

Tetrahedron Letters 42 (2001) 6151-6154

TETRAHEDRON LETTERS

Synthesis, structure, and reactivity of iminosulfonium ylides bearing an α -carbonyl group

Takayoshi Fujii,^{a,*} Tetsuya Suzuki,^a Takashi Sato,^a Ernst Horn^b and Toshiaki Yoshimura^{a,*}

^aDepartment of Material Systems Engineering and Life Science, Faculty of Engineering, Toyama University, Gofuku, Toyama 930-8555, Japan

^bDepartment of Chemistry, Rikkyo University, 3-34-1 Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8501, Japan

Received 4 June 2001; revised 27 June 2001; accepted 29 June 2001

Abstract—Treatment of methyl(methylimino)diphenylsulfonium tetraphenylborate (3) with NaH and subsequent acylation produced a new type of iminosulfonium ylides bearing an α -carbonyl group 5. The molecular structure of iminosulfonium phenacylide 5a was determined by X-ray crystallographic analysis. The ylide 5 reacted further with methyl triflate affording the corresponding novel alkylidenesulfonium salts 6. © 2001 Elsevier Science Ltd. All rights reserved.

Sulfur ylides have been extensively utilized as reagents for organic syntheses.¹ The sulfur ylides such as sulfonium, oxosulfonium, and (dimethylamino)oxosulfonium methylides are the most generally useful in oxiraneand cyclopropane-forming reactions.¹ On the other hand, a large number of stable sulfonium ylides bearing electronegative groups such as cyano and carbonyl groups on the ylidic carbon have long been known.^{1a,2} Iminosulfonium ylides belong to the isoelectronic compounds of oxosulfonium ylides, but very little has been reported to date on these compounds. This is mainly due to the lack of a facile preparation of this class of compounds, especially the difficult access to their parent iminosulfonium salts. Recently, we prepared triphenyl- λ^6 -sulfanenitrile bearing a sulfur–nitrogen triple bond from fluorodiphenyl- λ^6 -sulfanenitrile (1) with phenyllithium and found it easily reacts with several electrophiles to give the corresponding *N*-substituted iminosulfonium salts.³ These results prompted us to examine the deprotonation of methyl-(methylimino)diphenylsulfonium salts **3** and subsequent acylation which might lead to the isolation of stable iminosulfonium acylmethylides **5**. Here we describe the first preparation and crystal structure determination of the iminosulfonium ylides bearing an α -carbonyl group and their methylation, which gives the corresponding novel alkylidenesulfonium salts **6** with a sulfur–carbon double bond.



Scheme 1. Reagents and conditions: (i) TfOCH₃, CH₂Cl₂, -20°C; (ii) NaBPh₄, acetone; (iii) NaH, DMSO-d₆ or THF, rt; (iv) trans-benzalacetophenone, THF, rt.

0040-4039/01/\$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved. PII: S0040-4039(01)01186-8

Keywords: iminosulfonium ylides; alkylidenesulfonium salts; iminosulfonium salts; methyl- λ^6 -sulfanenitrile; methylation; X-ray crystallographic analysis.

^{*} Corresponding authors. Fax: +81-76-445-6850 (T.Y.); fax: +81-76-445-6853 (T.F.); e-mail: yosimura@eng.toyama-u.ac.jp; tfujii@eng.toyama-u.ac.jp

The reaction of methyldiphenyl- λ^6 -sulfanenitrile (2),⁴ which was prepared by the reaction of 1 with methyllithium, with methyl triflate (TfOMe) in dichloromethane at -20°C gave the corresponding methyl(methylimino)diphenylsulfonium triflate. This iminosulfonium salt is very hygroscopic, and was therefore isolated by converting it into tetraphenylborate salt 3 upon treatment with NaBPh₄.⁵ Treatment of 3 with sodium hydride in DMSO-d₆ at room temperature resulted in the formation of a yellow solution of iminosulfonium methylide 4 (Scheme 1). The ${}^{1}H$ and ${}^{13}C$ NMR signals of the methylene moiety in 4 appear at $\delta_{\rm H}$ 1.41 and $\delta_{\rm C}$ 13.2, respectively. Addition of 1 equiv. of trans-benzalacetophenone to the solution of ylide 4 in THF resulted in the production of *trans*-1-benzoyl-2phenylcyclopropane and N-methyldiphenylsulfimide in 75 and 86% yields, respectively (Scheme 1). The formation of cyclopropane presented here should proceed via a reaction pathway similar to that suggested for oxosulfonium and (dimethylamino)oxosulfonium methylides.⁶

