3802 *J. Org. Chem.* **1997,** *62,* 3802−3803

First Preparation and X-ray Crystallographic Structure Determination of *S,S,S*-Triphenylthiazyne

Toshiaki Yoshimura,* Kohki Hamada,
Masahiro Imado, Kouki Hamata, Kazumi Tomoda,
Takayoshi Fujii, Hiroyuki Morita,
Choichiro Shimasaki, Shin Ono, Eiichi Tsukurimichi,
Naomichi Furukawa,[†] and Takeshi Kimura[†]

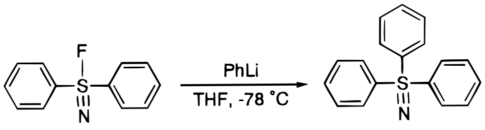
Department of Chemical and Biochemical Engineering,
Faculty of Engineering, Toyama University,
Gofuku, Toyama 930, Japan, and Department of Chemistry,
University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Received March 3, 1997

Formation of thiazyl fluoride ($FS{\equiv}N$) and thiazyl trifluoride ($F_3S{\equiv}N$) bearing an SN triple bond was first suggested and their chemistry developed by Glemser et al.[1] Despite a long history of this class of compounds in fluorine and inorganic chemistry, they had remained unrecognized in the field of organic chemistry.[2] The only example of an organic thiazyne was *S,S*-diphenyl-*S*-fluorothiazyne, which was first reported and named "thiazyne" by Clifford et al.,[2] although it was not isolated in pure form. Recently, we prepared *S,S*-diphenyl-*S*-fluorothiazyne (**1**) in pure crystalline form from *N*-bromo-*S,S*-diphenylsulfilimine and further reported the formation of *S*-alkoxy-*S,S*-diphenylthiazynes and *S*-amino-*S,S*-diphenylthiazynes from the reaction of **1**.[3] However, the spectral data of the *S*-fluorothiazyne **1** were much different from those reported by Clifford et al.[2] One possible explanation for this discrepancy is that these compounds might be their isomers, *N*-substituted sulfilimines, and our assignments of their characteristic IR bands at 1280−1360 cm^{-1} as $\nu_{S{\equiv}N}$ were tentative.[3] Therefore, more definitive evidence for the structure assignment has been required. Every thiazyne so far prepared has at least one electronegative atom such as fluorine, oxygen, and nitrogen on the sulfur atom.[1−4] Since the electronegative atom on the sulfur atom is considered to stabilize the SN multiple bond, a thiazyne bearing three carbon ligands, *S,S,S*-triphenylthiazyne (**2**), is an interesting target and will show three equivalent phenyl groups on the NMR spectra to distinguish it from the structure of *N*-phenylsulfilimine. Here, we report the first preparation and X-ray crystallographic structure determination of a new thiazyne **2** having three carbon ligands.

The reaction of *S*-fluorothiazyne **1** with 1.1 equimolar amount of phenyllithium in anhydrous THF under Ar atmosphere at −78 °C gave a new thiazyne **2** (Scheme 1). The compound **2** was isolated by silica gel column chromatography and recrystallized from CH_2Cl_2−hexane in 43% yield.[5] ^1H and ^{13}C NMR, IR, and mass spectral data and elemental analysis were consistent with the structure of hydrated *S,S,S*-triphenylthiazyne (**2**) ($Ph_3S{\equiv}N{\cdot}H_2O$), and elemental analysis of the dehydrated product by heating at 80 °C (10^{-2} Torr) also gave satisfactory results. ^1H and ^{13}C NMR spectra of **2** showed the three equivalent phenyl groups. Furthermore, the IR absorption of **2** due to the SN stretching band is present at 1267 cm^{-1}, which is higher than that of *S,S*-diphenylsulfilimine (ν_{SN}, 940 cm^{-1})[6] and that of *S,S*-diphenylsulfoximine ($\nu_{OSN,}$ 1217 and 965 cm^{-1}),[7] clearly suggesting that the SN bond of the thiazyne **2** has a higher bond order than both sulfilimines and sulfoximines. The wavenumber 1267 cm^{-1} is lower than that of any other type of thiazynes, *S*-alkoxy-*S,S*-diphenylthiazynes (1322−1340 cm^{-1}),[3c] *S*-amino-*S,S*-diphenylthiazynes (1285−1300 cm^{-1}),[3b] *S,S*-diphenyl-*S*-fluorothiazyne (1361 cm^{-1}),[3a] or thiazyl trifluoride (1515 cm^{-1}),[1c] which is considered to be due mainly to the effect of the lower electronegativity of the carbon ligand of **2**.

