

0040-4039(95)00401-7

First Detection of 2,2'-Biphenylylenediphenylsulfurane and -Selenurane [10-M-4(C4), M = S, Se] by Low Temperature NMR Experiments and Isolation of the Tellurane

Soichi Sato[†] and Naomichi Furukawa*

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Abstract : Formation of 2,2'-biphenylylenediphenylsulfurane and -selenurane was detected in the reactions of 2,2'biphenylylenephenylchalcogenium compounds with phenyllithium by ${}^{1}H$, ${}^{13}C$, ${}^{77}Se$, and CH-COSY NMR studies at low temperature. Isolation of the tellurane (C) was reported as an example of the tellurane bearing four carbon ligands.

Several stable organic hypervalent compounds having group 16 elements as a central atom have been reported.¹ However, those having only carbon ligands are unstable and less popular. Particularly both sulfurane [10-S-4 (C4)] and selenurane [10-Se-4 (C4)] have been considered as an intermediate or a transition state for the reaction of the corresponding onium salts or oxides with various organometallic reagents.² Trost and Hori studied the reaction of 2,2'-biphenylylenearylsulfonium salts with aryllithium extensively to detect



a) 1.0 eq. PhLi in THF at -105 °C or -78 °C b) 1.0 eq. 2,2'-dilithiobiphenyl in THF at -78 °C c) aq. HBF₄ or HBr



[†] Research Fellow of the Japan Society for the Promotion of Science.

2,2'-biphenylylenediarylsulfuranes as intermediates, but they were unsuccessful in the direct detection or isolation of these compounds.³ Recently, we have succeeded not only in the first detection of tetraphenylsulfurane and selenurane by NMR⁴ but also in the isolation and determination of the structure of bis(2,2'-biphenylylene)sulfurane by X-ray crystallographic analysis.^{5,7} We report here that the formation of 2,2'-biphenylylenediphenylsulfurane (A) and -selenurane (B) can be confirmed by low temperature ¹H, ¹³C, ⁷⁷Se, HH- and CH-COSY NMR spectra and the tellurane (C) can be isolated.

When an equimolar amount of PhLi (1.02 M in cyclohexane/ether solution) was added to a suspension of 2,2'-biphenylylenephenylchalcogenium salt (1) or (2) [counter anion: BF_4^- (S), Br^- (Se)] in anhydrous tetrahydrofurane (THF) under an argon atmosphere at -100 ° or -78 °C, both mixtures turned to a yellowish homogeneous solution. Subsequently, each mixture was treated with 0.2 M aqueous tetrafluoroboric acid (HBF4) solution at -100 °or -78 °C to give the recovered chalcogenium salt 1 or 2 quantitatively. By elevating the temperature to room temperature, each solution turned to colorless to give phenyl o-terphenyl sulfide (5) or selenide (6) quantitatively, after work-up. The present results suggested that a stable intermediate like σ sulfurane A or σ -selenurane B would be formed in solution at low temperature. In order to confirm the formation of this sulfurane A or selenurane B as a discrete intermediate, the ¹H and ¹³C NMR spectra of the reaction mixture were measured in THF-dg at -100 °C and -78 °C, and it was observed that the new sets of each spectrum differed either from that of each substrate or the ligand coupling products.⁶ The ¹H and ¹³C NMR chemical shifts of A or B were determined by each cross peak observed in the ¹H¹H, and ¹³C¹H-COSY NMR spectra (Fig. 1.), and the corresponding ¹H and ¹³C NMR data of A or B are summarized in ref. 8.



Fig. 1. ¹³C¹H-COSY NMR spectra of sufurane A (left) and selenurane B (right).

Furthermore, when an equimolar amount of 2,2'-dilithiobiphenyl was added to a suspension of dichloro diphenyl tellurane 4 in anhydrous ether under an argon atmosphere at -78 °C, the mixture turned to a yellowish homogeneous solution at room temperature. After filtration of the residue, the solvent was evaporated to leave a pale yellow solid estimated as a σ -tellurane (C). The tellurane C was treated with 0.2 M aqueous tetrafluoroboric acid (HBF4) solution to give the corresponding telluronium salt (3) quantitatively. At higher temperature around 140 °C in situ, it decomposed to give the coupling product, phenyl o-terphenyl telluride (7) (8 %), dibenzotellurophene (10) (69 %) and biphenyl 11 (36 %) (Scheme 1). In order to confirm the

structure of this σ -tellurane C, the ¹H¹H, ¹³C¹H-COSY, and ¹²⁵Te NMR spectra of C were measured in THFdg at room temperature to give new sets of the spectrum different from that of the substrate 4 and the ligand coupling product 7 (Fig. 2.).⁸ The ¹H and ¹³C NMR chemical shifts of C were determined similarly.⁸

