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First Preparation and Reactions of S,S-Diaryl-S-fluorothiazynes, $Ar_2SF(N)$

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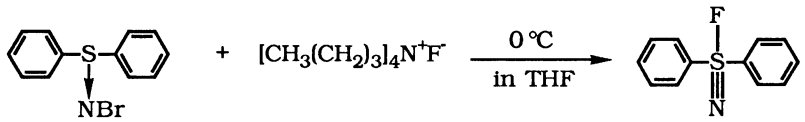
S,S-Diaryl-S-fluorothiazynes, $Ar_2SF(\equiv N)$, were prepared by the reaction of S,S-diaryl-N-bromosulfilimines with tetrabutylammonium fluoride. The thiazyne structure was assigned by the spectral data, physical properties, and is consistent with reactions with sodium alkoxides and primary amines. The thiazyne prepared previously by Clifford et al. is doubtful.

Thiazynes[1] $R\text{-}\overset{X}{\underset{\|}{S}}\text{-}R$ bearing an S≡N triple bond are little known and investigations for their structures and reactions are very interesting. Only a few examples of inorganic compounds bearing SN triple bond have been known, thiazyl trifluoride (F_3SN)[2] and thiazyl fluoride (FSN),[2] while there are few examples of organic compounds, e.g., S,S-diphenyl-S-fluorothiazyne $Ph_2SF(N)$ (**4'a**) was claimed to be prepared by A. F. Clifford et al. in 1978,[3] though it was not purified. We reported recently that the alkaline hydrolysis of S,S-diphenyl-N-bromosulfilimine (**1a**) in aqueous methanol affords S,S-diphenyl-S-methoxythiazyne,[4] $Ph_2S(OMe)(N)$ (**2a**), and that the further hydrolysis of **2a** gives S,S-diphenylsulfoximine, $Ph_2S(O)(NH)$ (**3a**), quantitatively.[4] We also reported that the methoxythiazyne **2a** is a good methylating reagent of thiols and the reaction mechanism was investigated kinetically.[5] Among these thiazynes, the S-fluorothiazyne is especially expected to be a useful reagent to prepare a variety of thiazynes and other SN compounds. Therefore, we tried to prepare the S-fluorothiazyne **4'a** by an alternative method, since the Clifford's method using F_3SN is dangerous.

N-Bromosulfilimine **1a** was allowed to react with tetrabutylammonium fluoride (TBAF) at 0 °C in dry THF in the presence of molecular sieves 4A. After completion of the reaction, the solution was diluted with excess water, extracted with chloroform and then the chloroform layer was washed with water repeatedly.



1a **4a**

Chloroform was evaporated to give a compound (**4a**) in 90% yield, which was recrystallized from benzene under cooling (mp 66 °C). The compound **4a** gave a satisfactory elemental analysis for S,S-diphenyl-S-fluorothiazyne (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%). ^{13}C NMR ($CDCl_3$, δ=126.3, 128.9, 132.8, 143.6 ppm) depicted only the phenyl group carbons. Pyrolysis of the compound **4a** at 100 °C gave quantitatively diphenyl sulfide. Similarly the mass spectrum showed only the pattern of the sulfide. The compound **4a** is hydrolyzed under both acidic (55%-H_2SO_4 in aq. MeOH) and alkaline conditions (4%-NaOH in aq. MeOH) to give S,S-diphenylsulfoximine quantitatively. ^{15}N NMR was observed at 66.1 ppm downfield from NH_3 in $CDCl_3$, though no ^{15}N-^{19}F coupling was observed which may be caused by fast exchange of fluorine atom with contaminated HF or TBAF, because addition of HF to F_3SN is known to form F_5SNH_2[6] reversibly and thus reversible addition of HF to **4a** is possible.

However the spectral data of the synthesized **4a** are completely different from the Clifford's compound **4'a**. The ^{19}F NMR of **4a** was observed at 86.6 ppm (downfield from $CFCl_3$ in $CDCl_3$) but that of **4'a** at 102.9 ppm.[3] A possible isomer, S,S-diphenyl-N-fluorosulfilimine, $Ph_2S{\rightarrow}NF$, is unlikely for the present compound **4a** because of the following reasons. The splitting of ^1H NMR of the phenyl group of **4a** (ortho: 7.85-8.00 ppm, meta and para: 7.30-7.63 ppm) is similar to such sulfone type compounds as the methoxythiazyne **2a** (ortho: 7.80-8.05 ppm, meta and para: 7.35-7.60 ppm) and S,S-diphenyl sulfone (ortho: 7.80-8.05 ppm, meta and para: 7.31-7.60 ppm) rather than sulfilimine type compounds, e.g., S,S-diphenyl-N-chlorosulfilimine (7.52 ppm)[10] and S,S-diphenylsulfilimine (7.20-7.70 ppm),[11] while the splitting of the phenyl group for **4'a** (7.15-7.95 ppm) is not clear. The IR SN stretching band of **4a** (1361 cm^{-1}) is higher than those of S,S-diphenyl-N-chlorosulfilimine (860 cm^{-1}),[10] S,S-diphenyl-N-bromosulfilimine (860 cm^{-1})[10] or S,S-diphenylsulfilimine (940 cm^{-1})[11] but close to those of **2a** (1340 cm^{-1})[4] or thiazyl trifluoride (1524 cm^{-1}),[12] though the band of **4'a** is similar (1428 cm^{-1}).[3] These spectral data suggest that our compound (**4a**) does not have a sulfilimine structure but a thiazyne $Ph_2SF(N)$. The substituted S,S-diphenyl-S-fluorothiazynes (**4a-e**) were also prepared and the results are shown in Table 1.

