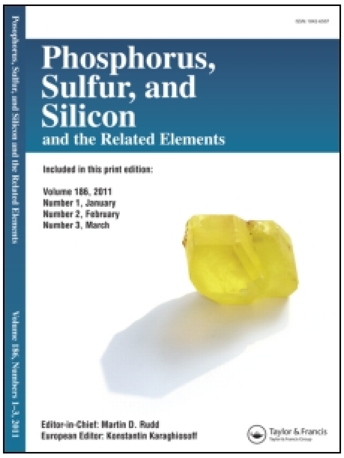
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Novel Disproportionation Reaction of Stable Stibabismuthene Via 1,2,3,4-Distibadibismetane Derivative

Takahiro Sasamori; Nobuhiro Takeda; Norihiro Tokitoh

To cite this Article Sasamori, Takahiro , Takeda, Nobuhiro and Tokitoh, Norihiro(2001) 'Novel Disproportionation Reaction of Stable Stibabismuthene Via 1,2,3,4-Distibadibismetane Derivative', Phosphorus, Sulfur, and Silicon and the Related Elements, 169: 1, 89 — 92

To link to this Article: DOI: 10.1080/10426500108546597

URL: http://dx.doi.org/10.1080/10426500108546597

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur and Silicon, 2001, Vol. 169, pp. 89-92
Reprints available directly from the publisher
Photocopying permitted by license only

© 2001 OPA (Overseas Publishers Association) N.V.
Published by license under the
Gordon and Breach Science Publishers imprint.

Novel Disproportionation Reaction of Stable Stibabismuthene Via 1,2,3,4-Distibadibismetane Derivative

TAKAHIRO SASAMORI[a], NOBUHIRO TAKEDA[b] and NORIHIRO TOKITOH[b]

[a]*Graduate School of Science, Kyushu University, 6–10–1 Hakozaki, Higashi-ku, Fukuoka 812–8581, Japan and* [b]*Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611–0011, Japan*

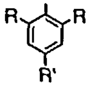
Downloaded At: 12:42 28 January 2011

The first stable stibabismuthene has been successfully synthesized by taking advantage of an efficient steric protection group, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt). Thermolysis and photolysis of the stibabismuthene resulted in the formation of homonuclear double-bond compounds. This disproportionation reaction is most likely interpreted in terms of the dimerization of the stibabismuthene giving 1,2,3,4-distibadibismetane derivative followed by the dissociation into the homonuclear double-bond compounds.

Keywords: stibabismuthene; 1,2,3,4-distibadibismetane; distibene; dibismuthene; disproportionation reaction

Downloaded At: 12:42 28 January 2011

INTRODUCTION



Tbt: R = R' = $CH(SiMe_3)_2$
Bbt: R = $CH(SiMe_3)_2$,
R' = $C(SiMe_3)_3$

The syntheses, structures and reactivities of multiple bonds between heavier main group elements have attracted wide interest as one of the active areas of chemical research. As for the case of group 15 elements, a number of kinetically stabilized diphosphenes (RP=PR) and diarsenes (RAs=AsR) have already been isolated [1]. We have recently succeeded in the synthesis and characterization of the first stable distibenes (RSb=SbR) [2] and dibismuthenes (RBi=BiR) [3], much heavier congeners of azo compounds, by taking advantage of efficient steric protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)-methyl]phenyl (Bbt). On the other hand, as for the heteronuclear double-bond compounds between heavier group 15 elements, several stable phosphaarsenes and phosphastibenes have been synthesized [1,4], but there is no example of a stibabismuthene, a heteronuclear doubly bonded system between antimony and bismuth. This paper presents the first synthesis of stable stibabismuthene **1**, and its interesting disproportionation reaction into the homonuclear double-bond species **2** and **3** via an intermediary 1,2,3,4-distibadibismetane derivative **4**.

