15.0	0.428	48.6	
iso-AmOH	15.7	0.306	47.0	
DMSO	77.5	—	45.0	
Sulfolane	74.7	4.18	44.0	
<i>tert</i> -BuOH	13.2	0.225	43.9	−3.260
DMF	64.9	4.05	43.8	
TMU	18.8	—	41.0	
Anisole	7.18	—	37.2	

TABLE II. Activation Parameters for Solvolyses of Ib, c

Solvent	E_a (kcal/mol)		$\Delta S^\ddagger$ (e.u.)	
	Ib	Ic	Ib	Ic
EtOH	23.2	26.6	−7.2	−3.5
DMF	22.0	23.3	−8.5	−10.5
DMSO	18.5	— ^{a)}	−18.7	— ^{a)}
<i>o</i> -ClC ₆ H ₄ OH	17.8	20.6	−19.0	−18.1
<i>p</i> -ClC ₆ H ₄ OH	— ^{b)}	21.1	— ^{b)}	−11.5

a) A side reaction occurred with DMSO. b) The rate is too rapid to be measured even at room temperature.

Chart 2

as an oil.

The reaction rates were determined in various solvents by measuring the decrease of the C=S chromophore. The absorption data were automatically collected and analyzed by using a non-weighted least-squares program. In all cases, good first-order rate plots were obtained. The results are summarized in Table I. The activation parameters calculated from the data are presented in Table II.

The proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra of the solvolysis products of Ib showed the presence of a mixture of isomeric dithiol esters, *S*-(1-phenylallyl) (IIb) and *S*-cinnamyl *S*-methyl dithiocarbonate (IIb'). The amounts of IIb' were as follows: ca. 35.8% in phenol; 10.3% in 80% aqueous ethanol; and 4% in ethanol.

Solvolysis of *O*-(2-methylthioethyl) *S*-methyl xanthate (Ic) also caused thione-thiol rearrangement to afford the corresponding dithiol ester (IIc). However, the rearrangement could not be observed in solvents having low ionizing power, e.g., benzene.

Correlation to E_T Values To examine the general features of the correlation between the reaction rates and empirical parameters of solvent polarity, the logarithms of

the rate constants were plotted against the E_T values of Reichardt,⁵⁾ based on the transition energy for the longest-wavelength solvatochromic absorption band of pyridinium *N*-phenoxide betaine dye (Fig. 1). As shown in Fig. 1, a plot of $\log k$ vs. E_T values in all solvents used exhibits some scattering of points. Plots of $\log k$ vs. E_T values for aprotic and protic solvent systems show nearly linear relationships with slopes $a=0.143$ and 0.0792 , respectively. In the protic solvents, the rate constant for 80% aqueous EtOH deviates from the expected value.

Correlation to Y Value A plot of $\log k$ vs. Grunwald-Winstein Y values shows an excellent linear relationship for alcohols (Y value for 80% aqueous EtOH = 0.0) with slope $m=0.310$ (correlation coefficient, $r=0.999$, see Fig. 2), suggesting that the rate of reaction depends moderately on the ionizing power of the solvent as compared with the case of *O*-allyl *S*-methyl xanthate (Id) ($m=0.141$).^{1a)} It is of interest to note that a [3,3]-sigmatropic rearrangement of this type is affected by introduction of a γ -substituent into the allylic moiety. The m value for the solvolysis of Ib in aqueous EtOH is 0.316 ($r=0.993$) (Fig. 3 and Table IV),

Fig. 1. Plots of $\log k$ vs. E_T Values for the Solvolysis of Ib, c

●, Ib aprotic; ○, Ib protic; □, Ic protic.

