Preparation and Reactivity of *N*-Substituted *S,S,S*-Triphenyliminosulfonium Salts

Toshiaki Yoshimura,* Takayoshi Fujii,* Kouki Hamata, Masahiro Imado, Hiroyuki Morita, Shin Ono, and Ernst Horn†
Department of System Engineering of Materials and Life Science, Faculty of Engineering, Toyama University, Gofuku, Toyama 930-8555
†*Tsukuba Advanced Research Alliance Center, Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571*

(Received June 23, 1998; CL-980471)

N-Substituted *S,S,S*-triphenyliminosulfonium salts were prepared by the reaction of *S,S,S*-triphenylthiazyne with several electrophiles. The molecular structure of *N*-methyl-*S,S,S*-triphenyliminosulfonium perchlorate was determined by the X-ray crystallographic analysis. Furthermore, their reactivities were investigated.

Heteroatom-substituted sulfonium salts and sulfoxonium salts are interesting compounds because of their anomalous reactivity.[1] Iminosulfonium salts belong to the isoelectronic compounds of oxosulfonium salts[1,2] but only a few have been reported to date.[3] Mews et al. have reported that the reaction of *S,S,S*-trifluorothiazyne with $(ROSO)^+AsF_6^-$ (R = Me, Et, ^{i}Pr) as a powerful alkylating reagent leads to the corresponding *N*-alkylated iminosulfonium salts ($RNSF_3^+AsF_6^-$).[3b] Recently, we prepared *S,S,S*-triphenylthiazyne (**1**) bearing an SN triple bond and found that its nitrogen atom has a nucleophilic character.[4] These results prompted us to investigate the preparation and reactivity of various *N*-substituted iminosulfonium salts **2** bearing three carbon ligands. Here we describe the preparation and crystal structure of a new type of iminosulfonium salts **2** together with their reactivities.

N-Substituted *S,S,S*-triphenyliminosulfonium salts **2** were prepared in good yields by the reaction of thiazyne **1** with several electrophiles (Table 1). *N*-Tosyliminosulfonium chloride, *N*-acyliminosulfonium acetate, and *N*-benzoyliminosulfonium benzoate are very hydroscopic, and were therefore isolated by converting them into the corresponding perchlorates **2f**, **2h**, and **2i**. The characterizations of the compounds **2** were achieved with spectroscopic data such as ^{1}H-, ^{13}C-NMR, IR, and FAB mass as well as elemental analyses.[5] These data are consistent with the structure of **2**.

The crystal structure of **2a'**, which is perchlorate salt of **2a**, was determined by X-ray crystallographic analysis (Figure 1).[6] The X-ray analysis clearly reveals that the configuration around the sulfur atom in **2a'** is a slightly distorted tetrahedral structure with one SN bond and three SC bonds. The bond length of S1-N1 is 1.514(3) Å which is significantly longer than that of triphenylthiazyne **1** (1.462(3) Å)[4] and very close to those of *S,S*-dimethylsulfonediimine (1.533(2) Å, electron diffraction)[7] and *S,S*-dimethylsulfoximine (1.521(3) Å, electron diffraction)[8]. This suggests that the double bond character of the S-N bond of **2a'** is similar to that of sulfonediimines and sulfoximines.

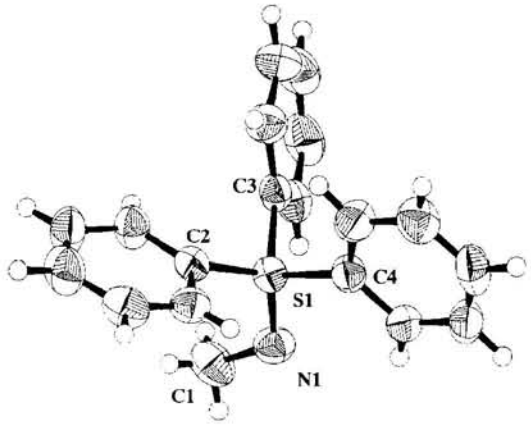
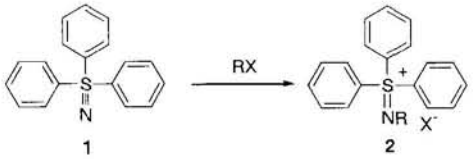


Figure 1. An ORTEP plot (50% probability ellipsoids) of the molecular structure of **2a'**. For clarity, the perchlorate anion is omitted. Selected bond distances (Å) and bond angles (deg): S1-N1, 1.514(3); S1-C2, 1.776(3); S1-C3, 1.785(3); S1-C4, 1.768(3); N1-C1, 1.478(5); N1-S1-C2, 116.3(2); N1-S1-C3, 115.3(2); N1-S1-C4, 106.1(2); C2-S1-C3, 105.6(1), C2-S1-C4, 107.0(2); C3-S1-C4, 105.8(1); S1-N1-C1, 118.6(3).

