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Synthesis, Structure, and Thermolysis Mechanism of *S*-Alkoxythiazynes

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S-Alkoxy-*S*,*S*-diarylthiazynes were prepared by two methods: the alkaline hydrolysis of *S*,*S*-diaryl-*N*-halosulfilimines in aqueous alcohols and the reaction of *S*,*S*-diaryl-*S*-fluorothiazynes with sodium alkoxides. The structure of *S*,*S*-diphenyl-*S*-propoxythiazyne was determined by an X-ray crystallographic analysis, which showed a short SN bond length of 1.441(3) Å. The thermolysis of *S*-alkoxythiazynes gave elimination products, which were identified as the corresponding carbonyl compounds and *N*-unsubstituted *S*,*S*-diarylsulfilimines. Kinetic experiments for the thermolysis of the *S*-alkoxy-*S*,*S*-diarylthiazynes were carried out. The first-order kinetic behavior, a large kinetic isotope effect ($k_H/k_D = 6.1$) using *S*,*S*-diphenyl-*S*-[1,1-$^2H_2$]propoxythiazyne, a negative activation entropy ($\Delta S^{\ddagger} = -30\ J\ K^{-1}mol^{-1}$), and a negative Hammett ρ-value ($\rho = -0.35$) on the phenyl group were obtained, suggesting that the reaction proceeds via a concerted five-membered cyclic transition state. A deviation from the ideal concerted transition state is discussed in comparison with that for sulfoxides.

Thiazynes are unusual compounds bearing a sulfur–nitrogen triple bond; their chemistry has been developed by Glemser et al.[1] in the field of fluorine and inorganic chemistry. However, their chemistry in the organic area had remained unrecognized, until we recently prepared a series of organic thiazynes.[2] The first thiazyne in this series which we have reported is *S*-methoxy-*S*,*S*-diphenylthiazyne,[2a] which is formed as an intermediate in the alkaline hydrolysis of *N*-halosufilimines to the corresponding sulfoximines. Later, we briefly reported on the first preparation of *S*-fluorothiazynes,[2b] from which the *S*-alkoxythiazynes[2b] were found to be formed in a reaction with alkoxide anions. However, the alkoxythiazynes could not be isolated from the sulfoximine and more definitive evidence has been required. Recently, we prepared a thiazyne having three carbon ligands, *S*,*S*,*S*-triphenylthiazyne,[2d] for the first time and determined its structure by an X-ray crystallographic analysis. In this paper we describe the synthesis, successful crystalline isolation, the X-ray crystallographic structure, and a kinetic investigation concerning the mechanism of the thermolysis of *S*-alkoxy-*S*,*S*-diarylthiazynes, together with the preparation of the key *S*,*S*-diaryl-*S*-fluorothiazyne compounds.

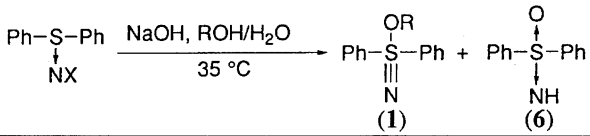
Results and Discussion

Synthesis of *S*-Alkoxythiazynes 1: Previously, we briefly reported on the formation of the *S*-alkoxythiazynes **1** as an oily mixture with the sulfoximine **6** in two separated reactions: the alkaline hydrolysis of *S*,*S*-diphenyl-*N*-halosulfilimines[2a] and the treatment of *S*-fluorothiazynes **2**—**5**[2b] with various alkoxides. In order to delineate the scope and limitations of these reactions as synthetic methods of *S*-alkoxythiazynes **1**, the reaction conditions were further examined. (Tables 1 and 2)

Though the method involving the alkaline hydrolysis of *N*-halosulfilimines has the advantage of a shorter synthetic sequence than the latter, this method gave a much greater amount of the sulfoximine **6** to prevent any separation of the thiazynes, and also gave the *N*-unsubstituted sulfilimine, which is formed by a reduction with alcohols depending on the *N*-halogen atom when higher alcohols as 1-propanol were used. The *N*-iodosulfilimine underwent the reduction even with methanol. The alkaline hydrolysis in absolute methanol is unfavorable, because the reaction requires a prolonged time and the yield is not improved. Though the reason for the longer time requirement had been unclear in a previous report,[2a] based on the later mechanistic investigation it was found to be due to a solvent effect in the S_N1-like mechanism.[3]

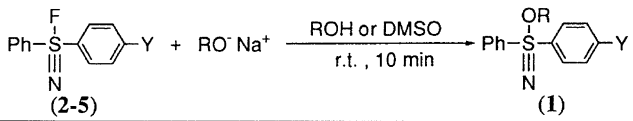
Meanwhile, the reaction of *S*-fluorothiazynes **2**—**5**[2b] with sodium alkoxides afforded many more types of *S*-alkoxythiazynes **1** in higher yields, and some of them were obtained as crystalline solids by a careful work-up. The corresponding alcohol was used as a solvent in each reaction. However, since longer-chain, expensive alcohols and solid alcohols, such as neopentyl alcohol, are not available as a solvent, in such cases the reaction was carried out in DMSO. The yields of the alkoxythiazynes were often poor, due mainly to the character of the facile hydrolysis of the alkoxythiazynes during the work-up washing with water and to a partial rearrangement to *N*-alkylsulfoximines when kept in an oily state. In such cases the work-up in the presence of a small amount of DBU improved the yields from about 30 to 50—90%. The

Table 1. Formation of *S*-Alkoxythiazynes by the Alkaline Hydrolysis of *N*-Halosulfilimines



Compound	R	X	Solvent	Time	Yield/%	Other products
1a	Me	Cl	$MeOH/H_2O$	17 min	43	**6** (50)
1a	Me	Br	$MeOH/H_2O$	92 min	60	**6** (34)
1a	Me	Br	MeOH	4.5 h	58	**6** (40)
1a	Me	Br	MeONa/MeOH	4.8 h	21	**6** (78)
1a	Me	I	$MeOH/H_2O$	12 h	Not detected	$Ph_2S{\rightarrow}NH{\cdot}H_2O$ (92)
1b	Et	Br	$EtOH/H_2O$	3.4 h	22	**6** (22), $Ph_2S{\rightarrow}NH{\cdot}H_2O$ (44)
1c	*n*-Pr	Cl	*n*-$PrOH/H_2O$	3 h	24	**6** (63), $Ph_2S{\rightarrow}NH{\cdot}H_2O$ (trace)
1c	*n*-Pr	Br	*n*-$PrOH/H_2O$	2 h	Not detected	**6** (18), $Ph_2S{\rightarrow}NH{\cdot}H_2O$ (71)