TABLE III. First-Order Rate Constants for Solvolyses of Ib, c in Alcohols at 60 °C

Solvent	$k \times 10^5 \text{ (s}^{-1}\text{)}$		Y value
	Ib	Ic	
80% EtOH	132.0	4.52	0.000
MeOH	64.2	1.98	-1.090
AcOH	42.8	1.01	-1.639
EtOH	29.8	0.792	-2.033
<i>tert</i> -BuOH	13.2	0.225	-3.260

Fig. 2. Plots of $\log k$ vs. Y Values for the Solvolysis of Ib, c in Alcohols

Ib, slope = 0.310; Ic, slope = 0.402.

TABLE IV. First-Order Rate Constants for Solvolyses of Ib in Aqueous EtOH at 60 °C

Aqueous EtOH (v/v%)	$k \times 10^5 \text{ (s}^{-1}\text{)}$	Y value
100	29.8	-2.033
90	61.9	-0.747
80	132	0.000
70	213	0.595
60	265	1.124

Fig. 3. Plots of $\log k$ vs. Y Values for the Solvolysis of Ib in EtOH- H_2O Solvents

Slope = 0.316.

Fig. 4. Plots of $\log k$ vs. Y Values for the Solvolysis of Ib in Protic Solvents

Slope = 0.303.

consistent with that for alcoholic solvent ($m=0.310$). The m value for all the protic solvents tested (alcohols and aqueous EtOH) is 0.303 ($r=0.996$) (see Fig. 4).

Correlation to Y Value of Binary Mixtures of Phenol with Benzene Next, we studied the correlations between the rate constants and Y values for phenol–benzene solvents (Fig. 5).

In phenol–benzene solvents, linear correlations were observed. The m value for the solvent system is calculated to be 0.583 ($r=0.996$), larger than the value for protic solvents ($m=0.303$), indicating that the phenolysis reaction proceeds through a more ionic intermediate than that for protic solvents.

Solvolysis of *O*-(2-Methylthioethyl) *S*-Methyl Xanthate (Ic) Solvolyses of Ic in various solvents were studied in the same way as mentioned above. The reaction rates in

TABLE V. First-Order Rate Constants for Solvolyses of Ib, c in Phenol–Benzene at 60 °C

PhOH (w/v%)	$k \times 10^5$ (s ⁻¹)		Y value
	Ib	Ic	
90	556	29.9	1.427
70	307	17.5	1.101
50	166	9.96	0.425
40	—	5.81	—
30	56.9	3.42	-0.192
20	30.4	1.46	-0.711

Fig. 5. Plots of $\log k$ vs. Y Values for the Phenolysis of Ib, c in Phenol–Benzene Solvents

Ib, slope=0.583; Ic, slope=0.597.

various solvent studied were smaller than those for Ib. The plot of $\log k$ vs. E_T values showed a scattered pattern (Fig. 1). In contrast, a linear relationship with the Y values was observed ($m=0.402$, $r=0.997$) (Fig. 2).

Structure of the Transition State for the Rearrangement of Allylic Xanthate To understand the solvent effect on the rate for allylic xanthates, we performed modified intermediate neglect of differential overlap (MINDO/3)⁶⁾ calculations on the rearrangement reaction. To reduce computation time, the simplest compound, *i.e.*, *O*-allyl *S*-methyl xanthate (Id), was chosen as a model compound.

The molecular geometry of Id was determined by combining the known geometries for *O*-ethyl *S*-carboxyethyl xanthate⁷⁾ plus the allyl moiety followed by variation of all the interatomic distances plus bond and dihedral angles, until the heat of formation of the system was minimized. The minimum energy structure (A) is shown in Fig. 6.⁸⁾

Likewise, the minimum energy geometry for the [3,3]-sigmatropic rearrangement product, *i.e.*, *S*-allyl *S*-methyl

TABLE VI. Heats of Formation and Dipole Moment Calculated by MINDO/3 for the [3,3]-Sigmatropic Rearrangement of *O*-Allyl *S*-Methyl Xanthate (Id) to *S*-Allyl *S*-Methyl Dithiocarbonate (IId) via Concerted Six-Membered Transition State