Table 1. Reaction of **1** with several electrophiles[a]



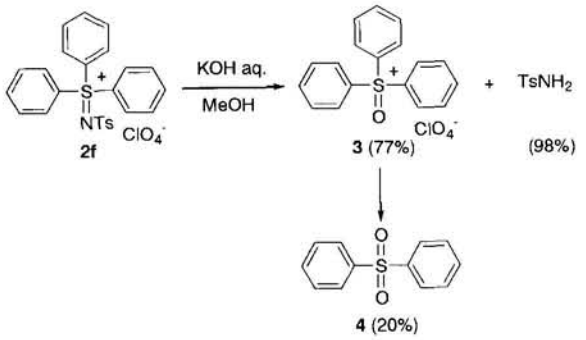
1 2

2	R	Electrophile	X	Temp (°C)	Time (h)	Yield of **2** (%)[b]
a	Me	MeI	I	50	6	93[c]
b	Et	EtI	I	50	24	97[c]
c	^{n}Pr	^{n}PrI	I	reflux	10	78[c]
d	^{i}Pr	^{i}PrI	I	reflux	36	77[c]
e	Bn	BnBr	Br	reflux	15	64[c]
f	Ts	TsCl/$NaClO_4$	ClO_4	rt	1	89[d]
g	NO_2	NO_2BF_4	BF_4	rt	1	66[d]
h	Ac	Ac_2O/$NaClO_4$	ClO_4	rt	1	98[d]
i	Bz	Bz_2O/$NaClO_4$	ClO_4	rt	1	82[d]

[a] substrate (1 mmol), electrophile (3 mmol), solvent (10 ml). [b] Isolated yield. [c] Benzene. [d] CH_3CN.

The reactivities of the iminosulfonium salts of **2** in acidic and alkaline conditions are expected to be influenced by the substituent on the terminal nitrogen atom. The *N*-alkylated iminosulfonium salts are not hydrolyzed under either acidic or alkaline conditions at room temperature. Whereas, the iminosulfonium salts **2f** - **i** with electron-withdrawing substituents on the nitrogen atom were easily hydrolyzed under the above conditions. For example, treatment of **2f** with aqueous methanolic potassium hydroxide at room temperature for 1 h gave the corresponding *S,S,S*-triphenyloxosulfonium salts **3**, sulfone **4**, and tosylamide in 77, 20, and 98% isolated yield, respectively (Scheme 1).[9] Similarly, **2g** could be hydrolyzed smoothly to the corresponding **3** and **4** in 54 and 30% isolated yield, respectively.[9] In these cases, the initial product **3** will be produced by a nucleophilic attack of hydroxide anion at the central sulfur atom of **2f** and **2g**, and then hydrolyzed to **4**.[10]

Scheme 1.



Interestingly, the alkaline hydrolysis of *N*-acyl iminosulfonium salts **2h** and **2i** at room temperature afforded the deacylated product **1** quantitatively. This reaction shows that an attack by a hydroxide anion occurred at the carbonyl carbon rather than at the sulfur atom of **2h** and **2i**. *N*-Acylsulfilimines and *N*-acyl-*N*-alkylaminosulfonium salts are known to undergo hydrolysis under neutral and alkaline conditions giving sulfoxides and amides.[11] The compounds **2h** and **2i** are therefore expected for an acylating reagent. In fact, treatment of **2h** and **2i** with sodium 2-propoxide gave the corresponding esters and thiazyne **1** in good yields (yields of ester and **1** were determined by GC and ^{1}H-NMR. R = Ac, 89, >99%, respectively.; R = Bz, 95, >99%, respectively). Further investigations are now in progress in this area.

This work was supported in part by a Grant-in-Aids for Scientific Research on Priority Areas (A) of the Chemistry of Inter-element Linkage Chemistry (No. 09239218 and 10133218) and Scientific Research Grant (No. 09740466) from the Ministry of Education, Science, Sports and Culture.

References and Notes

1 S. Oae, T. Numata, and T. Yoshimura, "The chemistry of the sulphonium group, part 2," ed by C. J. M. Stirling, John Wiley & Sons, New York (1981), pp. 571 and references therin.

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

3 a) O. Glemser and R. Mews, *Angew. Chem., Int. Ed. Engl.*, **19**, 883 (1980). b) R. Bartsch, H. Henle, T. Meier, and R. Mews, *Chem. Ber.*, **121**, 451 (1988).

4 T. Yoshimura, K. Hamada, M. Imado, K. Hamata, K. Tomoda, T. Fujii, H. Morita, C. Shimasaki, S Ono, .E. Tsukurimichi, N. Furukawa, and T. Kimura, *J. Org. Chem.*, **62**, 3802 (1997).