Table 2. Reaction of *S*-Fluorothiazynes **2**—**5** with Sodium Alkoxides



Compound	R	Y	Solvent	Yield/%
1a	Me	H	MeOH	88[a]
1b	Et	H	EtOH	80[a]
1c	*n*-Pr	H	*n*-PrOH	73[b]
1d	*i*-Pr	H	*i*-PrOH	63[b]
1e	*n*-Bu	H	*n*-BuOH	51[b]
1f	Me_3CCH_2	H	DMSO	61[b]
1g	*n*-Pr	Me	*n*-PrOH	92[a]
1h	*n*-Pr	Cl	*n*-PrOH	95[a]
1i	*n*-Pr	NO_2	*n*-PrOH	90[a]
1j	*t*-Bu	H	DMSO	Not detected
1k	$PhCH_2$	H	DMSO	Not detected

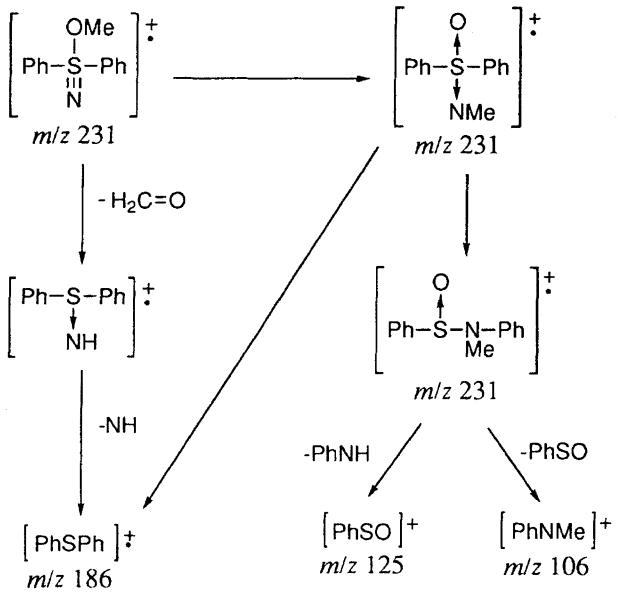
a) Yield was determined by ^1H NMR analysis. b) Isolated yield.

reactions with potassium *t*-butoxide and with sodium benzyloxide did not give the corresponding thiazynes. Although the *S*-alkoxythiazynes **1c**—**f** were successfully purified by recrystallization (benzene/hexane), **1a**,**b**,**g**—**i** could not be separated from the sulfoximines. The key point concerning the success of the purification is not only the higher melting point but also the exclusive formation of the *S*-alkoxythiazynes compared to the sulfoximine. Also, the use of DBU is one of the best ways.

The characterization of *S*-alkoxythiazynes **1** was achieved with ^1H and ^{13}C NMR, IR, and elemental analyses or HRMS. All of the spectral data of **1a**—**i** are consistent with the structure of the alkoxythiazynes **1**. Our previous report[2a] concerning the GC-mass spectrum of **1a** was found to be in error. The GLC peak of the sample was found to have the same retention time as that of *N*-methyl-*S*,*S*-diphenylsulfoximine. The alkoxythiazyne was thermally too unstable to be detected by GC and the previously observed mass spectrum was completely the same as that of the thermally stable *N*-methyl-*S*,*S*-diphenylsulfoximine.[4]

The mass spectrum of **1a** (**1a** : **6** = 83 : 17) in the present work by the direct method also showed almost the same pattern (231 (9), 186 (7), 125 (7), 106 (100), 92 (12)) as that for a mixture of the *N*-methylsulfoximine (231 (12), 186 (11), 125 (10), 106 (100)) and *S*,*S*-diphenylsulfoximine (217 (4), 216 (5), 125 (50), 92 (100)). In spite of not containing any *N*-methylsulfoximine in the sample, the strong pattern of the *N*-methylsulfoximine was observed, suggesting that the fragmentation of methoxythiazyne proceeds via a rearrangement to the *N*-methylsulfoximine due to electron impact or thermal energy. Thus, the fragmentation pattern of **1a** may be proposed as shown in Scheme 1.

The mass spectrum of purified *S*-propoxythiazyne **1c** showed a parent peak at *m/z* 259 (very weak) and major fragment peaks at *m/z* 92 (81), 125 (49), 186 (95), 203 (27), and 230 (100). In the case of the *N*-propylsulfoximine,[5] major fragment peaks were observed at *m/z* 186 (24), 203 (47), and 230 (100). The spectrum of the *S*-propoxythiazyne **1c** showed a different fragment pattern from that of the *N*-propylsulfoximine, i.e. the peaks at *m/z* 92, 125, and 186 for **1c** were weak for the latter. The fragmentation pattern of **1a**