Scheme 1



1 **2**

The crystal structure of the new thiazyne **2** was determined by X-ray crystallographic analysis (Figure 1).[8] The X-ray analysis clearly reveals that the configuration around the sulfur atom in **2** is a slightly distorted tetrahedral structure with one SN bond and three SC bonds. The bond length of S1−N1 is 1.462(3)°, which is very close to that of thiazyl trifluoride (1.416 Å)[9] determined by microwave spectroscopy and is shorter than that of *S,S*-diphenyl-*N*-tosylsulfilimine (1.628 Å, X-ray),[10] *S,S*-dimethylsulfoximine (1.521 Å, electron diffraction),[11] and *S,S*-dimethylsulfonediimine(1.533 Å, electron diffraction).[12]

The thiazyne **2** is thermally much more stable than other organic thiazynes hitherto prepared and is not hydrolyzed under either acidic or alkaline conditions,

---

[†] University of Tsukuba.

(1) (a) Glemser, O.; Schröder, H. *Allg. Chem.* **1955**, *279*, 28. (b) Glemer, O.; Richert, H.; Anorg, Z. *Allg. Chem.* **1961**, *307*, 313. (c) Richert, H.; Glemser, O. *Allg. Chem.* **1961**, *307*, 328. (d) Glemser, O.; Meyer, H.; Haas, A. *Chem. Ber.* **1964**, *97*, 1704. (d) Glemser, O.; Mews, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 883 and references therein.

(2) Clifford, A. F.; Howell, J. L.; Wooton, D. L. *J. Fluorine Chem.* **1978**, *11*, 433.

(3) (a) Yoshimura, T.; Kita, H.; Takeuchi, K.; Takata, E.; Hasegawa, K.; Shimasaki, C.; Tsukurimichi, E. *Chem. Lett.* **1992**, 1433. (b) Yoshimura, T.; Takata, E.; Miyake, T.; Shimasaki, C.; Hasegawa, K.; Tsukurimichi, E. *Chem. Lett.* **1992**, 2213. (c) Alkoxythiazyne was prepared from *S,S*-diphenyl-*N*-halosulfilimine: Yoshimura, T.; Tsukurimichi, E.; Kita, H.; Fujii, H.; Shimasaki, C. *Tetrahedron Lett.* **1989**, *30*, 6339.

(4) (a) Shaaz, L. J.; Andes, B. A.; Carsky, P.; Zahradnik, R. *Inorg. Chem.* **1984**, *23*, 2428. (b) Beach, D. B.; Jolly, W,; Mews, R.; Waterfeld, A. *Inorg. Chem.* **1984**, *23*, 4080.

(5) The side products were mainly biphenyl (24%) and diphenyl sulfide (13%), which may be formed by ligand-coupling reaction. A complex reaction mixture including some unidentified products was also obtained. **2**: mp 231−232 °C, 181−182 °C (monohydrate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.48−7.52 (m, 6H), 7.54−7.58 (m, 3H), 7.74−7.77 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.2, 129.0, 132.0, 145.8; IR (KBr) 1267 cm^{-1} (SN); MS *m/z* 277 (M^+). Anal. Calcd for $C_{18}H_{15}N_1S_1$: C, 77.94; H, 5.45; N, 5.05. Found: C, 77.70; H, 5.42; N, 5.03. Monohydrate. Anal. Calcd for $C_{18}H_{17}N_1O_1S_1$: C, 73.19; H, 5.80; N, 4.74. Found: C, 73.34; H, 5.69; N, 4.93.

