Synthesis and Reactivity of *S*-Sulfiliminothiazynes

Masanori Ohkubo, Takayoshi Fujii, Shin Ono, Hiroyuki Morita, Toshiaki Yoshimura,* Ernst Horn,† and Soichi Sato†
Department of Chemical and Biochemical Engineering, Faculty of Engineering, Toyama University, Gofuku, Toyama 930
†*Tsukuba Advanced Research Alliance Center, Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305*

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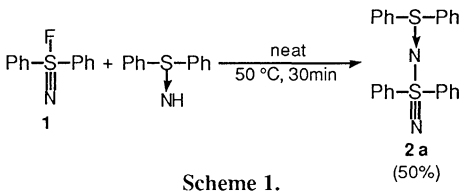
Reaction of *S,S*-diphenyl-*S*-fluorothiazyne with *N*-unsubstituted *S,S*-diphenylsulfilimine afforded the corresponding *S*-sulfiliminothiazyne. Measurement of the pKa value of *S*-sulfiliminothiazyne and its reactivity were examined. The molecular structure of the sulfonediiminosulfonium salt was determined by the X-ray crystallographic analysis.

Thiazynes[1,2] bearing an SN triple bond are rare but their structures and reactions are very interesting. Their chemistry has been studied in the field of inorganic chemistry[2] using thiazyl trifluoride and thiazyl fluoride but not in organic chemistry. Recently we reported that the treatment of *S,S*-diphenyl-*N*-bromosulfilimine with tetrabutylammonium fluoride gave *S*-fluoro-*S,S*-diphenylthiazyne (**1**) in THF at 0 °C.[3] Furthermore, **1** was allowed to react with nucleophiles such as sodium alkoxides and cyclic amines, which gave the corresponding *S*-alkoxy-*S,S*-diphenylthiazynes[3] and *S*-amino-*S,S*-diphenylthiazynes,[4] respectively. In a further extension of these studies, we prepared *S,S*-diphenyl-*S*-sulfiliminothiazyne (**2a**) by the reaction of **1** with *N*-unsubstituted *S,S*-diphenylsulfilimine. In the present paper we wish to report the preparation of *S,S*-disubstituted-*S*-sulfiliminothiazynes **2** and their reactivity. Furthermore, the crystal and molecular structure of the perchlorate salt of *S,S*-diethyl-*S*-sulfiliminothiazyne **2d** was determined by X-ray analysis.

S-Fluorothiazyne **1** was treated with a 2 equimolar amount of *N*-unsubstituted *S,S*-diphenylsulfilimine affording the corresponding *S*-sulfiliminothiazyne **2a** at 50 °C for 30 min in 50% yield (Scheme 1).



Scheme 1.

The IR band due to the S≡N bond stretching in **2a** is observed at 1260 cm^{-1}, which is lower than that of *S*-fluoro- (1361 cm^{-1}),[3] *S*-alkoxy- (1322-1340 cm^{-1})[3,5] and *S*-aminothiazynes (1285-1298 cm^{-1}).[4] The sulfilimine type S-N stretching band is also observed at 920 cm^{-1}. The pKa value of 9.37 for **2a** was measured by potentiometric titration using 0.1M hydrochloric acid at 25 °C. The basicity was found to be large compared to *S,S*-diphenylsulfilimine (8.56),[6] *S,S*-diphenylsulfonediimine (3.97),[6] and *S*-aminothiazynes (pKa=6.14-7.72).[4] Certainly the protonated site is not the sulfilimino nitrogen but the thiazyne nitrogen atom, because the hydrochloride salt of **2a** when treated with hydrochloric acid showed a disappearance of the S≡N bond stretching band. The large basicity of **2a** can be explained by the polarization of the S≡N bond as in the case of sulfilimine[6] and the resonance stabilization of the sulfonium cation.

In order to confirm the new S-N bond formation in **2a**,

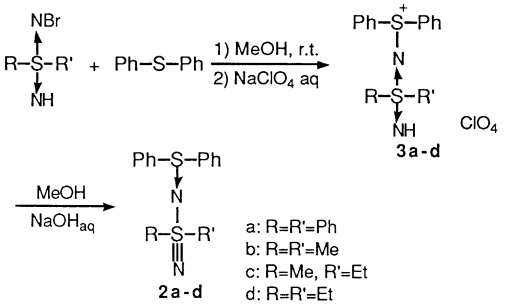
Table 1. Spectral data of *S*-sulfiliminothiazynes (**2a-d**) and sulfonediiminosulfonium salts (**3a-d**)