Distance for $>C=S \cdots CH_2=C$ (Å)	ΔH_f (kcal/mol)	Rel. ΔH_f (kcal/mol)	μ_p (debye)
5.790 ^{a)}	-47.17	0.0	7.20
5.0	-47.06	+0.11	7.19
4.0	-46.53	+0.64	6.82
3.1	-44.18	+2.09	6.31
2.5	-40.88	+6.29	5.78
2.0	-38.67	+8.50	4.43
1.8	-31.88	+15.29	3.46
1.78	-30.67	+16.50	3.56
1.77	-56.87	-9.70	2.32
1.75	-55.83	-8.66	2.31
1.779 ^{b)}	-59.91	-12.74	2.14

a) All parameters were optimized on a conformation in which the methyl group of MeS- is *anti* to the oxygen atom of $>C=S$. Using this structure as a starting geometry, all parameters except $>C=S \cdots CH_2=C$ distance were optimized from 5.0 Å to 1.75 Å. b) All parameters were optimized on a conformation in which the methyl group of MeS- is *syn* to the oxygen atom of $>C=O$.

Fig. 6. MINDO/3 Heats of Formation and Optimized Structures of Id, IId and the Transition State for [3,3]-Sigmatropic Rearrangement of Id

dithiocarbonate (II_d), was determined. The calculated geometry⁹⁾ (C) is shown in Fig. 6.

The relative energies for the related compounds obtained from the MINDO/3 calculations appear in Table VI. Inspection of these values that *S*-allyl *S*-methyl dithiocarbonate (II_d) is *ca.* 12 kcal/mol more stable than *O*-allyl *S*-methyl xanthate (Id), suggesting that the thione–thiol isomerization is exothermic.¹⁰⁾

To obtain further information about the nature of the transition state, cyclic transition states were calculated along the reaction coordinate, taking the length of the forming $>\text{C}=\text{S}\cdots\text{CH}_2=$ bond as the reaction coordinate. The heat of formation for each structure is summarized in Table VI. As can be seen in Table VI, the optimized structure in which the thione sulfur atom was forced to be located 2.0 Å apart from the γ carbon is *ca.* 8.5 kcal/mol less stable than free *O*-allyl *S*-methyl xanthate (Id). As the $>\text{C}=\text{S}\cdots\text{CH}_2=$ distance is decreased, the heat of formation gradually increased and reached a maximum value ($\Delta H_f = -30.7$ kcal/mol) at *ca.* 1.78 Å (see B in Fig. 6). When the $>\text{C}=\text{S}\cdots\text{CH}_2=$ distance is 1.77 Å, the transition structure suddenly relaxed and transformed into *S*-allyl *S*-methyl dithiocarbonate (II_d). Concomitantly, reorganizations of π - and σ -electrons take place, accompanied with changes of bond distances and angles, resulting in electron delocalization all over the reaction system.

The optimized highest-energy structure along this pathway has a quasi-chair conformation. The structure shows enhanced double bond character at the $\text{S}=\text{C}-\text{O}$ - and $=\text{CH}-\text{CH}_2$ bonds and has a heat of formation equal to -30.7 kcal/mol, which is *ca.* 16.5 kcal/mol less stable than the starting material, *O*-allyl *S*-methyl xanthate (Id).

Discussion

In the phenolysis reaction of Ib, the formation of *S*-cinnamyl *S*-methyl dithiocarbonate (II_{b'}) was observed besides *S*-(1-phenylallyl) *S*-methyl dithiocarbonate (II_b). The magnitude of the *m* value for phenol–benzene solution is considerably larger than the values observed in typical *S*_N2 reactions.¹¹⁾ These results provide evidence for the formation of an intimate ion pair or an ion-pair intermediate, which collapses to products before the proper

structural orientation for [3,3]-sigmatropic rearrangement is attained.

