CHEMISTRY LETTERS, pp. 2213-2216, 1992.

Preparation and Reactivities of S,S-Diaryl-S-aminothiazynes, $Ar_2S(NR_2)(N)$[1)]

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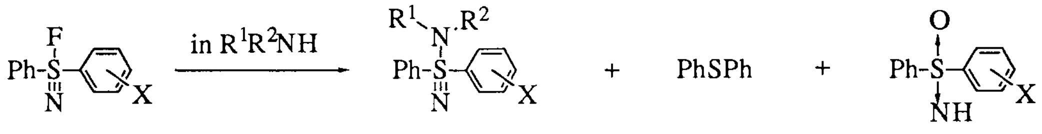
Reaction of S,S-diaryl-S-fluorothiazynes[6)] with cyclic secondary amines gave novel thiazynes, the corresponding S-aminothiazynes in good yields. Spectroscopic studies, measurement of pKa values, pyrolysis and alkylation reactions of the aminothiazynes were carried out.

Thiazynes[1)] have an unusual structure bearing an SN triple bond. However, their chemistry has been studied in the field of inorganic fluorine chemistry,[2)] but not in the organic heteroatom chemistry. Recently we reported the formation of S,S-diphenyl-S-methoxythiazyne[4)] in the alkaline hydrolysis of S,S-diphenyl-N-bromosulfilimine in $MeOH\text{-}H_2O$ and that the methoxythiazyne is a good methylating agent of thiols.[5)] Meanwhile, we prepared S,S-diaryl-S-fluorothiazynes (**1**)[6)] by the reaction of the corresponding N-bromosulfilimines with tetrabutylammonium fluoride (TBAF) in THF at 0 °C and also allowed the S-fluorothiazynes **1** to react with alkyl and aromatic primary amines to give the corresponding N-monosubstituted sulfonediimines in good yields.[6)] On the other hand, the reaction of **1** with secondary cyclic amines gave unusual S-aminothiazynes (**2**) and herein we wish to report the results.

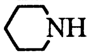
The fluorothiazynes **1** were allowed to react with various secondary amines and the results are summarized in Table 1. Though the reaction with an open chain amine, diethylamine, is very slow to give only decomposition products even under reflux conditions in diethylamine, the reaction with such cyclic amines as morpholine, pyrolidine, piperidine, and hexahydro-1H-azepine afforded the corresponding S,S-diaryl-S-aminothiazynes (**2**) in good yields. However, the reaction with morpholine at elevated temperature (100-120 °C) gave not the morpholinothiazyne (**2a**) but diphenyl sulfide in 70% yield. Unlike the thiazyne **1** the thiazynes **2** were stable under acidic conditions and thus purified by dissolving in 1% H_2SO_4 followed by treatment with charcoal, extraction under alkaline conditions, and recrystallization from acetone-hexane.



1 **2** **3** **4**

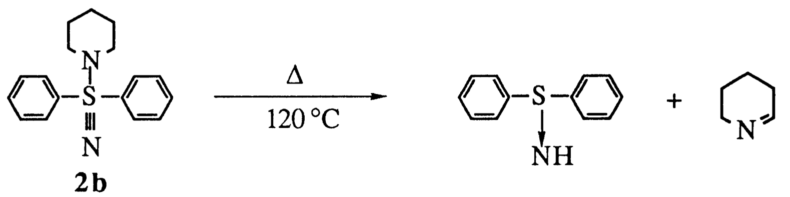
The assignment of the structure of the aminothiazyne was performed as follows. All aminothiazynes **2** gave satisfactory elemental analyses and high resolution mass spectral data. However, it is necessary to distinguish S-aminothiazynes from their isomers N-aminosulfilimines. As we reported previously,[4,6)] S,Sdiarylthiazynes show characteristic IR and ^{1}H NMR spectra. The IR spectra of the S-aminothiazynes **2** showed characteristic 3 bands at 880-900, 1065,and 1285-1298 cm^{-1}. The last band due to S≡N stretching is a little lower than that of S,S-diphenyl-S-fluorothiazyne (1361 cm^{-1})6) and S,S-diphenyl-S-alkoxythiazyne (1322-1340 cm^{-1}),4,6) but higher than that of sulfilimine type compounds (860-1000 cm^{-1}). The differences of the stretching bands of these three types of thiazynes are probably attributable to the differences of electronegativities of the atoms attached to the sulfur atom. The ^{1}H NMR spectra of **2** show splitting of the ortho-protons from meta- and para-protons in a similar manner to those of sulfones, sulfoximines, sulfonediimines and thiazynes4,6) though sulfilimine type compounds do not show such splitting. These spectral data suggests that compound **2** has a thiazyne structure.