Compound	R	R'	Yield/%	^{1}H NMR δ/ppm	^{13}C NMR δ/ppm	IR ν/cm^{-1}	mp/°C
2a	Ph	Ph	70[a]	7.29-7.35(m,6H), 7.40-7.48(m,6H) 7.63-7.66(m,4H), 7.96-7.99(m,4H)	126.6, 127.4, 128.1, 129.5, 130.3, 131.6, 138.1, 150.1	920(ν_{SN}) 1260($\nu_{S\equiv N}$)	105.0-107.0
2b	Me	Me	99[b]	3.09(s, 3H), 7.49-7.51(m,6H) 7.68-7.71(m,4H)	52.2, 127.1, 129.7, 131.6, 138.7	935(ν_{SN}) 1247($\nu_{S\equiv N}$)	oil
2c	Me	Et	98[b]	1.26(t, *J*=7.2Hz,6H), 3.04(s,3H) 3.14(q, *J*=7.2Hz,4H), 7.47-7.50(m,6H) 7.67-7.72(m,4H)	6.6, 49.7, 56.7, 126.8, 127.4, 129.6, 129.7, 131.4, 131.7, 139.0, 139.2	925(ν_{SN}) 1258($\nu_{S\equiv N}$)	oil
2d	Et	Et	44[b]	1.25(t, *J*=7.6Hz,6H), 3.09(q, *J*=7.6Hz,4H) 7.46-7.50(m,6H), 7.69-7.73(m,4H)	6.4, 54.1, 127.2, 129.7, 131.6, 139.2	943(ν_{SN}) 1254($\nu_{S\equiv N}$)	oil
3a	Ph	Ph	42[a]	7.52-7.63(m,12H), 7.80-7.82(m,4H) 8.06-8.08(m,4H)	127.4, 127.7, 129.9, 130.6, 133.2, 133.6, 134.3, 138.1	950(ν_{SN})	144.5-146.0
3b	Me	Me	52[a]	3.53(s,3H), 7.59-7.66(m,6H) 7.78-7.81(m,4H)	46.6, 127.6, 130.7, 133.6, 134.4	960(ν_{SN})	146.0-147.0
3c	Me	Et	73[a]	1.39(t, *J*=7.6Hz,3H), 3.45(s,3H) 3.63(q, *J*=7.6Hz,2H), 7.56-7.62(m,6H) 7.77-7.80(m,4H)	7.3, 43.3, 53.3, 127.4, 127.7, 130.6, 133.3, 133.5, 134.7, 134.9	950(ν_{SN})	95.0-97.0
3d	Et	Et	81[a]	1.37(t, *J*=7.6Hz,6H), 3.52-3.65(m,4H) 7.57-7.7.64(m,6H), 7.77-7.82(m,4H)	6.7, 50.7, 127.5, 130.6, 133.4, 135.2	970(ν_{SN})	117.5-119.0

[a] Isolated yield. [b] Purity was determined by ^{1}H NMR analysis.

alkaline hydrolysis of the *S*-sulfiliminothiazyne was carried out in MeOH-H_2O under reflux conditions affording the corresponding *S,S*-diphenylsulfonediimine and diphenyl sulfoxide in 83 and 80% yields, respectively. The formation of the sulfonediimine suggests the structure of **2a**. This reaction shows that the sulfiliminyl sulfur is more subject to nucleophilic attack than the thiazyl sulfur of **2a**. *S*-Aryl-*S*-methyl-*N*-tosylsulfilimines are known to undergo alkaline hydrolysis in methanol at room temperature.[7] On the contrary, *S,S*-diphenyl-*N*-tosylsulfilimine was not hydrolyzed with KOH even under reflux condition. Meanwhile, diphenyl-(*S',S'*-diphenylsulfilimino)sulfonium salt is known to be hydrolyzed in methanol at 70 °C.[8] On the basis of these results, the character of the SN bond of **2a** is considered to be similar to that of sulfiliminosulfonium salt.

The information that the alkaline hydrolysis of **2a** gave the sulfonediimine inspired us to design the synthesis of *S*-sulfiliminothiazynes using sulfonediimines as starting materials.



Scheme 2.

Reaction of *S,S*-diphenyl-*N*-bromosulfonediimine[9] with diphenyl sulfide in methanol at room temperature for 24 h afforded the corresponding sulfonediiminosulfonium salt **3a** in 42% yield which is further treated with aqueous sodium hydroxide to give the *S*-sulfiliminothiazyne **2a** in 70% yield (Scheme 2). *S,S*-Dialkyl-*N*-bromosulfonediimines were also treated in a similar manner to the above to afford the corresponding *S*-sulfiliminothiazynes **2b-d** (Table 1).[11] Interestingly, this method can be applied to the *S,S*-dialkyl-*S*-sulfiliminothiazynes, because synthesis of the latter from the corresponding *S*-fluorothiazyne is very difficult since the alkyl type *S*-fluorothiazyne is not available. The *S,S*-Dialkyl-*S*-sulfiliminothiazynes **2b-d** were more sensitive to water and thermally less stable than **2a** and could not be crystallized. Therefore, X-ray crystallographic analysis was carried out using **3d** (Figure 1).[12] The molecular structure of the sulfonium salt **3d** was similar to that of sulfonediimine.[13] The S(2)-N(2) bond length (1.510Å) is almost the same as that of sulfonediimine (1.53Å).[13] The geometric configuration about S(2) in **3d** is a slightly distorted tetrahedral structure with two S-N bonds and two S-C bonds. Interestingly, the configuration of S(1) in **3d** bears a tetrahedral geometry similar to that of sulfonium salt[14] with a C-S-C bond angle of *ca* 105°, being indicative of the existence of plus charge on the S(1) atom.