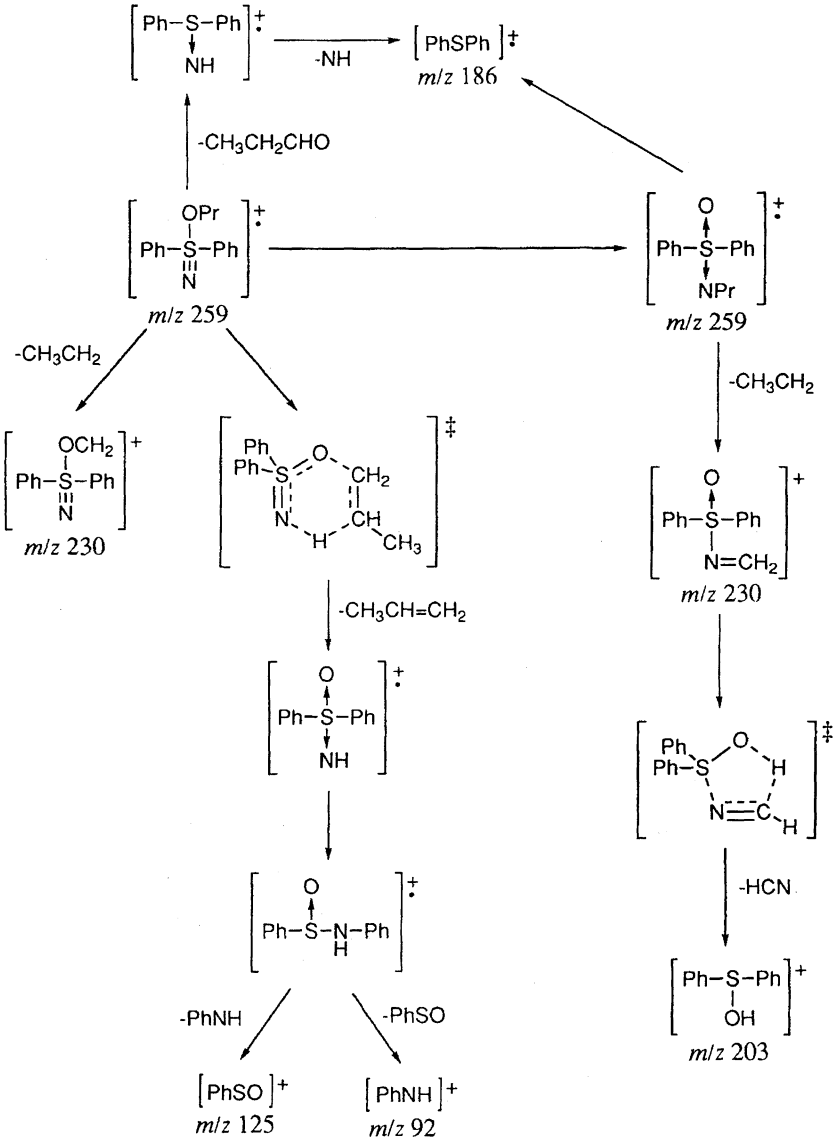


Scheme 1.

may be proposed as shown in Scheme 2.

The peaks at *m/z* 92 ([PhNH]$^+$) and 125 ([PhSO]$^+$) are considered to be generated by a rearrangement of the phenyl group to the N atom of *S,S*-diphenylsulfoximine,[6] which may be formed by a McLafferty-type elimination of propene from the parent ion. The peak at *m/z* 186 ([PhSPh]$^{+\bullet}$) may be due to deimination of the *N*-unsubstituted sulfilimine[7] formed by an initial elimination of propanal from the parent ion of **1c** via a five-membered transition state, like the thermolysis described later. The peak at *m/z* 230 is also the base peak in the spectrum of the *N*-propylsulfoximine and is considered to be formed by an elimination of the ethyl group of the *N*-propylsulfoximine. Since the carbocation in this peak is stabilized by the N atom, the release of the ethyl group from the parent peak of the *N*-propylsulfoximine may be dominated rather than phenyl migration, unlike the *N*-methylsulfoximine and the *N*-unsubstituted sulfoximine. This peak may further undergo the elimination of HCN via a similar five-membered cyclic transition state to form the fragment *m/z* 203 ([PhS(OH)Ph]$^+$). Therefore, in the case of the thiazyne **1c** the propyl group is also considered to migrate from the O atom to the N atom, like in the case of methoxythiazyne. However, comparing the relative intensity of the peaks at *m/z* 230 and 203 for **1c** with those for the *N*-propylsulfoximine, ca. 60% of the peak at *m/z* 230 is considered to be arised from the parent ion of *N*-propylsulfoximine, while the remaining part may be derived by an elimination of ethyl group from the parent ion of the *S*-propoxythiazyne.

The IR band due to the S–N bond stretching of *S*-alkoxythiazynes **1a**—**i** is observed at 1327—1335 cm^{-1}, which is similar to that of *S*-fluoro- (1361 cm^{-1}),[2b] *S*-amino- (1285—1298 cm^{-1}),[2c] *S*-sulfilimino- (1247—1260 cm^{-1}),[2c] *S,S,S*-triphenylthiazyne (1267 cm^{-1})[2d], and thiazyl trifluoride (1515 cm^{-1}),[1c] but higher than that of *S,S*-diphenylsulfilimine (940 cm^{-1}),[8] and *S,S*-diphenylsulfoximine (965, 1092, 1217 cm^{-1}).[6] These results imply



Scheme 2.

that the SN bond of *S*-alkoxythiazynes **1a**—**i** has a higher bond order than that of sulfilimine and sulfoximine.

X-Ray Crystallographic Analysis of *S*-Propoxythiazyne 1c: A detailed structural analysis of *S*-propoxythiazyne **1c** was performed by an X-ray crystallographic analysis. Selected bond distances and bond angles of *S*-propoxythiazyne **1c** are collected in Table 3. An ORTEP drawing of *S*-propoxythiazyne **1c** is depicted in Fig. 1.

Table 3. Selected Structural Data for *S*,*S*-Diphenyl-*S*-propoxythiazyne (**1c**)[a)]

Bond distance (Å)		Bond angle (Å)	
S(1)–N(1)	1.441(3)	O(1)–S(1)–N(1)	122.0(2)
S(1)–O(1)	1.615(3)	O(1)–S(1)–C(4)	97.5(1)
S(1)–C(4)	1.798(3)	O(1)–S(1)–C(10)	97.5(1)
S(1)–C(10)	1.798(3)	N(1)–S(1)–C(4)	116.1(1)
O(1)–C(1)	1.320(8)	N(1)–S(1)–C(10)	116.1(1)
C(1)–C(2)	1.326(10)	C(4)–S(1)–C(10)	104.0(2)
C(2)–C(3)	1.338(9)	S(1)–O(1)–C(1)	122.4(4)
		O(1)–C(1)–C(2)	126.7(7)
		C(1)–C(2)–C(3)	127.7(8)

a) Numbers in parentheses are estimated standard deviations in the least significant digits. The atom-labeling scheme is shown in Fig. 1.

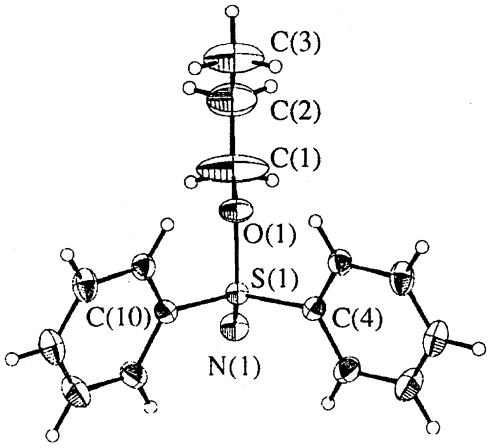


Fig. 1. ORTEP drawing of **1c**.