Table 1. Preparation of S,S-Diaryl-S-aminothiazynes

Amine	X	Conditionsa)		Yields/%b)			
		Temp/°C,	Time/h	**2**(Mp/°C)		**3**	**4**
Et_2NH	H	reflux	6	0		30	20
	H	0	1.5	92	(oil)	—	—
	H	r.t.	4	88	(120)	—	—
	H	100-120	3	0		70	3
	H	r.t.	5	94	(134)	—	—
	p-Me	r.t.	12	73	(135)	—	—
	p-Cl	r.t.	14	24	(143)	—	—
	p-NO_2	r.t.	20	99	(134)	—	—
	H	0	48	52	(oil)	—	—

a) Eight equivalent amounts of amines were used. b) Isolated yields.

When S,S-diphenyl-S-piperidinothiazyne (**2b**) was heated in situ at 120 °C for 0.5 min or refluxed in benzene for 4 h, N-unsubstituted diphenylsulfilimine was obtained in 93 or 85% yield, respectively. The ^{1}H NMR spectrum of the reaction mixture showed an existence of 3,4,5,6-tetrahydropyridine in a quantitative yield and it was further identified by IR and mass spectral analyses. The order of the instability for the ring size of the aminothiazynes is 5>7>6, especially S-pyrolidinothiazyne decomposed completely at room temperature in 12 h. One of the possible mechanisms of the pyrolysis of **2** is Ei reaction involving an abstraction of α-proton by the basic thiazyne nitrogen.



2b

The aminothiazynes are basic and therefore nucleophilic. It is important to measure the basicity of the aminothiazyne to estimate their nucleophilic reactivities and to examine the character of the SN bond. The pKa values of substituted S,S-diaryl-S-piperidinothiazynes and S,S-diphenyl-S-morpholinothiazyne were determined by potentiometric titration with a Horiba pH meter model F-13 using 0.1 mol/dm^3 hydrochloric acid at 23 °C. The results are summarized in Table 2 together with some related SN compounds.

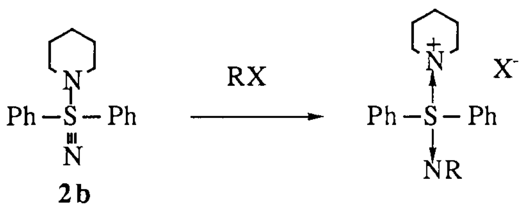
Table 2. pKa Values of S-Aryl-S-phenyl-S-aminothiazynes $Ph(XC_6H_4)S(N)(NR_2)$ at 23 °C and Related SN Compounds

X	R_2	pKa	
p-Me	$-(CH_2)_5-$	7.72	
H	$-(CH_2)_5-$	7.47	$\rho_X=-1.67$ (*vs.* σ)
p-Cl	$-(CH_2)_5-$	7.05	(r=0.999)
$p-NO_2$	$-(CH_2)_5-$	6.14	
H	$-(CH_2)_2O(CH_2)_2-$	6.43	
PhS(NH)Ar		8.56 (Ar=Ph)[7)]	ρ=-1.61
$PhS(NH)_2Ph$		3.92[7)]	
PhS(NH)(O)Ph		2.60[7)]	
MeS(NH)(O)Ar		2.73 (Ar=Ph)[8)]	ρ=-1.49