In the previous paper,^{1b)} we reported that the catalytic activity of phenols in phenolysis of homoallylic xanthates is probably a consequence of the formation of a complex of the type $\text{RO}(\text{RS})\text{C}=\text{S}\cdots\text{H}-\text{OAr}$ between the catalyst and substrate (see Chart 3). The mechanism for solvolysis of Ib in protic solvents is very similar to that proposed for phenol-catalyzed thione–thiol rearrangement of homoallylic xanthates.

This assumption is supported by the difference in the activation parameters between protic and aprotic solvents. The activation energies of Ib and Ic in ethanol are 1–3 kcal/mol higher than those in dimethyl formamide (DMF). This may be due to additional desolvation energy in going from the ground state to the transition state. In the rearrangements of Ib and Ic in phenols, the activation entropies are highly negative in comparison with those for EtOH. The low entropy of activation may be due to a highly ordered transition state in which the motion of a phenol molecule might be frozen out. The rate constants in *o*-chlorophenol are smaller than those in *p*-chlorophenol. The rate retardation may be attributed to steric interference and intramolecular hydrogen bonding with the *o*-chloro group.^{1b)}

According to Swain, the nucleophilic substitution reaction might be pictured as resulting from the combination of “pushing” and “pulling” actions.¹²⁾ The “pull” may be exerted by solvent and the “push” is exerted by the nucleophile. The resulting carbonium ion may be stabilized by solvation with solvent molecules. Swain’s relationship is $\log k/k_0 = n \times S_n + e \times S_e$ where *n* is a nucleophilicity parameter associated with a nucleophilic reagent, *e* is an electrophilicity parameter associated with an electrophilic reagent, *S_n* is the sensitivity of the reaction under consideration to nucleophilic push, and *S_e* is the sensitivity of this reaction to electrophilic pull. For a group of substitution reactions that are essentially insensitive to nucleophilic push, the Swain equation may, in principle, be simplified to $\log k/k_0 = e \times S_e$, which is identical to the Grunwald–Winstein equation, $\log k/k_0 = Y \times m$.

While a plot of $\log k$ vs. *Y* values shows a linear

Chart 3

Chart 4

relationship, a plot of $\log k$ vs. E_T values exhibits some scattering (Fig. 1). In our solvolysis, xanthates mainly act as hydrogen-bond acceptors for protic solvents in a similar manner to *tert*-BuCl, used for evaluation of Y values. As stated above, E_T values are calculated from the results of spectroscopy, and pyridinium *N*-phenoxide betaine dye used for the determination of E_T values exhibits a large permanent dipole moment and has a large π -electron system in addition to being a hydrogen-bond acceptor. In particular, the large dipole moment of the betaine dye reflects the registration of dipole-dipole and dipole-induced dipole interactions between solute and solvent. These considerations may explain why the plot of $\log k$ vs. E_T values exhibits considerable scattering.

In the dissociation process, the dithiocarbonate moiety, besides being an effective leaving group by hydrogen bonding with protic solvents, acts as a very strong nucleophile by changing the anionic part from $^-\text{O}(\text{C}=\text{S})\text{SMe}$ to $^-\text{S}(\text{C}=\text{O})\text{SMe}$. Consequently, thione–thiol rearrangement of allylic xanthates is considered to be independent of the degree of the nucleophilic push, showing a linear relationship toward Y values.