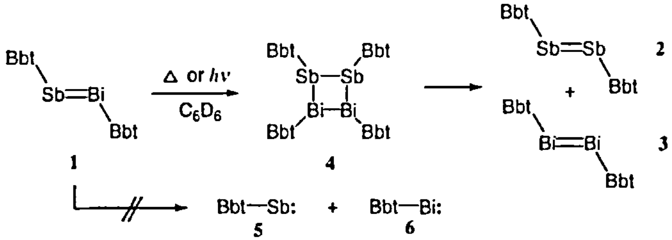
RESULTS AND DISCUSSION

The condensation reaction of $BbtBiBr_2$ with $BbtSbH_2$ in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded stibabismuthene **1** as red-purple crystals quantitatively. All the spectroscopic properties of stibabismuthene **1** including the Raman and UV/vis spectra indicated that **1** features a double bond between antimony and bismuth [5].

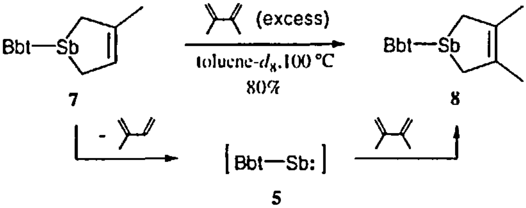
Although **1** is stable at ambient temperature in the absence of air

Downloaded At: 12:42 28 January 2011

and light, thermolysis of the benzene-d_6 solution of **1** at 70 °C showed very slow disproportionation leading to the formation of distibene **2** and dibismuthene **3**. On the other hand, photolysis of **1** in benzene-d_6 (100 W/Pyrex filter/r. t./4 h) resulted in the complete disproportionation giving a 1:1 mixture of **2** and **3**.



Two different pathways can be postulated for the disproportionation reactions of stibabismuthene **1**. The first one is the dimerization of **1** by heating or irradiation followed by the decomposition of the resulting 1,2,3,4-distibadibismetane derivative **4** into the homonuclear double-bond species **2** and **3**, while the other one is that based on the dissociation of **1** giving the corresponding monovalent species, i. e., stibinidene **5** and bismuthinidene **6**, both of which might undergo ready dimerization leading to the formation of **2** and **3**, respectively. On the other hand, we have already found that the stibinidene **5** generated by thermal cycloreversion of the corresponding overcrowded stibolene derivative **7** readily undergoes cycloaddition with 2,3-dimethyl-1,3-butadiene to give the stable stibinidene adduct **8** in good yields. Although we have examined the thermolysis and photolysis of **1** in the presence of 2,3-dimethyl-1,3-butadiene in expectation of trapping the intermediary monovalent species **5** and **6**, no [4+1] cycloadducts of **5** and **6** but only **2** and **3** were obtained in high yields. Taking the previous reports on the disproportionation reaction of unsymmetrically substituted diphosphenes [1,6] into consideration, the disproportionation reactions of **1** are not rationalized by the mechanism via stibinidene and bismuthinidene intermediates but most likely interpreted in terms of the association–dissociation mechanism via the 1,2,3,4-distibadibismetane derivative **4**.



7 **8** **5**

Acknowledgments. This work was partially supported by Grants-in-Aid for Scientific Research on Priority Areas (No. 09239101 and 11166250) from the Ministry of Education, Science, Sports and Culture of Japan. T. S. thanks Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists. We are also grateful to Shin-Etsu Chemical Co., Ltd., for the generous gifts of chlorosilanes.

Downloaded At: 12:42 28 January 2011

References

[1] For reviews see: (a) L. Weber, *Chem. Rev.*, **92**, 1839 (1992); (b) M. Yoshifuji, *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Geore Thieme Verlag, Stuttgart, Germany, p. 321 (1990); (c) A.H. Cowley, J.E. Kilduff, J. G. Lasch, S. K. Mehrotra, N. C. Norman, M. Pakulski, B. R. Whittlesey, J. L. Atwood, and W. E. Hunter, *Inorg. Chem.*, **23**, 2582 (1984).

[2] N. Tokitoh, Y. Arai, T. Sasamori, R. Okazaki, S. Nagase, H. Uekusa, and Y. Ohashi, *J. Am. Chem. Soc.*, **120**, 433 (1998).

[3] N. Tokitoh, Y. Arai, R. Okazaki, and S. Nagase, *Science*, **277**, 78 (1997).

[4] B. Twamley and P. P. Power, *Chem. Commun.*, 1979 (1998).

[5] T. Sasamori, N. Takeda, and N. Tokitoh, *Chem. Commun.*, 1353 (2000).

[6] M. Yoshifjui, T. Sato, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **62**, 2394 (1989).