5 **2a**: 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); FABMS (m/z) 292 (M^+ - I$^-$); Found: C, 54.38; H, 4.32; N, 3.38%. Calcd for $C_{19}H_{18}INS$: C, 54.42; H, 4.33; N, 3.34%. **2b**: 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); FABMS (m/z) 306 (M^+ - I$^-$); Found: C,55.33; H, 4.52; N, 3.09%. Calcd for $C_{20}H_{20}INS$: C, 55.43; H, 4.65; N, 3.23%. **2c**: 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); FABMS (m/z) 320 (M^+- I$^-$); Found: C, 56.34; H, 4.82; N, 3.00%. Calcd for $C_{21}H_{22}INS$: C, 56.38; H, 4.96; N, 3.13%. **2d**: 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); FABMS (m/z) 320 (M^+- I$^-$); Found: C, 56.35; H, 4.95; N, 3.02%. Calcd for $C_{21}H_{22}INS$: C, 56.38; H, 4.96; N, 3.13%. **2e**: m.p. 182-183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.34 (s, 2H), 7.28-7.34 (m, 5H), 7.85-7.96 (m, 9H), 8.06-8.09 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.8, 127.2, 127.7, 128.6, 129.1, 128.4, 131.4, 136.6, 137.7; IR (KBr) 1129 cm^{-1} (SN); FABMS (m/z) 368 (M^+ - Br$^-$); Found: C, 66.69; H, 4.96; N, 3.14%. Calcd for $C_{25}H_{22}BrNS$: C, 66.96; H, 4.95; N, 3.12%. **2f**: m.p. 260-261 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 7.14 (d, J = 8.6 Hz, 2H), 7.34 (d, J =8.6 Hz, 2H), 7.82-7.86 (m, 6H), 7.94-7.98 (m, 3H), 8.13-8.16 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 126.3, 126.8, 129.8, 130.1, 131.7, 137.8, 138.0, 144.9; IR (KBr) 1335, 1160 cm^{-1} (SO_2); FABMS (m/z) 432 (M^+ - ClO_4^-); Found: C, 56.43; H, 4.12; N, 2.70%. Calcd. for $C_{25}H_{22}ClNS_2O_6$: C, 56.44; H, 4.17; N, 2.63%. **2g**: m.p. 138-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.89 (m, 6H), 7.95-7.98 (m, 3H), 8.16-8.18 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.9, 130.7, 132.3, 138.6; IR (KBr) 1537, 1269 cm^{-1} (NO_2); FAB (m/z) 323 (M^+ - BF_4^-); Found: C, 53.06; H, 3.75; N, 6.92%. Calcd. for $C_{18}H_{15}N_2SO_2BF_4$: C, 52.71; H, 3.69; N, 6.83%. **2h**: m.p. 157-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 7.83-7.88 (m, 6H), 7.92-7.96 (m, 3H), 8.09-8.11 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.5, 126.4, 130.1, 131.6, 137.3, 179.3; IR (KBr) 1666 cm^{-1} (CO); FABMS (m/z) 320 (M^+ - ClO_4^-); Found: C, 57.05; H, 4.39; N, 3.17%. Calcd. for $C_{20}H_{18}ClNSO_5$: C, 57.21; H, 4.32; N, 3.34%. **2i**: m.p. 193-194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (t, J = 7.6 Hz, 2H), 7.67 (t, J =7.6 Hz, 1H), 7.86-7.90 (m, 6H), 7.93-7.97 (m, 3H), 8.18-8.24 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.7, 128.7, 129.9, 130.0, 131.7, 133.1, 134.1, 137.4, 173.4; IR (KBr) 1634 cm^{-1} (CO); FABMS (m/z) 382 (M^+ - ClO_4^-); Found: C, 62.68; H, 4.18; N, 2.63%. Calcd. for $C_{25}H_{20}ClNSO_5$: C, 62.30; H, 4.18; N, 2.91%.

6 The crystal data for **2a'**: $C_{19}H_{18}ClNO_4S$, monoclinic, $P2_1/n$, a = 8.747(1) Å, b = 20.214(2) Å, c = 10.908(9) Å, β = 99.472(9)°, V = 1902.4(4) Å^3, Z = 4, ρ = 1.368 g/cm^3, μ(Mo-Kα) = 3.34 cm^{-1}, R = 0.051 (R_W = 0.047), 2791 with $F_o^2 > 3.0\sigma(F_o^2)$.

7 H. Oberhammer and W. Zeil, *Z. Naturforsch., A*, **24**, 1612 (1969).

8 H. Oberhammer and W. Zeil, *Z. Naturforsch., A*, **25**, 845 (1970).

9 The hydrolyzed products were identified on the basis of a comparison of the ^{1}H- and ^{13}C-NMR data of the authentic samples and from literature[3] values.

10 Treatment of *S,S,S*-triphenyloxosulfonium perchlorate (**3**-ClO_4^-) with aqueous methanolic potassium hydroxide at room temperature for 24 h gave *S,S*-diphenylsulfone (**4**) and biphenyl in 92 and 5% isolated yield, respectively.

11 H. Kise, G. F. Whitfield, and D. Swern, *J. Org. Chem.*, **37**, 1121 (1972); J. A. Franz and J. C. Martin, *J. Am. Chem. Soc.*, **97**, 583 (1975).