The mechanism of [3,3]-sigmatropy could involve either a one-stage, concerted process, or ionization to a rigidly oriented intimate ion pair followed by internal return of the sulfur atom of the dithiocarbonate anion ($^-\text{SCOSR}$) to give the rearranged product. For a decision between these alternatives, the response of the rearrangement reaction to changes in solvent composition provides valuable information. The rates of *O*-allyl *S*-methyl dithiocarbonate (Id)³⁾ are insensitive to the ionizing power of solvents as compared with *O*-(2-methylthioethyl) *S*-methyl xanthate (Ic), which undergoes thione–thiol rearrangement *via* a solvent-separated ion-pair or a free carbonium intermediate [$k(80\%$ aqueous EtOH)/ $k(tert\text{-BuOH}) = 20$, $m = 0.402$]. In the case of Id, $m = 0.141$; a threefold increase in rate was observed for the rearrangement in going from *tert*-BuOH to 80% aqueous EtOH [$k(80\%$ aqueous EtOH)/ $k(tert\text{-BuOH}) = 3.0$]. On the other hand, the rearrangement of *O*-cinnamyl *S*-methyl xanthate (Ib) was moderately accelerated by increased polarity of the solvent, $m = 0.310$; the reaction is about ten times faster in 80% aqueous EtOH than *tert*-BuOH [$k(80\%$ aqueous EtOH)/ $k(tert\text{-BuOH}) = 10$], which indicates a mechanism with more ionic character than that of Id. The solvent effect of phenols is noteworthy. The rearrangement is more than a thousand times faster in

Fig. 7. Change of Net Charges and Dipole Moment in Id Calculated by MINDO/3

phenolic solvent, a highly polar solvent, than in *n*-hexane, which shifts the mechanism of the rearrangement toward an ionic process.

These facts indicate that the transition state of allylic xanthate rearrangement has an inherently polarizable structure and may be affected by substituents attached to the allyl moiety and by solvent polarity.

The net charges calculated by MINDO/3 along the reaction coordinate (Table VI) indicate that the electrons participating in the [3,3]-sigmatropic rearrangement delocalize gradually with decreasing $>\text{C}=\text{S} \cdots \text{CH}_2=$ distance, during which the dipole moment changes from 7.20 debye ($> 5 \text{ \AA}$) to 3.46 debye (1.8 $\text{\AA}$, cyclic transition state). This indicates that an early stage of the [3,3]-sigmatropic rearrangement may be affected by solvation of the reaction medium used (Table VI and Fig. 7).

In strongly ionizing solvents such as phenols, which have strong hydrogen-bonding ability to the anionic center, the degree of electron delocalization might be affected both in the ground state and in the transition state, causing alteration of the mechanism from nonionic to ionic. The MINDO/3 calculation on phenylallyl cation indicates that the magnitudes of the LUMO (lowest unoccupied molecular orbital) coefficient and net charge of the γ -position of the phenylallyl cation ($[\text{Ph-C}\gamma\text{H}=\text{C}\beta\text{H}=\text{C}\alpha\text{H}_2]^+$) are larger

Fig. 8. The LUMO Coefficients and Net Charges of Cinnamyl Cation Calculated by MINDO/3

than those of the α -position, suggesting that nucleophilic attack at the γ -position predominates over that at the α -position, which is consistent with the product ratio observed in the phenolysis reaction (Fig. 8). It is reasonable to expect that a thermodynamically stable localized ion ($\text{PhCH}=\text{CHCH}_2^+$)¹³ would not intervene in the reaction and the cyclic transition state may ionize to a loosely oriented intimate ion pair (see Chart 4) followed by internal return of the anion ($^-\text{SCOSMe}$) to give the thione-thiol rearranged products.

In summary, the concerted rearrangement of *O*-cinnamyl *S*-alkyl xanthate in aprotic solvents and the ionic rearrangement in phenolic solvents are considered to be the extremes in a continuous spectrum of mechanisms, and the transition state may have considerable polar character.

The rate constants obtained may be useful as a new scale of solvent ionizing power for solvent-sensitive chemical reactions, in particular as a measure of the hydrogen-bonding capacity of solvents with a sulfur atom.

Experimental

¹H-NMR spectra were taken with Hitachi R-600 and JEOL GX-400 spectrometers for ca. 10% (w/v) solution, with tetramethylsilane (TMS) as an internal standard; chemical shifts are expressed in δ values. Infrared (IR) spectra were recorded on a Hitachi 270-30 infrared spectrophotometer equipped with a grating. Ultraviolet (UV) spectra were recorded on a Hitachi 150-20 spectrophotometer.