(6) Yoshimura, T.; Omata, T,; Furukawa, N.; Oae, S. *J. Org. Chem.* **1976**, *41*, 1728.

(7) Oae, S.; Harada, K.; Tsujihara, K.; Furukawa, N. *Int. J. Sulfur Chem. Part A* **1972**, *2*, 49.

(8) The crystal data for **2**: $C_{18}H_{15}N_1S_1{\cdot}H_2O$, monoclinic, $P2_1/n$, a = 9.213(2) Å, b = 16.486(4) Å, c = 11.098(2) Å, β = 111.64(1)°, V = 1566.8 Å^3, z = 4, ρ = 1.25 g/cm^3, μ(Mo Kα) = 1.9 cm^{-1}, R = 0.057 (R_w = 0.056), 1911 with $F_o^2 > 3.0\sigma(F_o^2)$. The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(9) The S−N bond length of thiazyl trifluoride was determined by microwave spectroscopy. Kirchhoff, W. H.; Wilson, E. B., Jr. *J. Am.Chem. Soc.* **1962**, *84*, 334.

(10) Kalman, A.; Duffin, B.; Kucsman, A. *Acta. Crystallogr., Sect. B* **1971**, *27*, 586.

(11) Oberhammer, H.; Zeil, W. *Z. Naturforsch., A* **1970**, *25*, 845.

(12) Oberhammer, H.; Zeil, W. *Z. Naturforsch., A* **1969**, *24*, 1612.

S0022-3263(97)00391-5 CCC: $14.00

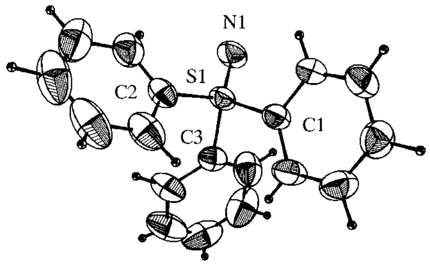
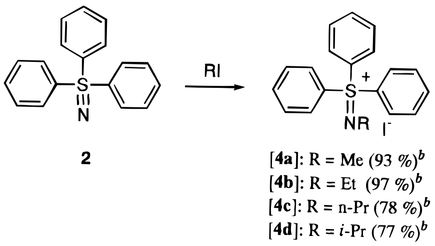


Figure 1. Crystal structure of **2**. For clarity, the monohydrate is omitted. Selected bond distances (Å) and bond angles (deg): S1−N1, 1.462(3); S1−C1, 1.810(4); S1−C2, 1.799(4); S1−C3, 1.812(3); N1−S1−C1, 116.6(2); N1−S1−C2, 116.0(2); N1−S1−C3, 115.6(2); C1−S1−C2, 101.7(2), C1−S1−C3, 101.4(1); C2−S2−C3, 103.3(2).

though the corresponding *S*-fluoro- and *S*-alkoxy-thiazynes are readily hydrolyzed to *S*,*S*-diphenylsulfoximine under acidic conditions. The thiazyne **2** is considerably basic. Treatment of the compound **2** with hydrochloric acid afforded quantitatively the corresponding *S*,*S*,*S*-triphenyliminosulfonium chloride (**3**),[13] which is also a new type of compound and is of interest in relation to the isoelectronic triphenyloxosulfonium salt.[14] Measurement of the basicity of **2** is important for estimating its nucleophilicity and the character of the SN bond. The pK_a value of the conjugate acid of **2** was determined by potentiometric titration using 0.1 M hydrochloric acid at 25 °C to be 7.44. This value is very close to that of *S*,*S*-diphenyl-*S*-piperidinothiazyne (7.44)[3b] and is large compared to that of *S*,*S*-diphenylsulfoximine (2.60)[7,15] and *S*,*S*-diphenylsulfonediimine (3.92).[15] The high basicity of **2** is attributable to polarization of the SN bond, which is similar to the case of sulfilimines.[15]

The electron-rich nature of the nitrogen atom in thiazyne **2** is manifest not only in the basicity but also in the nucleophilicity at the nitrogen. Treatment of **2** with several alkyl halides such as methyl iodide, ethyl iodide, and isopropyl iodide gave the corresponding *N*-alkylated compounds **4** in good yields (Scheme 2).[16] *N*-Alkyliminosulfonium halides are also first examples in the field of organosulfur chemistry. Further investigations are now in progress in this area.