The molecular structure of *S*-propoxythiazyne **1c** has a mirror symmetry co-planar with about the atoms N(1), S(1), O(1), and C(1) and the configuration around the sulfur atom is a slightly distorted tetrahedral geometry involving an S–N bond, an S–O bond, and two S–C bonds. The triple bond length of S(1)–N(1) is 1.411(3) Å. This S–N bond length is similar to that of thiazyl trifluoride (1.416(3) Å, microwave spectroscopy)[9)] and *S*,*S*,*S*-triphenylthiazyne (1.462(3) Å, X-ray)[2d)] and is shorter than that of *S*,*S*-diphenyl-*N*-tosylsulfilimine (1.628(7) Å, X-ray),[10)] *S*,*S*-dimethylsulfoximine (1.521(3) Å, electron diffraction),[11)] and *S*,*S*-dimethylsulfonediimine (1.533(2) Å, electron diffraction).[12)] The shorter SN bond length of *S*-propoxythiazyne **1c** again suggests that the SN bond order of thiazynes is higher than that of sulfilimines, sulfoximines, and sulfonediimines.

Stability: Since the *S*-alkoxythiazynes **1** have been isolated as intermediates[2a)] in the alkaline hydrolysis of *N*-halosulfilimines to the corresponding sulfoximines, the hydrolysis of *S*-methoxythiazyne **1a** is expected to be very facile. Therefore, the thermal stability and facility toward hydrolysis were examined, as shown in Table 4.

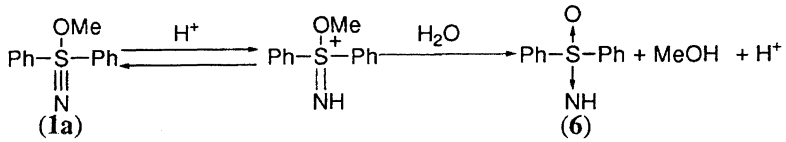
The hydrolysis of *S*-alkoxythiazynes is apparently catalyzed by 5% sulfuric acid. The *S*-methoxythiazyne **1a** is very sensitive to the acidic conditions, e.g. **1a** was almost completely hydrolyzed to give the sulfoximine **6** by bubbling CO_2 into a CD_3OD/D_2O solution for 1 min, and was also hydrolyzed while stirring with silica gel in methanol for 23 h, while resulted in a difficulty to isolate **1a** by silica-gel column chromatography. The susceptibility of alkoxythiazynes to acid-catalyzed hydrolysis induced us to maintain alkaline conditions during the work-up procedures for the isolation of alkoxythiazynes. According to previous results,[13)] the reaction of *S*-methoxythiazyne **1a** with benzenethiol proceeds via nucleophilic substitution on the alkyl carbon atom to give the corresponding sulfoximine **6** and methyl phenyl sulfide. The mechanism of the hydrolysis of **1a** may also be substitution on the methyl carbon atom of the protonated thiazyne **1a** (Scheme 3).

When the oily thiazyne **1a** was kept at room temperature without solvent, the alkyl group was sometimes found to

Table 4. Thermolysis and Hydrolysis of *S*-Alkoxy-*S*,*S*-diphenylthiazynes (**1**)

R	Conditions	Products and yield (%)
Me[a)]	5% H_2SO_4 in MeOH/H_2O, r.t., 1 h	**6** (98)
Me[a)]	In CD_3OD/D_2O, CO_2, r.t., 1 min	**6** (95),[b)] recovered **1a** (5)[b)]
Me[a)]	SiO_2 in MeOH, r.t., 23 h	**6** (90)
Me[a)]	In MeOH, 50 °C, 24 h	**6** (90)
Me[a)]	In benzene, reflux, 39 h	**6** (36), Ph_2S (43), $Ph_2S{\rightarrow}NH{\cdot}H_2O$ (21)
n-Pr	In benzene, reflux, 24 h	Ph_2S (25), $Ph_2S{\rightarrow}NH{\cdot}H_2O$ (73)
n-Pr	In benzene-d_6, 110 °C	$Ph_2S{\rightarrow}NH{\cdot}H_2O$ (98),[b)] EtCHO (85)[b)]
i-Pr	In benzene-d_6, 110 °C	$Ph_2S{\rightarrow}NH{\cdot}H_2O$ (98),[b)] Me_2CO (88)[b)]
n-Bu	In benzene-d_6, 110 °C	$Ph_2S{\rightarrow}NH{\cdot}H_2O$ (95),[b)] PrCHO (65)[b)]

a) Reactions were carried out using the mixture of **1a** and **6** and the yields are conversion yields.
b) Yields were determined by ^1H NMR analysis.



Scheme 3.

partially rearrange to the nitrogen atom to give *S*,*S*-diphenyl-*N*-alkylsulfoximine. This migration may be interpreted as proceeding via an intermolecular alkylation catalyzed by contamination with acid, which is consistent with the observation of such an occurrence under high-concentration conditions of alkoxythiazynes.

In the crystalline state or in an aprotic solvent the *S*-alkoxythiazynes are relatively stable at room temperature. However, the *S*-alkoxythiazynes decomposed in benzene under reflux conditions to give *N*-unsubstituted *S*,*S*-diphenylsulfilimine and carbonyl compounds (Scheme 4).

The formation of diphenyl sulfide is explained by a secondary reaction of *N*-unsubstituted diphenylsulfilimine and aldehydes once formed.[14] Considering the basicity of *S*,*S*-diphenyl-*S*-piperidinothiazyne ($pK_a = 7.47$),[2c] the nitrogen atom of the *S*-alkoxythiazynes is also expected to be basic. Therefore, an intramolecular *cis*-elimination via a five-membered cyclic transition state is one of the possible mechanisms.

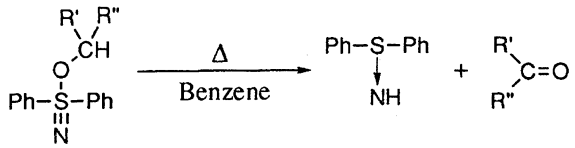
Mechanism of Thermolysis: The thermolysis of tricoordinated sulfur compounds as sulfoxides or sulfilimines having β-hydrogens gives the corresponding alkenes and sulfenic acids or sulfenamides.[15] The results of kinetic studies on the thermolysis of these compounds have suggested that the reaction proceeds through an intramolecular *cis*-elimination process.[16] This mechanism involves concurrent S–C bond cleavage and proton migration in the transition state (Scheme 5).