Molecular orbital calculations were performed on a Facom M-360 computer in the Computer Center of Kumamoto University. Molecular modeling and least-squares calculations were performed on a Fujitsu FM-16 β or FMR-60 personal computer.

Preparation of *O,S*-Dialkyl Xanthates (Ia–c) *O*-Cinnamyl³⁾ (Ib) and *O*-(2-methylthioethyl)⁴⁾ (Ic) *S*-methyl xanthates were prepared according to the reported methods.

Compound Ic was purified by column chromatography on silica gel and obtained as an oil (yield 95%). IR (liquid film) cm^{-1} : 1218, 1070 ($-\text{O}(\text{C}=\text{S})\text{SMe}$). ¹H-NMR (in CDCl_3): 2.20 (3H, s, SMe), 2.59 (3H, s, $-\text{O}(\text{C}=\text{S})\text{SMe}$), 2.89 (2H, d, $-\text{SCH}_2-$), 4.79 (2H, d, $-\text{OCH}_2-$).

Solvolysis of *O*-Cinnamyl *S*-Methyl Xanthate (Ib) in Aqueous EtOH A solution of Ib in aqueous EtOH was heated at 60 °C on a water bath until the completion of the reaction had been confirmed by UV spectrophotometry. The product was extracted with CHCl_3 . The solvent was evaporated off to leave I Ib and I Ib' as a colorless oil.

The solvolysis of Ib in 80% EtOH gave a mixture of I Ib (89.7%) and I Ib' (10.3%). The structures of I Ib and I Ib' were determined by analysis of the 400 MHz ¹H-NMR spectrum. I Ib: IR (liquid film) cm^{-1} : 1644, 872

($-\text{S}(\text{C}=\text{O})\text{S}-$), 926, 980 ($-\text{CH}=\text{CH}_2$). ¹H-NMR (in CDCl_3): 2.41 (3H, s, SMe), 5.22 (1H, d, $=\text{CH}_2$), 5.27 (1H, d, $=\text{CH}_2$), 5.42 (1H, 2, $>\text{CHS}-$), 6.09 (1H, ddd, $-\text{CH}=\text{CH}-$). I Ib': IR (liquid film) cm^{-1} : 1644, 872 ($-\text{S}(\text{C}=\text{O})\text{S}-$), 968 ($-\text{CH}=\text{CH}-$). ¹H-NMR (in CDCl_3): 2.44 (3H, s, SMe), 3.83 (2H, d, $-\text{CH}_2\text{S}-$), 6.19 (1H, td, $=\text{CH}-\text{C}-\text{S}-$), 6.58 (1H, d, $\text{PhCH}=\text{CH}-$).

The solvolysis of Ib in 100% EtOH gave a mixture of I Ib (96%) and I Ib' (4%).

Phenolysis of Ib in Phenol-Benzene Solution A solution of Ib (200 mg, 0.89 mmol) in phenol (21.3 mmol) was heated at 60 °C for 0.5 h. The product was purified by chromatography on silica gel and obtained as a colorless oil (yield 190 mg, 95%). The ¹H-NMR spectrum showed the ratio of I Ib: I Ib' to be 64.2: 35.8.

Kinetics The reaction rates were followed at a given temperature by measuring the decrease of the thiocarbonyl absorption at ca. 350 nm (14.3–27.7 mmol/l), using a ground-glass-stoppered 10 $\times$ 10 mm Pyrex cell, which was thermostated with flowing water at constant temperature. The absorption data were collected automatically. The first-order rate constants were calculated from a plot of $\ln(A_t - A_\infty)$ vs. time by a least-squares method, where A_t is the absorbance at time t and A_∞ is the absorbance after about 10 half-lives. All spectra were calculated by means of a nonweighted least-squares program written in F-BASIC86 V3.1.

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