In order to further ascertain the structure, reactions of the S-fluorothiazyne **4a** with some nucleophiles were investigated. Reactions of **4a** with sodium alkoxides in alcohols gave S,S-diphenyl-S-alkoxythiazynes, $Ph_2S(OR^1)(N)$ (**5a**) in moderate yields (27-51%) together with sulfoximine **3a** as shown in Table 2. S,S-Diphenyl-S-methoxythiazyne (**5a-Me**) and -S-ethoxythiazyne (**5a-Et**) were identical with those obtained

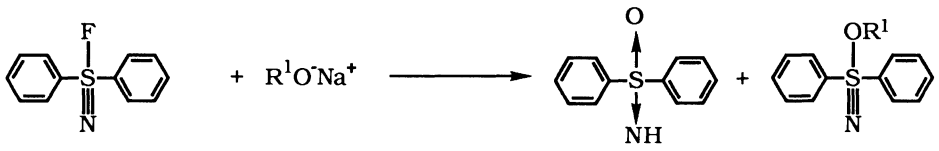
Table 1. Preparation of S,S-Diaryl-S-fluorothiazynes $XC_6H_4PhSF(N)$ (**4a-e**)

		Conditions		Yield	Mp
	X	**1** : TBAF	Time/h	%	°C
a	H	1 : 2	3	90	66.0-66.5
b	p-Cl	1 : 2	50	98	117-118
c	p-Me	1 : 2	2	99	oil
d	o-Me	1 : 2	4	90	oil
e	$p\text{-}NO_2$	1 : 2	1	99	77

previously by the alkaline hydrolysis of N-bromosulfilimine **1a** in aqueous alcohol.[4] This method is better than the previous one for the preparation of S,S-diaryl-S-alkoxythiazynes since more kinds of alkoxythiazynes can be obtained.

Furthermore, **4a** was allowed to react with primary amines as shown in Table 3. Both alkyl and aryl amines gave the corresponding sulfonediimines $Ph_2S(NR^2)(NH)$ (**6a**). In comparison with the method for preparation of diarylsulfonediimines from N-halosulfilimines,[9] the present reaction has a characteristic to give N-arylsulfonediimines. Since only a few methods are known for preparation of sulfonediimines,[7-9] S-fluorothiazynes **4** are expected to be valuable reagents. These reactions also confirm indirectly that the structure of **4** is not the N-fluorosulfilimine but is the thiazyne. Further work on these and related reactions is now under way in these laboratories.

Table 2. Reactions of S,S-Diphenyl-S-fluorothiazyne (**4a**) with Sodium Alkoxides

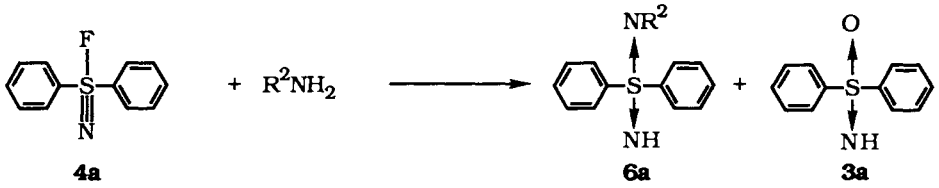


4a **3a** **5a**

R^1	Conditions				Yields/%[a]	
	[R^1ONa]/[**4a**]	Temp/°C	Time/min	Solvent	**3a**	**5a**
Me	3	r.t.	1	MeOH	24	51
Et	3	r.t.	1	EtOH	20	46
n-Pr	3	r.t.	1	n-PrOH	24	48
i-Pr	3	r.t.	1	i-PrOH	33	41
n-Bu	3	r.t.	1	n-BuOH	27	27
i-Bu	3	r.t.	1	i-BuOH	32	31

a) Since the separation of **5a** from **3a** is very difficult,[4] yields were determined by ^1H NMR integral ratio.

Table 3. Reaction of S,S-Diphenyl-S-fluorothiazynes (**4a**) with Primary Amines



4a **6a** **3a**

R^2	Conditions				Yields/%[a]	
	$[R^2NH_2]/[\mathbf{4a}]$	Temp/°C	Time/h	Solvent	**6a**	**3a**
H	excess	30	17	MeOH	23	66
$CH_3(CH_2)_2$	excess	30	16	$CH_3(CH_2)_2NH_2$	71	-
$CH_3(CH_2)_3$	2	30	14	Et_2O	79	-
Ph	excess	30	16	$PhNH_2$	54	-
m-ClC_6H_4	excess	30	13	m-$ClC_6H_4NH_2$	53	-
o-MeC_6H_4	excess	30	16	o-$MeC_6H_4NH_2$	37	-

a) Isolated yield.

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" was first used by Clifford et al.[3] for Ph_2FSN as diphenylfluorothiazyne.

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