Unlike these tricoordinated sulfur compounds, there has been to no example of an E*i* reaction of tetracoordinated sulfur compounds. Therefore, a comparison of the thermolysis of *S*-alkoxythiazynes having a polar N atom with that of sulfoxides and sulfilimines is interesting.

In order to clarify the mechanism, a kinetic study was performed by following the decreasing ^{1}H NMR signals of alkyl protons of the thiazynes. The reaction was found to fit a first-order kinetic equation; the results are summarized in Table 5. Unlike the products listed in Table 4, when the kinetics was carried out under dilute conditions using a predried sample and a solvent, the thermolysis of **1a** did not show any increase in the hydrolysis product **6**, and the *N*-unsubstituted sulfilimine was formed quantitatively.

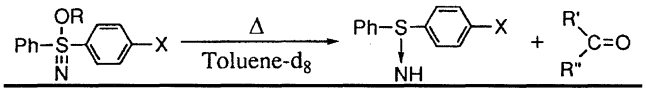
A large deuterium kinetic isotope effect using *S*,*S*-diphenyl-*S*-[1,1-^{2}H$_2$]propoxythiazyne (**1c–d$_2$**) was observed suggesting the involvement of proton migration in the rate-controlling step. However, the first-order kinetic behavior does not agree with a bimolecular elimination.

The activation parameters for the thiazyne **1c** ($\Delta H^{\ddagger}$ = 99.9 kJ mol^{-1}, $\Delta S^{\ddagger} = -30$ JK^{-1} mol^{-1}) are similar to those of alkyl phenyl sulfoxides ($\Delta H^{\ddagger} = 105$—117 kJ mol^{-1}, $\Delta S^{\ddagger} = -63$——4 J K^{-1} mol^{-1})[15,17,18] and sulfilimines ($\Delta H^{\ddagger}$ = 87—111 kJ mol^{-1}, $\Delta S^{\ddagger} = -36$——24 J K^{-1} mol^{-1}).[19] The negative activation entropy suggests that the transition state is more rigid than the starting state. The large kinetic isotope effect, the small Hammett substituent effect, and the negative activation entropy are inconsistent with an ionic or radical mechanism involving a rate-determining S–O bond cleavage. All of these data support a mechanism involving an intramolecular concerted *cis*-elimination via a five-membered cyclic transition state, as in the case of sulfoxides and sulfilimines. Inspection of the data in Table 5 shows some structural dependency of the rate constants on the alkyl group. In spite of a reduction of the number of β-hydrogens of the propoxythiazyne **1c** compared to the methoxythiazyne **1a**, the rate of thermolysis of **1c** is 1.8 times faster than that

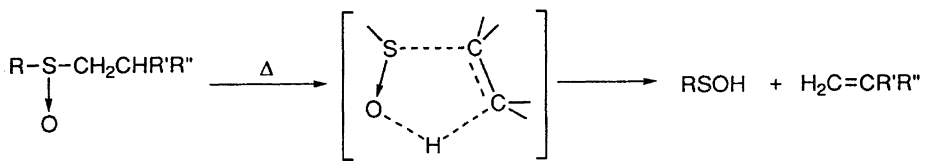


Scheme 4.

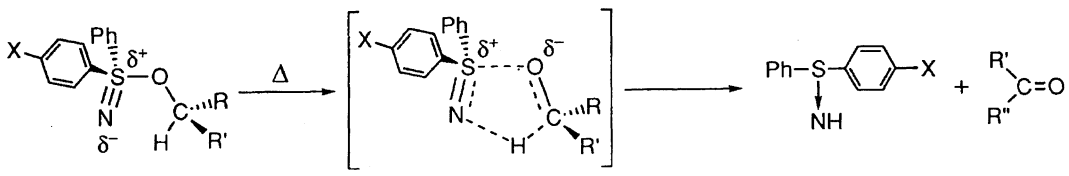
Table 5. Kinetic Data for Thermolysis of *S*-Alkoxythiazyne **1**



Compound	R	X	Temp/°C	$k \times 10^4$/s^{-1}
1a	Me	H	74.1	1.01±0.02
1c	*n*-Pr	H	64.1	0.621±0.006
1c	*n*-Pr	H	74.1	1.83±0.03
1c	*n*-Pr	H	84.1	4.80±0.05
1d	*i*-Pr	H	74.1	1.00±0.05
1g	*n*-Pr	Me	74.1	2.09±0.02
1h	*n*-Pr	Cl	74.1	1.37±0.02
1i	*n*-Pr	NO_2	74.1	1.01±0.01
1c-d$_2$	$CD_2CH_2CH_3$	H	74.1	0.301±0.003



Scheme 5.



Scheme 6.

of **1a**. The acceleration effect of the β-alkyl group is explained by hyper-conjugation of the alkyl group with C–O π orbital formation, as in the case of an E2 elimination of alkyl halide.[20]

The magnitude of the kinetic isotope effect of β-hydrogen ($k_H/k_D = 6.1$) is larger than that of sulfoxides ($k_H/k_D = 2.3$—4.3)[18,21] and sulfilimines ($k_H/k_D = 2.9$—3.5),[17] suggesting that the proton transfer in the transition state for **1c** is more concerted than that for sulfoxides and sulfilimines.

A substituent effect for the thermolysis of the *S*-alkoxythiazynes **1** showed a negative Hammett ρ-value (-0.35), which is an opposite trend to that for many sulfoxides. For example, the Hammett ρ-values on the *S*-phenyl group of the thermolysis of aryl propyl sulfoxides, aryl *t*-butyl sulfoxides, and aryl 1-phenylethyl sulfoxides are positive ($\rho = +0.51$,[15a] $+0.695$,[15b] and $+0.60$,[17] respectively). Though the E*i*-reaction of sulfoxides is generally recognized as a concerted process, a balance of the extent of the C–S bond cleavage and proton migration from the β-carbon to the oxygen causes a deviation to an E1-like or a carbanion-like mechanism in the five-membered cyclic transition state.[17,18] Namely, in the E1-like mechanism the departure of the leaving group progresses more than proton abstraction, thus developing a partially positive charge at the α-carbon, while in the carbanion-like mechanism the reverse relation develops a partially negative charge at the β-carbon in the transition state, as shown in Fig. 2. Although the development of the charge at the α- or β-carbon is small unlike in E2 reactions, the positive Hammett ρ-values for the sulfoxides are consistent with an E1-like mechanism. On the other hand, the negative ρ-value for the thermolysis of aryl 2-cyanoethyl sulfoxides ($\rho = -0.49$) suggests a carbanion-like mechanism.[18]

The negative trend for the present system might suggest the importance of proton abstraction by the nitrogen atom, i.e., involvement of a carbanion-like transition state. β-Proton abstraction by the basic nitrogen instead of oxygen will contribute to deviate the mechanism to carbanion-like. However, unlike in the case of sulfoxides, the α-position of *S*-alkoxythiazynes is not the carbon, but the electronegative α-oxygen atom, which may withdraw the developing β-carbanion electron to form a C–O π-bond to cancel the negative charge on the β-carbon. Therefore, the negative ρ-value is considered to be the result of a migration of the electron of the SN bond to the oxygen atom through the basic nitrogen, β-proton, and β-carbon atoms, as shown in Scheme 6.