Stable iminosulfonium ylides, iminosulfonium phenacylide **5a** and trifluoroacetylmethylide **5b** were formed by the reaction of 4 with 0.5 equiv. of benzoyl chloride and trifluoroacetic anhydride, respectively, and subsequent deprotonation of parent iminosulfonium salts by 4 in THF at 0°C (Scheme 2). The iminosulfonium ylides 5a and 5b were purified by column chromatography on silica gel followed by recrystallization from dichloromethane/hexane in 89 and 54% yields, respectively. NMR, IR, and mass spectroscopy and elemental analyses were consistent with the structure of $5.^7$ In the ¹³C NMR spectra of **5a** and **5b**, the ylidic carbon appears at δ 58.2 and 61.4, respectively. In the IR spectra, C=O and S=N streching bands were observed at 1590–1608 and 1160–1164 cm⁻¹, respectively.

The crystal structure of the novel iminosulfonium ylide **5a** was determined by X-ray crystallographic analysis (Fig. 1).⁸ The X-ray analysis clearly reveals that the configuration around the sulfur atom in **5a** is a slightly distorted tetrahedral structure with one SN bond and three SC bonds. The bond length of the sulfur–ylidic carbon (S(1)–C(1)) is 1.672(2) Å, which is shorter than the sum of the covalent radii of S and C (1.81 Å),⁹ and those of sulfonium ylides, 2-dimethylsulfuranylidene-malononitrile (1.719(8) Å)² and 2-dimethylsulfuranylidene-1,3-indanedione (1.707(3) Å).² The S(1)–N(1)

bond length (1.538(2) Å) is close to that of (methylimino)triphenylsulfonium perchlorate (1.514(4) Å).^{3b} The O(1)–C(4) bond length (1.248(2) Å) is significantly longer than that of a typical C=O double bond (1.21 Å),¹⁰ and the C(1)–C(4) bond length (1.408(3) Å) is significantly shorter than that of a typical C–C single bond (1.51 Å).¹⁰ These findings are indicative of a hybrid of the canonical forms **5aA**, **5aB**, and **5aC** (Scheme 2).

The acyl-stabilized iminosulfonium ylides **5** conceivably have three reaction sites, carbonyl oxygen, ylidic carbon, and imino nitrogen toward electrophiles. The reaction of **5** with TfOMe in CDCl₃ at 0°C was examined (Scheme 2). For example, in the ¹H NMR of **5a**, the peaks of **5a** at δ 2.95 (s, NCH₃) and 5.06 (s, CH) gradually reduced on addition of TfOMe, and the two sets of peaks of the expected *N*-methylated **6a** (δ 3.25 (s, N(CH₃)₂, 5.44 (s, CH)) and *O*-methylated compound **7a** (δ 3.05 (s, NCH₃), 3.38 (s, OCH₃), 6.32 (s, CH)) appeared. The product ratio of **6a** and **7a** in the reaction of **5a** is approximately 1.2 : 1, while only *N*methylated compound **6b** was obtained in **5b**. The *N*-methylated compound **6a** is sufficiently stable in CDCl₃ at 0°C, but it completely decomposed at room



Figure 1. The molecular structure of **5a**. Selected bond distances (Å) and bond angles (°): S(1)-N(1), 1.538(2); S(1)-C(1), 1.672(2); S(1)-C(2), 1.783(2); S(1)-C(3), 1.803(2); O(1)-C(4), 1.248(2); N(1)-C(5), 1.460(3); C(1)-C(4), 1.408(3); N(1)-S(1)-C(1), 122.0(1); N(1)-S(1)-C(2), 103.39(9); N(1)-S(1)-C(3), 113.20(9); C(1)-S(1)-C(2), 111.24(10); C(1)-S(1)-C(3); 101.44(9); C(2)-S(1)-C(3), 104.54(9); S(1)-N(1)-C(5), 116.7(2); S(1)-C(1)-C(4), 118.4(2); O(1)-C(4)-C(1), 122.8(2).



Scheme 2. Reagents and conditions: (i) NaH, THF, 0°C; (ii) PhCOCl or (CF₃CO)₂O, 0°C-rt; (iii) TfOCH₃, CDCl₃, 0°C.



