

Synthesis and Reactivity of *S*-Sulfiliminothiazynes

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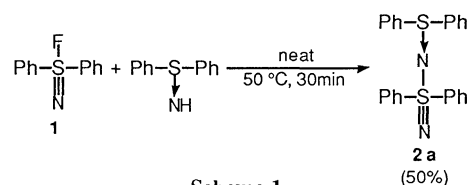
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Reaction of *S,S*-diphenyl-*S*-fluorothiazynyl with *N*-unsubstituted *S,S*-diphenylsulfilimine afforded the corresponding *S*-sulfiliminothiazynyl. Measurement of the p*K*_a value of *S*-sulfiliminothiazynyl and its reactivity were examined. The molecular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

Thiazynes^{1,2} bearing an S≡N triple bond are rare but their structures and reactions are very interesting. Their chemistry has been studied in the field of inorganic chemistry² 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*-diphenylthiazynyl (**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*-diphenylthiazynes³ and *S*-amino-*S,S*-diphenylthiazynes,⁴ respectively. In a further extension of these studies, we prepared *S,S*-diphenyl-*S*-sulfiliminothiazynyl (**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*-sulfiliminothiazynyl **2d** was determined by X-ray analysis.

S-Fluorothiazynyl **1** was treated with a 2 equiv amount of *N*-unsubstituted *S,S*-diphenylsulfilimine affording the

corresponding *S*-sulfiliminothiazynyl **2a** at 50 °C for 30 min in 50% yield (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 p*K*_a 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 (p*K*_a=6.14-7.72).⁴ Certainly the protonated site is not the sulfilimino nitrogen but the thiazynyl 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 sulfilimine⁶ and the resonance stabilization of the sulfonium cation.

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

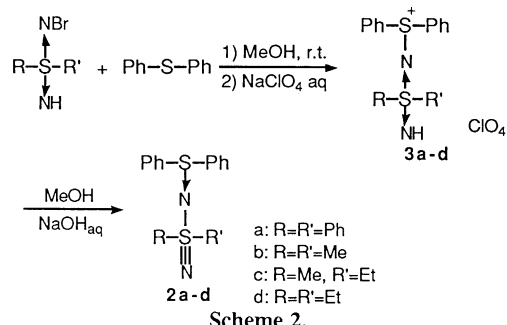
Table 1. Spectral data of *S*-sulfiliminothiazynes (**2a-d**) and sulfonediiminosulfonium salts (**3a-d**)

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(ν _{S≡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(ν _{S≡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(ν _{S≡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(ν _{S≡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) 7.57-7.74(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 ¹H NMR analysis.

alkaline hydrolysis of the *S*-sulfiliminothiazine was carried out in MeOH-H₂O 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 sulfiliminy 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'*-diphenyl-sulfilimino)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*-sulfiliminothiazines using sulfonediimines as starting materials.



Reaction of *S,S*-diphenyl-*N*-bromosulfonediimine⁹ 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*-sulfiliminothiazine **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*-sulfiliminothiazines **2b-d** (Table 1).¹¹ Interestingly, this method can be applied to the *S,S*-dialkyl-*S*-sulfiliminothiazines, because synthesis of the latter from the corresponding *S*-fluorothiazine is very difficult since the alkyl type *S*-fluorothiazine is not available. The *S,S*-Dialkyl-*S*-sulfiliminothiazines **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 (1.510 Å) is almost the same as that of sulfonediimine (1.53 Å).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 salt¹⁴ with a C-S-C bond angle of *ca* 105°, being indicative of the existence of plus charge on the S(1) atom.

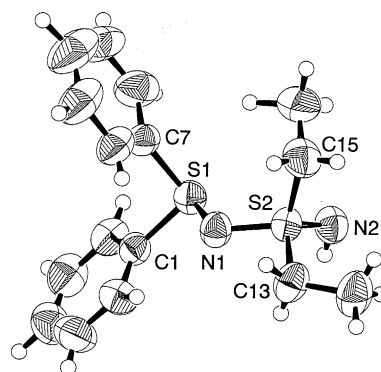


Figure 1. The ORTEP drawing of **3d**.

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References and Notes

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- The sulfonediimine was prepared according to the known method¹⁰ and *S,S*-diphenyl-*N*-bromosulfonediimine was prepared by treatment of the corresponding sulfonediimine with NBS.
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- Elemental analysis of **2a** and **3a-d**: **2a**: Found: C, 71.60; H, 5.07; N, 7.06%. Calcd for C₂₄H₂₀N₂S₂: C, 71.96; H, 5.03; N, 6.99%. **3a**: Found: C, 57.50; H, 4.19; N, 5.64%. Calcd for C₂₄H₂₁ClN₂O₄S₂: C, 57.53; H, 4.22; N, 5.59%. **3b**: Found: C, 44.42; H, 4.36; N, 7.24%. Calcd for C₁₄H₁₇ClN₂O₄S₂: C, 44.62; H, 4.55; N, 7.43%. **3c**: Found: C, 45.91; H, 4.87; N, 7.12%. Calcd for C₁₅H₁₉ClN₂O₄S₂: C, 46.09; H, 4.90; N, 7.17%. **3d**: Found: C, 47.29; H, 5.18; N, 6.90%. Calcd for C₁₆H₂₁ClN₂O₄S₂: 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]⁺.
- Crystal data for **3d**: C₁₆H₂₁ClN₂S₂O₄, M=404.93, monoclinic, P2₁/n, a=9.876(1), b=12.214(1), c=16.575(2) Å, β=103.04(1)°, V=1947.8(3) Å³, z=4, D_{calc}=1.381 g/cm³, 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).
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