A Reinvestigation of Paneth's Violet Compound. The Synthesis of Tetramethyldibismuthine

Arthur J. Ashe, III,* and Edward G. Ludwig, Jr.

Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109

Received June 28, 1982

Summary: Tetramethyldibismuthine was prepared from the reaction of trimethylbismuthine with sodium in liquid ammonia followed by treatment with 1,2-dichloroethane. Like tetramethyldistibine it shows thermochromic properties on freezing.

In 1935, Paneth reported that the reaction between methyl radicals and a heated bismuth mirror gave a trace of a violet solid which melted to a yellow liquid prior to decomposition.[1] On the basis of analogy to the thermochromic behavior (red → yellow) of tetramethyldistibine **1b**, the violet compound was assigned the structure of tetramethyldibismuthine **1a**. No other characterization of tetramethyldibismuthine has appeared in the literature, although several other dibismuthines have recently been reported.[2–5] We now wish to report on a synthesis of **1a** and on a comparison of its properties with those of **1b**[6] and other compounds of group V elements.

The reaction of trimethylbismuthine[7] with sodium in liquid ammonia afforded a red solution of $NaBi(CH_3)_2$ which on reaction with 1,2-dichloroethane gave a 70% yield of tetramethyldibismuthine as a viscous red oil ($d_{20\,°C}$ = 2.85 g/cm^3).[8] The ^1H NMR and ^{13}C NMR spectra (C_7D_8) consist of broad singlets at δ 1.62 and δ_C −18.92, respectively. The mass spectrum (70 eV) shows the expected peaks for sequential fragmentation at m/e (relative intensity) 478 (2.6, M^+), 463 (3.7), 448 (2.0), 434 (3.4), 418 (4.9), 254 (35.8), 239 (79.3), 224 (62.3), and 209 (100). The Raman spectrum of solid **1a** shows intense polarized peaks at 110 (Bi–Bi) and 445 (BiC) cm^{-1}. The corresponding bands for solid tetramethyldistibine, tetramethyldiarsine,[9] and tetramethyldiphosphine[10] occur at 179 (Sb–Sb), 271 (AsAs), 455 (PP), and 505 (SbC), 570 (AsC), and 668 (PC) cm^{-1}. This shift to lower frequency exceeds that expected for increasing mass and is consistent with a progressive weakening of the vibrational force constants.[11]

$$Me_3Bi \xrightarrow[NH_3]{Na} Me_2BiNa \xrightarrow{C_2H_4Cl_2} Me_2BiBiMe_2$$

$$Me_2BiBiMe_2 \xrightarrow[\Delta]{} Me_3Bi + Bi$$

Tetramethyldibismuthine is an extremely labile compound. It decomposes thermally at 25 °C with nearly quantitative formation of trimethylbismuthine and bismuth metal. In a dilute benzene solution, **1a** has a half-life of approximately 6 h. Tetramethyldistibine shows the analogous reaction at 160–200 °C.[12] Reaction of **1a** with I_2 occurs instantly at 25 °C with the formation of $(CH_3)_2BiI$, $(CH_3)BiI_2$, BiI_3, and Bi. Tetramethyldibismuthine fumes in air but is stable toward water.

As reported by Paneth, the red-yellow liquid tetramethyldibismuthine freezes reversibly at −12.5 °C to well-formed iridescent violet-blue crystals. The diffuse reflectance spectrum of solid **1a** shows a broad maximum at λ 665 nm. Pentane solutions of **1a** show only λ_{max} at 220 (ϵ 37 000) and 264 (7200) with a featureless low intensity tail to 700 nm. In comparison solid **1b** (mp 17.5 °C) shows a diffuse reflectance max at 530 nm, while cyclohexane solutions show λ_{max} <215 with a featureless tail to 360 nm. Neither tetramethyldiarsine nor tetramethyldiphosphine show thermochromic properties on melting.

This red shift between solid and liquid phase is similar to that reported for molecular iodine,[13] certain distibines,[1,14] ditellurides[15] and diselenides.[15] It appears to be a common property of many of the diatomic-like compounds of elements in the lower right-hand corner of the periodic table. Several of these compounds have been shown to display extended bonding in the solid phase.[16] Whether the solid phase colors of **1a** and **1b** are due to this effect must await the results of X-ray crystal structure determinations now in progress.