Figure 2. The molecular structure of **6b**'. For clarity, the tetraphenylborate is ommited. Selected bond distances (Å) and bond angles (°): S(1)-N(1), 1.647(4); S(1)-C(1), 1.660(5); S(1)-C(2), 1.772(4); S(1)-C(3), 1.768(4); O(1)-C(4), 1.201(6); N(1)-C(5), 1.490(6); N(1)-C(6), 1.474(6); C(1)-C(4), 1.414(7); N(1)-S(1)-C(1), 122.0(2); N(1)-S(1)-C(2), 103.7(2); N(1)-S(1)-C(3), 103.5(2); C(1)-S(1)-C(2), 111.6(2); C(1)-S(1)-C(3); 108.6(2); C(2)-S(1)-C(3), 106.1(2); S(1)-N(1)-C(5), 112.7(3); S(1)-N(1)-C(6), 117.3(3); S(1)-C(1)-C(4), 118.2(4); O(1)-C(4)-C(1), 127.0(4).

temperature. The *N*-methylated **6b** and *O*-methylated compound **7a** could be isolated by converting them into the corresponding tetraphenylborates **6b**' and **7a**', respectively.¹¹ Furthermore, the molecular structure of a novel alkylidenesulfonium tetraphenylborate **6b**' was determined by X-ray crystallographic analysis (Fig. 2).¹² Further investigation of the chemistry of iminosulfonium ylides and alkylidenesulfonium salts is now in progress.

Acknowledgements

This work was supported in part by a Grants-in-Aid for Research (No. 09239218, 10133218, and 11120219) from the Ministry of Education, Science, Sports and Culture and by the Asahi Glass Foundation.

References

- For reviews, see: (a) Trost, B. M.; Melvin, Jr., L. S. Sulfur Ylides; Academic Press: New York, 1975; (b) Block, E. In The Chemistry of the Sulfonium Group; Stirling, C. J. M.; Patai, S., Eds.; Wiley: New York, 1981; Chapter 16, pp. 673–702; (c) Aggarwal, V. K. Synlett 1998, 329–336 and references cited therein.
- Perozzi, E. F.; Paul, I. C. In *The Chemistry of the Sulfonium Group*; Stirling, C. J. M.; Patai, S., Eds.; Wiley: New York, 1981; Chapter 2, pp. 15–77 and references cited therein.
- (a) Yoshimura, T.; Hamada, K.; Imado, M.; Hamata, K.; Tomoda, K.; Fujii, T.; Morita, H.; Shimasaki, C.; Ono, S.; Tsukurimichi, E.; Furukawa, N.; Kimura, T. J. Org.

Chem. **1997**, *62*, 3802–3803; (b) Yoshimura, T.; Fujii, T.; Hamata, K.; Imado, M.; Morita, H.; Ono, S.; Horn, E. *Chem. Lett.* **1998**, 1013–1014.