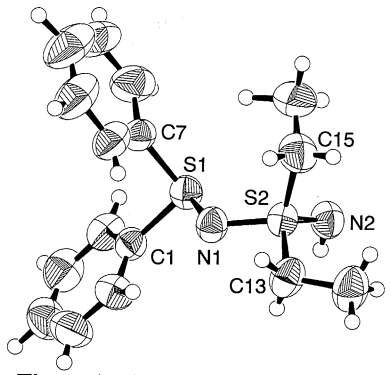


Figure 1. The ORTEP drawing of **3d**.

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References and Notes

1 A. F. Clifford, J. L. Howell, and D. L. Wooton, *J. Fluorine Chem.*, **11**, 433 (1978).
2 O. Glemser and R. Mews, *Angew. Chem.*, **92**, 904 (1980).
3 T. Yoshimura, H. Kita, K. Takeuchi, E. Takata, H. Hasegawa, C. Shimasaki, and E. Tsukurimichi, *Chem. Lett.*, **1992**, 1433.
4 T. Yoshimura, E. Takata, T. Miyake, C. Shimasaki, K. Hasegawa, and E. Tsukurimichi, *Chem. Lett.*, **1992**, 2213.
5 T. Yoshimura, E. Tsukurimichi, H. Kita, H. Fujii, and C. Shimasaki, *Tetrahedron Lett.*, **30**, 6339 (1989).
6 N. Furukawa, T. Yoshimura, T. Omata, and S. Oae, *Chem. Ind. (London)*, **1974**, 702.
7 J. Day and D. J. Cram, *J. Am. Chem. Soc.*, **87**, 4398 (1965).
8 T. Yoshimura, N. Furukawa, T. Akasaka, and S. Oae, *Tetrahedron*, **33**, 1061 (1977).
9 The sulfonediimine was prepared according to the known method[10] and *S,S*-diphenyl-*N*-bromosulfonediimine was prepared by treatment of the corresponding sulfonediimine with NBS.
10 N. Furukawa, K. Akutagawa, T. Yoshimura, T. Akasaka, and S. Oae, *Synthesis*, **1979**, 289.
11 Elemental analysis of **2a** and **3a-d**: **2a**: Found: C,71.60; H,5.07; N,7.06%. Calcd for $C_{24}H_{20}N_2S_2$: C,71.96; H,5.03; N,6.99%: **3a**: Found: C,57.50; H,4.19; N,5.64%. Calcd for $C_{24}H_{21}ClN_2O_4S_2$: C,57.53; H,4.22; N,5.59%: **3b**: Found: C,44.42; H,4.36; N,7.24%. Calcd for $C_{14}H_{17}ClN_2O_4S_2$: C,44.62; H,4.55; N,7.43%: **3c**: Found: C,45.91; H,4.87; N,7.12%. Calcd for $C_{15}H_{19}ClN_2O_4S_2$: C,46.09; H,4.90; N,7.17%: **3d**: Found: C,47.29; H,5.18; N,6.90%. Calcd for $C_{16}H_{21}ClN_2O_4S_2$: C,47.46; H,5.23; N,6.92%. FAB mass spectrum of **2b-d**: **2b**: m/e 277 $[MH]^+$: **2c**: m/e 291 $[MH]^+$: **2d**: m/e 305 $[MH]^+$.
12 Crystal data for **3d**: $C_{16}H_{21}ClN_2S_2O_4$, M=404.93, monoclinic, $P2_1/n$, a=9.876(1), b=12.214(1), c=16.575(2)Å, β=103.04(1)°, V=1947.8(3)Å^3, z=4, D_{calc}=1.381 g/cm^3, μ(MoKα)=4.33 cm^{-1}, R=0.048 (Rw=0.044), unique reflections=4935. Selected bond lengths (Å) and angles (deg) : S(1)-N(1), 1.638(3); S(1)-C(1), 1.790(4); S(1)-C(7), 1.782(4); S(2)-N(1), 1.599(3); S(2)-N(2), 1.510(4); S(2)-C(13), 1.797(4); S(2)-C(15), 1.773(5); N(1)-S(1)-C(1), 102.5(2); N(1)-S(1)-C(7), 103.5(2); C(1)-S(1)-C(7), 100.2(2); N(1)-S(2)-N(2), 122.8(2); N(1)-S(2)-C(13), 96.3(2); N(1)-S(2)-C(15), 109.3(2); N(2)-S(2)-C(13), 117.8(2); N(2)-S(2)-C(15), 104.3(2); C(13)-S(2)-C(15), 105.1(2); S(1)-N(1)-S(2), 116.0(2)
13 N. S. Webb and R. A. Gloss, *Tetrahedron Lett.*, **1967**, 1043.
14 D. E. Zuccaro and J. D. McCullough, *Z. Kristalligr.*, **112**, 401 (1959).