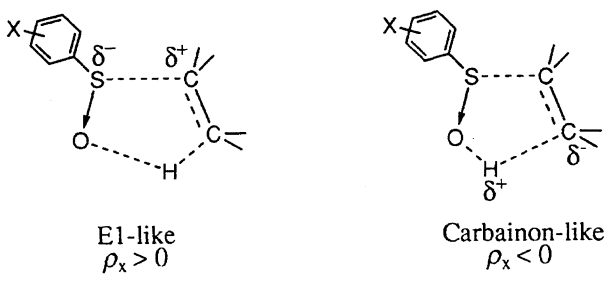


Fig. 2.

Experimental

General: ^{1}H and ^{13}C NMR spectra were taken on a JEOL-JNM 400 spectrometer with TMS as an internal standard. Mass spectra were obtained on a JEOL-JMS-D 300 spectrometer operating at 20 eV or 70 eV (HRMS). IR spectra were obtained on a Horiba FT-710 spectrometer. Elemental analyses were performed on a Yanaco MT-5 CHN CORDER. *S*-Aryl-*S*-phenyl-*N*-bromosulfilimines were prepared according to a method reported in previous literature.[22]

General Procedure for Synthesis of *S*-Aryl-*S*-fluoro-*S*-phenylthiazynes (2—5): The indicated *S*-aryl-*N*-bromo-*S*-phenylsulfilimine (10 mmol) was treated with 20 ml (20 mmol) of tetrabutylammonium fluoride (TBAF) (1 M in THF, 1 M = 1 mol dm^{-3}) at 0 °C for 3 h. The solution was diluted with four times the volume of chloroform and washed with water (20×50 ml) to remove tetrabutylammonium salt. The combined organic phases were dried over anhydrous magnesium sulfate and evaporated to dryness to give **2—5** as a yellowish solid. This solid was purified by recrystallization from benzene by cooling.

***S*-Fluoro-*S*,*S*-diphenylthiazyne (2):** Yield 65%; mp 63.0—64.0 °C; IR (KBr disk) 1361 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.50$—7.64 (m, 6H), 7.91—7.94 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 127.0$, 129.4, 133.2, 143.6 (d, $^2J_{CF} = 22$ Hz). Found: C, 65.56; H, 4.69; N, 6.15%. Calcd for $C_{12}H_{10}FNS$: C, 65.73; H, 4.60; N, 6.39%.

***S*-Fluoro-*S*-phenyl-*S*-*p*-tolylthiazyne (3):** Yield 53%; mp 84.5—85.5 °C; IR (KBr disk) 1360 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2.43$ (s, 3H), 7.32—7.36 (m, 2H), 7.50—7.54 (m, 2H), 7.57—7.61 (m, 1H), 7.80—7.82 (m, 2H), 7.89—7.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 21.1$, 126.4, 126.7, 129.0, 129.6, 132.7, 140.3 (d, $^2J_{CF} = 22$ Hz), 143.7 (d, $^2J_{CF} = 23$ Hz), 144.0. Found: C, 67.06; H, 5.18; N, 5.93%. Calcd for $C_{13}H_{12}FNS$: C, 66.93; H, 5.18; N, 6.00%.

***S*-*p*-Chlorophenyl-*S*-fluoro-*S*-phenylthiazyne (4):** Yield 60%; mp 119.5—120.5 °C; IR (KBr disk) 1364 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.49$—7.57 (m, 4H), 7.61—7.65 (m, 1H), 7.85—7.88 (m, 2H), 7.90—7.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 127.0$, 128.4, 129.5, 129.6, 133.5, 139.9, 142.1 (d, $^2J_{CF} = 23$ Hz), 143.4 (d, $^2J_{CF} = 22$ Hz). Found: C, 56.82; H, 3.60; N, 5.40%. Calcd for $C_{12}H_9ClFNS$: C, 56.81; H, 3.58; N, 5.52%.

***S*-Fluoro-*S*-*p*-nitrophenyl-*S*-phenylthiazyne (5):** Yield 72%; mp 110.5—111.5 °C; IR (KBr disk) 1361 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.59$—7.63 (m, 2H), 7.68—7.72 (m, 1H), 7.94—7.97 (m, 2H), 8.08—8.11 (m, 2H), 8.37—8.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 124.4$, 127.0, 127.8, 129.5, 133.8, 141.9 (d,

$^2J_{CF}$ = 20 Hz), 148.6 (d, $^2J_{CF}$ = 25 Hz), 149.7. Found: C, 54.30; H, 3.46; N, 10.35%. Calcd for $C_{12}H_9FN_2O_2S$: C, 54.54; H, 3.43; N, 10.60%.

General Procedure for Synthesis of *S*-Alkoxy-*S*-aryl-*S*-phenylthiazynes (1): Method A: A solution of the *S*,*S*-diphenyl-*N*-halosulfilimine (0.5 mmol) in the corresponding alcohol (35 ml) was added to a stirred solution of 35 ml of NaOH (0.1 M in water or alcohol) at 35 °C for the period of time indicated in Table 1. The reaction mixture was poured into water and extracted with chloroform (4×15 ml) in the presence of a drop of DBU. The combined organic extracts were washed with water (2×30 ml) and dried over anhydrous magnesium sulfate and concentrated under reduced pressure.

Method B: The indicated *S*-fluorothiazyne **2**—**5** (1 mmol) was treated with the sodium alkoxide (3 mmol) in the corresponding alcohol (20 ml) at room temperature for 10 min. The reaction mixture was poured into water and extracted with chloroform (10×5 ml) in the presence of a drop of DBU. The combined organic extracts were washed with water (3×30 ml) and dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give **1** as an oil or a solid. This solid was purified by recrystallization from benzene/hexane.