Scheme 2[a]



[a] Substrate **2** (0.5 mmol), electrophiles (3 mmol), benzene (10 mL). [b] Isolated yield.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research (No. 04804035) from the Ministry of Education, Science and Culture.

Supporting Information Available: Experimental procedure and spectral data, including copies of ^{1}H NMR and ^{13}C NMR spectra, for compounds **2**−**4**; structure determination summaries and tables of X-ray structure data for **2** (27 pages).

JO9703919

---

(13) Experimental data: mp 219−222 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 (t, *J* = 7.6 Hz, 6H), 7.83 (t, *J* = 7.6 Hz, 3H), 7.96 (d, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 128.7, 130.5, 134.2, 135.6; IR (KBr) 2950 (NH), 1077 cm^{-1} (SN). Anal. Calcd for $C_{18}H_{16}Cl_1N_1S_1$: C, 68.89; H, 5.14; N, 4.46. Found: C, 68.67; H, 5.02; N, 4.39.

(14) Mori, M.; Takeuchi, H.; Minato, H.; Kobayashi, M.; Yoshida, M.; Matsuyama, H.; Kamigata, N. *Phosphorus, Sulfur, Silicon* **1990**, *47*, 157.

(15) Furukawa, N.; Yoshimura, T.; Omata, T.; Oae, S. *Chem. Ind.* **1972**, *A2*, 1972.

(16) **4a**: mp 222−223 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.99 (s, 3H), 7.85−7.95 (m, 9H), 8.03−8.06 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 31.7, 129.0, 129.3, 131.5, 136.5; IR (KBr) 1197 cm^{-1} (SN). Anal. Calcd for $C_{19}H_{18}I_1N_1S_1$: C, 54.42; H, 4.33; N, 3.34. Found: C, 54.38; H, 4.32; N, 3.38. **4b**: mp 197−198 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.34 (t, *J* = 7.2 Hz, 3H), 3.17 (q, *J* = 7.2 Hz, 2H), 7.84−7.94 (m, 9H), 8.05−8.07 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 17.4, 40.8, 129.0, 129.7, 131.5, 136.5; IR (KBr) 1172 cm^{-1} (SN). Anal. Calcd for $C_{20}H_{20}I_1N_1S_1$: C, 55.43; H, 4.65; N, 3.23. Found: C, 55.33; H, 4.52; N, 3.09. **4c**: mp 196−197 °C; ^{1}H NMR(400 MHz, CDCl$_3$) δ 0.99 (t, *J* = 7.2 Hz, 3H), 1.74 (sext, *J* = 7.2 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H), 7.84−7.94 (m, 9H), 8.05−8.07 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 11.6, 25.0, 47.3, 129.0, 129.7, 131.4, 136.5; IR (KBr) 1166 cm^{-1} (SN). Anal. Calcd for $C_{21}H_{22}I_1N_1S_1$: C, 56.38; H, 4.96; N, 3.13. Found: C, 56.34; H, 4.82; N, 3.00. **4d**: mp 211−212 °C ^{1}H NMR(400 MHz, CDCl$_3$) δ 1.21 (d, *J* = 6.4 Hz, 6H), 3.51 (sept, *J* = 6.4 Hz, 1H), 7.84−7.95 (m, 9H), 8.04−8.06 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 25.6, 48.9, 129.0, 130.9, 131.4, 136.4; IR (KBr) 1168 cm^{-1} (SN). Anal. Calcd for $C_{21}H_{22}I_1N_1S_1$: C, 56.38; H, 4.96; N, 3.13. Found: C, 56.35; H, 4.95; N, 3.02.