- 4. For **2**: hygroscopic compound; mp 177°C (decomp.); ¹H NMR (400 MHz, CDCl₃): δ 3.52 (s, 3H), 7.50–7.55 (m, 6H), 7.83–7.86 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 48.2, 125.5, 129.2, 131.8, 147.5; IR (KBr) 1250 cm⁻¹ (SN); HRMS, calcd. for C₁₃H₁₃NS: 215.0769. Found: 215.0736.
- 5. For **3**: mp 158–159°C; ¹H NMR (400 MHz, CD₃CN): δ 2.84 (s, 3H), 3.99 (s, 3H), 6.84 (t, J=7.4 Hz, 4H), 6.99 (t, J=7.4 Hz, 8H), 7.25–7.29 (m, 8H), 7.77–7.81 (m, 4H), 7.89–7.95 (m, 6H); ¹³C NMR (100 MHz, CD₃CN): δ 31.9, 39.1, 122.8, 126.6 (q, J_{CB} =2.5 Hz), 128.9, 131.5, 131.9, 136.7, 137.3, 164.8 (q, J_{CB} =49.3 Hz); IR (KBr) 1209 cm⁻¹ (SN); FAB (m/z) 230 (M⁺–BPh₄). Elemental analysis calcd for C₃₈H₃₆BNS: C, 83.05; H, 6.60; N, 2.55. Found: C, 83.43; H, 6.73; N, 2.55.
- Johnson, C. R.; Schroeck, C. W.; Shanklin, J. R. J. Am. Chem. Soc. 1973, 95, 7424–7431.
- 7. For **5a**: mp 140°C; ¹H NMR (400 MHz, CDCl₃): δ 2.95 (s, 3H), 5.06 (s, 1H), 7.36-7.43 (m, 3H), 7.50-7.57 (m, 6H), 7.91-7.93 (m, 2H), 8.03-8.06 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 30.9, 58.2, 126.9, 127.0, 128.0, 129.6, 130.4, 132.5, 138.5, 139.7, 182.9; IR (KBr) 1590 cm⁻¹ (CO), 1164 cm⁻¹ (SN); MS (m/z) 333 (M⁺). Elemental analysis calcd for C₂₁H₁₉NOS: C, 75.64; H, 5.74; N, 4.20. Found: C, 75.85; H, 5.83; N, 4.10. For 5b: mp 120°C; ¹H NMR (400 MHz, CDCl₃): δ 2.93 (s, 3H), 4.96 (s, 1H), 7.54–7.64 (m, 6H), 7.95–7.98 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 30.9, 61.4, 117.7 (q, J_{CF} =289.6 Hz), 126.9, 129.9, 133.4, 136.6, 171.4 (q, J_{CF}=32.9 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ –76.6; IR (KBr) 1608 cm⁻¹ (CO), 1160 cm⁻¹ (SN); MS (m/z) 325 (M⁺). Elemental analysis calcd for C₁₆H₁₄F₃NOS: C, 59.07; H, 4.34; N, 4.31. Found: C, 59.37; H, 4.23; N, 4.39.
- 8. Crystal data of **5a**: C₂₁H₁₉NOS, M=333.45, monoclinic, a=9.974(1), b=8.670(1), c=20.516(2) Å, $\beta=91.620(9)^\circ$, U=1773.6(3) Å³, T=242 K, space group $P2_1/c$ (no. 14), Z=4, μ (Mo K α) = 1.89 cm⁻¹, 5467 reflections measured, 5153 unique ($R_{int}=0.020$); R ($I>3\sigma(I)$)=0.041, $R_w=0.050$ for 3249 reflections and 293 parameters. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 163270 for compound **5a**.
- 9. Emsley, J. *The Elements*, 3rd ed.; Oxford Univerity Press: Oxford, 1998.
- Smith, M. B.; March, J. March's Advanced Organic Chemistry, 5th ed.; Wiley: New York, 2001; Table 1.5, pp. 21.
- 11. For **6b**': mp 127°C (decomp.); ¹H NMR (400 MHz, CD₃CN): δ 3.09 (s, 6H), 5.45 (s, 1H), 6.83 (t, J=7.2 Hz, 4H), 6.98 (t, J=7.2 Hz, 8H), 7.25–7.29 (m, 8H), 7.79–7.83 (m, 4H), 7.95–7.99 (m, 2H), 8.03–8.06 (m, 4H); ¹³C NMR (100 MHz, CD₃CN): δ 41.3, 51.2, 122.8, 125.1, 126.6 (q, J_{CB} =2.5 Hz), 130.0, 133.0, 136.7, 138.8, 164.8 (q, J_{CB} =49.4 Hz), 175.9 (q, J_{CF} =36.2 Hz); IR (KBr) 1646 cm⁻¹ (CO); FAB (m/z) 340 (M⁺-BPh₄). Elemental analysis calcd for C₄₁H₃₇BF₃NOS: C, 74.66; H, 5.65; N, 2.12. Found: C, 74.78; H, 5.74; N, 2.31. For **7a**': mp 149–150°C; ¹H NMR (400 MHz, CD₃CN): δ 3.01 (s, 3H), 3.41 (s, 3H), 6.35 (s, 1H), 6.83 (t, J=7.2 Hz, 4H), 6.98 (t, J=7.2 Hz, 8H), 7.24–7.29 (m, 8H), 7.56–7.60 (m, 2H), 7.65–7.76 (m, 7H), 7.81–7.85 (m, 2H), 8.05–8.08 (m),

4H); ¹³C NMR (100 MHz, CD₃CN): δ 32.0, 61.2, 94.2, 122.7, 126.6 (q, J_{CB} =2.5 Hz), 128.2, 130.0, 130.1, 130.7, 131.7, 133.9, 134.6, 136.3, 136.7, 164.7 (q, J_{CB} =49.4 Hz); IR (KBr) 1265, 1084 cm⁻¹ (COC), 1194 cm⁻¹ (SN); FAB (m/z) 348 (M⁺-BPh₄). Elemental analysis calcd for C₄₆H₄₂BNOS: C, 82.74; H, 6.34; N, 2.10. Found: C, 82.71; H, 6.38; N, 2.11.

12. Crystal data of **6b**': $C_{41}H_{37}BF_3NOS$, M = 659.61, mono-

clinic, a=9.541(2), b=16.739(2), c=10.902(2) Å, $\beta=95.23(1)^{\circ}$, U=1733.8(4) Å³, T=296 K, space group $P2_1$ (no. 4), Z=2, μ (Mo K α)=1.43 cm⁻¹, 5501 reflections measured, 5428 unique ($R_{int}=0.013$); R ($I>3\sigma(I)$)=0.042, $R_w=0.056$ for 2952 reflections and 436 parameters. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 163271 for compound **6b**'.