Method C: A solution of the *S*-fluorothiazyne **2** (1 mmol) in DMSO (3 ml) was added to a stirred solution of the alkoxide in DMSO (5 ml) at room temperature for 10 min under an argon atmosphere which was prepared by treatment of sodium hydride (3 mmol) with the alcohol (3.1 mmol) in DMSO (5 ml). The reaction mixture was poured into water and extracted with chloroform (5×5 ml) in the presence of a drop of DBU. The combined organic extracts were washed with water (3×20 ml) and dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give **1** as an oil or a solid. This solid was purified by recrystallization from benzene/hexane.

***S*-Methoxy-*S*,*S*-diphenylthiazyne (1a):** Method B; yield 88% (oil); IR (neat film) 1331 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.74 (s, 3H), 7.45—7.54 (m, 6H), 7.91—7.94 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 48.2, 127.1, 128.9, 132.0, 144.2. HRMS, Found: *m*/*z* 231.0723. Calcd for $C_{13}H_{13}NOS$: M, 231.0718.

***S*-Ethoxy-*S*,*S*-diphenylthiazyne (1b):** Method B; yield 80% (oil); IR (neat film) 1333 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.36 (t, *J* = 7.2 Hz, 3H), 4.16 (q, *J* = 7.2 Hz, 2H), 7.44—7.54 (m, 6H), 7.91—7.94 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 15.3, 58.1, 127.0, 128.9, 132.0, 145.0. HRMS, Found: *m*/*z* 245.0851. Calcd for $C_{14}H_{15}NOS$: M, 245.0870.

***S*,*S*-Diphenyl-*S*-propoxythiazyne (1c):** Method B; yield 73%; mp 118.0—119.0 °C (decomp); IR (KBr disk) 1334 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.98 (t, *J* = 7.2 Hz, 3H), 1.76 (sext, *J* = 7.2 Hz, 2H), 4.04 (t, *J* = 6.8 Hz, 2H), 7.44—7.52 (m, 6H), 7.92—7.94 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 10.4, 22.9, 63.3, 127.1, 128.9, 131.9, 145.1. Found: C, 69.83; H, 6.83; N, 5.43%. Calcd for $C_{15}H_{17}$ NOS: C, 69.46; H, 6.61; N, 5.40%.

***S*-Isopropoxy-*S*,*S*-diphenylthiazyne (1d):** Method B; yield 63%; mp 115.0—116.0 °C (decomp); IR (KBr disk) 1334 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.31 (d, *J* = 6.4 Hz, 3H), 5.07 (sept, *J* = 6.8 Hz, 2H), 7.43—7.52 (m, 6H), 7.90—7.94 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 23.7, 67.4, 127.0, 128.8, 131.8, 146.2, Found: C, 69.31; H, 6.59; N, 5.31%. Calcd for $C_{15}H_{17}NOS$: C, 69.46; H, 6.61; N, 5.40%.

***S*-Butoxy-*S*,*S*-diphenylthiazyne (1e):** Method B; yield 51%; mp 125.5—126.5 °C (decomp); IR (KBr disk) 1332 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.91 (t, *J* = 7.2 Hz, 3H), 1.43 (sext, *J* = 7.2 Hz, 2H), 1.72 (quint, *J* = 6.8 Hz, 2H), 4.08 (t, *J* = 6.8 Hz, 2H), 7.44—7.52 (m, 6H), 7.91—7.94 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.63, 19.1, 31.4, 61.6, 127.1, 128.9, 131.9, 145.1. Found: C, 70.50; H, 7.03; N, 4.95%. Calcd for $C_{16}H_{19}NOS$: C, 70.29; H, 7.00; N, 5.12%.

***S*-Neopentyloxy-*S*,*S*-diphenylthiazyne (1f):** Method C; yield 61%; mp 110.5—111.5 °C (decomp); IR (KBr disk) 1332 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.00 (s, 9H), 3.70 (s, 2H), 7.45—7.53 (m, 6H), 7.91—7.95 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 26.6, 31.8, 70.6, 127.1, 128.9, 131.9, 145.1. Found: C, 71.17; H, 7.36; N, 5.01%. Calcd for $C_{17}H_{21}NOS$: C, 71.04; H, 7.36; N, 4.87%.

***S*-Phenyl-*S*-propoxy-*S*-*p*-tolylthiazyne (1g):** Method B; yield 92% (oil); IR (neat film) 1334 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.98 (t, *J* = 7.2 Hz, 3H), 1.75 (sext, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 4.02 (dt, *J* = 6.8, 2.0 Hz, 2H), 7.25—7.27 (m, 2H), 7.43—7.51 (m, 3H), 7.80—7.83 (m, 2H), 7.90—7.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 10.4, 21.4, 22.9, 63.3, 127.0, 127.2, 128.9, 129.5, 131.8, 142.1, 142.7, 145.5. HRMS, Found: *m*/*z* 273.1204. Calcd for $C_{16}H_{19}NOS$: M, 273.1187.

***S*-*p*-Chlorophenyl-*S*-phenyl-*S*-propoxythiazyne (1h):** Method B; yield 95% (oil); IR (neat film) 1327 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.98 (t, *J* = 7.2 Hz, 3H), 1.76 (sext, *J* = 7.2 Hz, 2H), 4.04 (t, *J* = 6.8 Hz, 2H), 7.42—7.54 (m, 5H), 7.84—7.88 (m, 2H), 7.89—7.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 10.4, 20.9, 63.6, 127.1, 128.6, 129.1, 129.2, 132.2, 138.4, 143.7, 144.8. HRMS, Found: *m*/*z* 293.0650. Calcd for $C_{15}H_{16}ClNOS$: M, 293.0641.

***S*-*p*-Nitrophenyl-*S*-phenyl-*S*-propoxythiazyne (1i):** Method B; yield 90% (oil); IR (neat film) 1348 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.00 (t, *J* = 7.2 Hz, 3H), 1.79 (sext, *J* = 7.2 Hz, 2H), 4.10 (m, 2H), 7.51—7.60 (m, 3H), 7.93—7.96 (m, 2H), 8.07—8.10 (m, 2H), 8.29—8.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 10.4, 22.9, 64.1, 124.3, 127.4, 128.1, 129.4, 132.8, 143.7, 149.5, 150.9. HRMS, Found: *m*/*z* 304.0893. Calcd for $C_{15}H_{16}N_2O_3S$: M, 304.0882.