The ¹²⁵Te NMR spectrum of tellurane C appeared at 439.0 ppm [4: 981.0 ppm (CDCl₃), 7: 638.0 ppm (CDCl₃)], reveals that the structure of compound C should be a tellurane bound to four aryl ligand in solution because this value is roughly identical with those of the known telluranes, tetraphenyltellurane: 509.7 ppm (THF); bis(2,2'biphenylylene)tellurane: 482.1 ppm (THF).

The present studies on the temperature dependent NMR experiments provide the first and discrete evidence for the formation of 2,2'biphenylylenediphenylsulfurane and -selenurane as an intermediate, while 2,2'-biphenylylenediphenyl tellurane was isolated as a stable derivative. Further studies are in progress to detect and isolate the chalcogenanes having other carbon ligands.



Fig. 2. ¹³C¹H-COSY NMR spectra of tellurane C.

Acknowledgment. The authors wish to thank Dr. T. Erata, Institute of Applied Physics, University of Tsukuba, for the his valuable help in the two-dimensional NMR experiment by low temperature. This work was supported by the Ministery of Education, Science, and Culture, Japan [Priority area: Grant No. 05236205].

REFERENCES AND NOTES

- a) Hayes, R. A.; Martin, J. C. Sulfurane Chemistry. In Organic Sulfur Chemistry: Theoretical and Experimental Advances; Bernardi, F.; Csizmadia, I. G.; Mangini, A. Eds.; Elsevier: Amsterdam, 1985; pp. 408-483; and references therein. b) Bergman, J.; Engman, L.; Siden, J. Tetra- and higher-valent (hypervalent) derivatives of selenium and tellurium. In The chemistry of organic selenium and tellurium compounds; Patai, S.; Rappoport, Z. Eds.; John Wiley and Sons, Inc.: New York, Vol. 1, 1986; pp. 517-558, and references therein. c) Irgolic, K. J. Tetraorganyl Tellurium Compounds, R4Te. In The Organic Chemistry of Tellurium; Gordon and Breach, Inc.: New York, 1974; pp. 234-241, (see also references therein).
- a) Wittig, G.; Fritz, H. Liebigs Ann. Chem., 1952, 577, 39-46. b) Sheppard, W. A. J. Am. Chem. Soc., 1971, 93, 5597-5598. c) Sheppard, W. A.; Foster, S. S. J. Fluorine Chem., 1972/1973, 2, 53-62. d) Harrington, D.; Weston, J.; Jacobus, J.; Mislow, K. J. Chem. Soc., Chem. Commun., 1972, 1079-1080. e) Iwama, Y.; Aragi, M.; Sugiyama, M.; Matsui, K.; Ishii, Y.; Ogawa, M. Bull. Chem. Soc. Jpn., 1981, 54, 2065-2067.
- a) LaRochelle, R. W.; Trost, B. M. J. Am. Chem. Soc., 1971, 93, 6077-6086. b) Trost, B. M.; Arndt, H. C. *ibid.*, 1973, 95, 5288-5298. c) Hori, M.; Kataoka, T.; Shimizu, H.; Miyagaki, M. Chem. Lett.,

1972, 515-520. d) Hori, M.; Kataoka, T.; Shimizu, H.; Miyagaki, M. Chem. Pharm. Bull., 1974, 22, 2020-2029.