Acknowledgment. Support of our work by the A.F. O.S.R. (Grant No. 81-099) is gratefully acknowledged.

Registry No. 1a, 82783-70-8; trimethylbismuthine, 593-91-9; 1,2-dichloroethane, 107-06-2; I_2, 7553-56-2.

---

(1) Paneth, F. A.; Loleit, H. *J. Chem. Soc.* **1935**, 366.

(2) For possible early preparations of tetraphenyldibismuthine, see: (a) Gilman, H.; Yablunky, H. L. *J. Am. Chem. Soc.* **1941**, *63*, 212. (b) Wiberg, E.; Mödritzer, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem. Biochem., Biophys., Biol.* **1957**, *12B*, 132. (c) Dessy, R. E.; Chivers, T.; Kitching, W. *J. Am. Chem. Soc.* **1966**, *88*, 467.

(3) For low temperature dimers of bismabenzene see: Ashe, A. J., III *Tetrahedron Lett.* **1976**, *415*. Ashe, A. J., III; Diephouse, T. R.; El-Sheikh, M. Y. *J. Am. Chem. Soc.*, in press.

(4) Becker, G.; Rössler, M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *B37*, 91.

(5) Breunig, H. J.; Müller, D. *Angew. Chem.* **1982**, *94*, 448.

(6) Meinema, H. A.; Martens, H. F.; Noltes, J. G. *J. Organomet. Chem.* **1973**, *51*, 223.

(7) Long, L. H.; Sachman, J. F. *Trans. Faraday Soc.* **1954**, *50*, 1177.

(8) Experimental procedure: The addition of 0.5 g (22 mmol) of sodium to 2.9 g (11 mmol) of trimethylbismuthine in 100 mL of liquid ammonia at −33 °C gave a red solution of sodium dimethylbismuthide. After addition of 1.1 g (11 mmol) of 1,2-dichloroethane, the ammonia was allowed to evaporate. The residue was extracted with pentane and filtered. Three recrystallizations from pentane at −20 °C gave 2.6 g (70%) of pure tetramethyldibismuthine.

(9) Durig, J. R.; Casper, J. M. *J. Chem. Phys.* **1971**, *55*, 198.

(10) Durig, J. R.; DiYorio, J. S. *Inorg. Chem.* **1969**, *8*, 2796.

(11) On the basis of a diatomic model, the force constants are BiBi, 1.88 × 10^5 dyn cm^{-1}; SbSb, 2.31 × 10^5 dyn cm^{-1}; AsAs, 2.80 × 10^5 dyn cm^{-1}; PP, 3.01 × 10^5 dyn cm^{-1}.

(12) Burg, A. B.; Grant, L. R. *J. Am. Chem. Soc.* **1959**, *81*, 1.

(13) Pimentel, G. C. *J. Chem. Phys.* **1951**, *19*, 446. Hach, R. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4321.

(14) Ashe, A. J., III; Butler, W.; Diephouse, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 207.

(15) Sandman, D. J.; Stark, J. C.; Foxman, B. M. *Organometallics* **1982**, *1*, 739.

(16) For a molecular orbital model see: Hughbanks, T.; Hoffmann, R.; Whangbo, M.-H.; Stewart, K. R.; Eisenstein, O.; Canadell, E. *J. Am. Chem. Soc.* **1982**, *104*, 3876.

Synthesis Gas Incorporation into Acylmanganese Pentacarbonyls

John H. Freudenberger and Milton Orchin*

Department of Chemistry, University of Cincinnati
Cincinnati, Ohio 45221

Received June 25, 1982

Summary: Hexane solutions of $Ph(CH_2)_xC(O)Mn(CO)_5$ (x = 1 or 2) treated with 2400 psi of CO/H_2 at 70 °C gave $Ph(CH_2)_{x+1}$–$OC(O)Mn(CO)_5$. The incorporation of the syn gas probably occurs stepwise and may be represented as follows: $RC(O)Mn(CO)_5 \xrightarrow{H_2/CO} RCH_2OMn(CO)_4 \xrightarrow{2CO} RCH_2OC(O)Mn(CO)_5$. In contrast, the same reactions carried out in sulfolane yielded only the aldehydes, $Ph(CH_2)_xCHO$. Speculation on a mechanism consistent with these results is presented.

0276-7333/82/2301-1408$01.25/0 © 1982 American Chemical Society