Preparation of 1-[1,1-$^2H_2$]Porpanol: A solution of methyl propionate (4.6 ml, 57 mmol) in dry diglyme (15 ml) was added dropwise to a stirred solution of LAD (1.0 g, 24 mmol) in dry diglyme (35 ml) at 0 °C for 30 min under an argon atmosphere and the mixture was stirred for 1 h at room temperature. A solution of malonic acid (5.0 g, 48 mmol) in diglyme (15 ml) was added slowly to the stirred reaction mixture at room temperature over 30 min. The reaction mixture was distilled and the distillate of a fraction boiling at between 90.0—115.0 °C was collected. 1-[1,1-$^2H_2$]Porpanol (1.2 H, 34%) was obtained by distillation from the fraction boiling at between 94.0—98.0 °C.

Synthesis of *S*,*S*-Diphenyl-*S*-[1,1-$^2H_2$]propoxythiazyne (1c-d_2): *S*,*S*-Diphenyl-*S*-[1,1-$^2H_2$]propoxythiazyne was prepared by the method C using 1-[1,1-$^2H_2$]porpanol prepared above. The yield was 65% (deuterium content 99.5%): Mp 118.0—119.0 °C (decomp); IR (KBr disk) 1332 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.98 (t, *J* = 7.2 Hz, 3H), 1.74 (q, *J* = 7.2 Hz, 2H), 7.44—7.52 (m, 6H), 7.91—7.95 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 10.4, 22.7, 62.8 (quint), 127.1, 128.9, 131.9, 145.1. HRMS, Found: *m*/*z* 261.1157. Calcd for $C_{15}H_{15}D_2NOS$: M, 261.1156.

Acidic Hydrolysis of *S*-Methoxythiazynes 1a: A methanol solution (25 ml) of the mixture of **1a** and **6** (117 mg, **1a** : **6** = 27 : 25) was added to a stirred solution of 25 ml of aqueous H_2SO_4 (5%) at room temperature for 1 h. The reaction mixture was alkalized with aqueous sodium hydroxide. The solution was extracted with chloroform (5×20 ml) and the combined organic extracts were washed with water (2×50 ml). The organic layer was dried over anhy-

drous magnesium sulfate and concentrated under reduced pressure. The residue (112 mg) was almost pure sulfoximine **6**[4] (98%) in comparison with an authentic sample.

Hydrolysis of *S*-Methoxythiazynes 1a by CO_2: A mixture of **1a** and **6** (10 mg, **1a** : **6** = 30 : 9) was dissolved in CD_3OD/D_2O (1/1, v/v, 0.5 ml) in an NMR tube. To this, CO_2 gas was bubbled for 1 min, and then the ^1H NMR spectrum was measured.

Hydrolysis of *S*-Methoxythiazynes 1a by Silica gel: A methanol solution (25 ml) of **1a** and **6** (279 mg, **1a** : **6** = 88 : 35) in the presence of silica gel (2.0 g) was stirred at room temperature for 23 h. The silica gel was filtered off and washed with methanol. The filtrate was concentrated under reduced pressure. The residue (248 mg) was almost pure sulfoximine **6** (90%) in comparison with an authentic sample.

Hydrolysis of *S*-Methoxythiazynes 1a in MeOH: The mixture of **1a** and **6** (74 mg, **1a** : **6** = 24 : 8) was dissolved in 100 ml of methanol and stirred at 50 °C for 24 h. The reaction mixture was concentrated under reduced pressure. The residue (65 mg) was almost pure sulfoximine **6** (90%) in comparison with an authentic sample.

Thermolysis of *S*-Alkoxythiazynes 1: *S*-Alkoxythiazyne **1** (0.4 mmol) dissolved in benzene (10 ml) was heated under reflux for the period of time indicated in Table 4. The reaction mixture was concentrated under reduced pressure. The residue was chromatographed (Al_2O_3, $CHCl_3$) to give diphenyl sulfide and *N*-unsubstituted *S*,*S*-diphenylsulfilimine.[5] The products were identified by a comparison with an authentic sample.

Similarly, *S*-alkoxythiazyne **1** (0.04 mmol) was dissolved in benzene-d_6 (0.5 ml) in a sealed NMR tube. After the tube was heated at 110 °C the ^1H NMR spectra were measured in order to determine the yields of the carbonyl compounds.

Kinetics: Thermolyses of **1a** (0.05—0.07 M) were carried out in NMR tubes at the required temperature in toluene-d_8 using anisole as an internal standard. The reaction rate was determined by following the decrease in the integral intensity of the methylene proton of the propyl group. The rate constants were calculated by a least-squares method using 10—16 points accumulated during 75% completion of the reaction. When the data were plotted as $\ln(I_0/I_t)$ vs. time, where I_0 is the initial integral intensity of **1**, I_t is the integral intensity of **1** at time t, a good linear correlation was observed, suggesting that the reaction rate follows a first-order kinetics. The activation parameters were calculated by a least-squares method using three points on a plot of $\ln k$ vs. $1/T$. The Hammett ρ-value was calculated by a least-squares method using $\log k$ vs. σ.

Crystallographic Data for the *S*-Propoxythiazyne 1c: $[C_{15}H_{17}NOS]$, $M = 259.37$, orthorhombic, space group $Pmn2_1$ (No. 31), $a = 14.375(1)$, $b = 16.170(1)$, $c = 7.873(1)$ Å, $V = 698.3(1)$ Å^3, $d_{calcd} = 1.23$ g cm^{-3}, $Z = 2$, $F(000) = 276.0$, $\mu = 2.20$ cm^{-1}. A colorless block-shaped crystal having dimensions $0.13 \times 0.19 \times 0.27$ mm was mounted on a glass fiber and used for data collection on a Rikagaku AFC7R diffractometer employing graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) using the $\omega/2\theta$ scan technique. The cell dimensions were determined from the setting angles of 25 reflections ($13 < 2\theta < 27.5°$), and the total of 3209 reflections ($2\theta_{max}$ 55°) collected at 293 K were corrected for Lorentz and polarization effects. The structure was solved by direct methods. The H-atoms were introduced at calculated positions (C–H = 0.97 Å, phenyl C–H = 1.08 Å) but not refined. The final full-matrix least-squares refinement was based on F converged with $R = 0.042$ and $R_w = 0.054$ for 1299 unique reflections ($I > 3.0\sigma(I)$ and 91 parameters. All of calculations were performed on an Indy workstation using the teXsan crystallographic software package from Molecular Structure Corp. The atomic coordinates and thermal parameters have been reported elsewhere.[23]

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