- a) Ogawa, S.; Sato, S.; Erata, T.; Furukawa, N. *Tetrahedron Lett.*, 1991, 32, 3179-3182. b) Ogawa, S.; Matsunaga, Y.; Sato, S.; Erata, T.; Furukawa, N. *ibid.*, 1992, 33, 93-96. c) Ogawa, S.; Sato, S.; Furukawa, N. *ibid.*, 1992, 33, 7925-7928.
- 5. Ogawa, S.; Matsunaga, Y.; Sato, S.; Iida, I.; Furukawa, N. J. Chem. Soc., Chem. Commun., 1992, 16, 1141-1142.
- a) Ogawa, S.; Sato, S.; Erata, T.; Furukawa, N. Tetrahedron Lett., 1992, 33, 1915-1918.
 b) Furukawa, N.; Matsunaga, Y.; Sato, S. Synlett, 1993, 655-656.
 c) Sato, S.; Furukawa, N., Chem. Lett., 1994, 889-892.
- a) Hellwinkel, D.; Farbach, G.; Tetrahedron Lett., 1965, 23, 1823-1827. b) Hellwinkel, D.; Fahrbach, G. Justus Liebigs Ann. Chem., 1968, 712, 1-20. c) Hellwinkel, D.; Fahrbach, G. Justus Liebigs Ann. Chem., 1968, 715, 68-73. d) Hellwinkel, D.; Fahrbach, G. Chem.. Ber., 1968, 101, 574-584. e) Hellwinkel, D. Annals of the New York Academy of Sciences, 1972, 192, 158-166. f) Barton, D. H. R.; Glover, S. A.; Ley, S. V. J. Chem. Soc., Chem. Commun., 1977, 266-267. g) Glover, S. A. J. Chem. Soc., Perkin Trans. 1, 1980, 1338-1344. h) Jones, C. H. W.; Sharma, R. D. J. Organomet. Chem., 1987, 332, 115-121.
- A: ¹H NMR (270 MHz, THF-d₈, -90 °C) δ 6.88 (d, J=7.6 Hz, 2H, 3-ArH), 7.11 (d, J=7.3 Hz, 4H, 8-ArH), 7.16 (t, J=7.3 Hz, 2H, 10-ArH), 7.21 (t, J=7.6 Hz, 2H, 4-ArH), 7.21 (t, J=7.3 Hz, 4H, 9-ArH), 7.37 (t, J=7.6 Hz, 2H, 5-ArH), 8.14 (d, J=7.6 Hz, 2H, 6-ArH); ¹³C NMR (68.4 MHz, THF-d₈, -90 °C) δ 121.9, 128.0, 128.3, 128.4,



128.8, 129.0, 129.4, 134.8, 152.6, 156.8. **B** : ¹H NMR (270 MHz, THF-d₈, -70 °C) δ 7.13 (d, J=8.5 Hz, 4H, 8-ArH), 7.13 (t, J=9.0 Hz, 2H, 4-ArH), 7.17 (t, J=8.5 Hz, 4H, 9-ArH), 7.17 (d, J=9.0 Hz, 2H, 3-ArH), 7.20 (t, J=8.5 Hz, 2H, 10-ArH), 7.41 (t, J=9.0 Hz, 2H, 5-ArH), 8.14 (d, J=9.0 Hz, 2H, 6-ArH); ¹³C NMR (68 MHz, THF-d₈, -70°C) δ 122.7, 128.3, 128.6, 129.1, 129.5, 129.9, 130.9, 138.1, 151.9, 156.2; ⁷⁷Se NMR (51 MHz, THF-d₈, -70°C) δ 397.1.^{5a)} C : mp 122-126°C/ (decomp.) (pale yellow powder); ¹H NMR (270 MHz, THF-d₈, r.t.) δ 7.04 (d, J=7.3 Hz, 2H, 3-ArH), 7.13 (t, J=7.3 Hz, 2H, 4-ArH), 7.16 (t, J=7.6 Hz, 4H, 9-ArH), 7.23 (t, J=7.6 Hz, 2H, 10-ArH), 7.35 (d, J=7.3 Hz, 4H, 8-ArH), 7.40 (t, J=7.3 Hz, 2H, 5-ArH), 8.13 (d, J=7.3 Hz, 2H, 6-ArH); ¹³C NMR (68 MHz, THF-d₈, r.t.) δ 123.0, 128.6, 129.1, 129.9, 132.6, 134.4, 140.2, 142.7, 149.7; ¹²⁵Te NMR (85 MHz, THF-d₈, r.t.) δ 439.0; MS (m/z): 436 (M⁺), 359 (M⁺-77), 282 (M⁺-154), 152 (M⁺-284); Exact mass Calcd for C₂₄H₁₈Te: 436.0471, Found: 436.0501.

(Received in Japan 24 December 1994; revised 6 February 1995; accepted 23 February 1995)