Basicities of the S-aminothiazynes **2** were found to be very large compared to S,S-diphenylsulfoximine and S,S-diphenylsulfonediimine. The protonation site must be not the amino nitrogen but the thiazyne nitrogen, because the IR spectrum of the S-aminothiazyne hydrochloride (1200, 1075, 895 cm^{-1}) shows disappearance of stretching band of the SN triple bond and is similar to the spectra of S,S-diphenylsulfonediimine hydrochloride (1200, 1080, 1030, 920 cm^{-1}) and N-alkylated thiazynes shown later. If the electronic structure of the thiazyne nitrogen is the same as that of the nitrile nitrogen, the large basicity of the thiazyne cannot be expected. The present S≡N stretching band (1290 cm^{-1}) is too low compared to that of the triple bond (1790 cm^{-1}) calculated using the same force constant as nitrile (2250 cm^{-1}) and is rather in the double bond region. Therefore the large basicity and low frequency of the SN triple bond of the aminothiazyne **2** can be attributed to polarization of the SN bond as shown in the following equation like in the case of sulfilimine.[7)]

Furthermore, Hammett ρ value for the pKa values of the p-substituted S,S-diaryl-S-aminothiazynes is also given in the Table 2 together with that for the sulfoximine and the N-unsubstituted diarylsulfilimine. Magnitude of the ρ value for the aminothiazyne is similar to that for the sulfilimine while that for the sulfoximine is small, namely sensitivity of the effect of substituents on the aminothiazynes and sulfilimines is larger than that on the sulfoximine suggesting that the SN bond of the aminothiazynes and sulfilimines is more polarizable than that of the sulfoximine.

From the results of the measurement of pKa, S-aminothiazynes **2** were found to be strong bases and nucleophiles. Treatment of **2b** with methyl iodide and benzyl chloride gave the corresponding N-methylated (**5**) and N-benzylated products (**6**) in 100% and 92% yields, respectively. The alkylated position is probably the thiazyne nitrogen, because the IR spectra of **5** and **6** resemble sulfonediimine hydrochloride, and thus the thiazyne nitrogen is nucleophilic. N-Alkylsulfonediiminium halides are also a little known compounds in the field of sulfur chemistry. Further work on these and related reactions is now under way in these laboratories.



2b

5: $R=CH_3$, $X=I$[9]
6: $R=CH_2Ph$, $X=Cl$[10]

References

1) The compounds having an SN triple bond are called thiazyl compounds[2] like thiazyl trifluoride for F_3SN, but this name is not appropriate for the compounds substituted by carbon groups. Meanwhile, the name "thiazyne" is first used by Clifford et al.[3] for Ph_2FSN as diphenylfluorothiazyne.
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4) T. Yoshimura, E. Tsukurimichi, H. Kita, H. Fujii, and C. Shimasaki, *Tetrahedron Lett.*, **30**, 6339 (1989).
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7) N. Furukawa, T. Yoshimura, T. Omata, and S. Oae, *Chem. Ind.*, **1974**, 702.
8) S. Oae, K. Harada, K. Tsujihara, and N. Furukawa, *Int. J. Sulfur Chem.*, **1972**, **A2**, 49.
9) Mp 188 °C; IR (KBr): 1215, 1065, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.7-2.2 (6H, m, CH_2), 3.20 (3H, s, Me), 3.4-3.7 (4H, m, CH_2), 7.7-8.0 (6H, m, Ph m- and p-), 8.2-8.5 (4H, m, Ph o-).
10) Mp 191 °C; IR (KBr): 1210, 1185, 1065, 915 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.5-2.1 (6H, m, piperidino CH_2), 3.2-3.6 (4H, m, piperidino CH_2), 4.57 (2H, s, benzyl CH_2), 7.26 (5H, s, benzyl Ph), 7.5-7.9 (6H, m, Ph m- and p-), 8.1-8.4 (4H, m, Ph o-).

(Received July 30, 1992)