

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

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

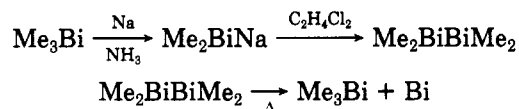
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109

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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 trimethylbismuthine⁷ with sodium in liquid ammonia afforded a red solution of NaBi(CH₃)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/cm³).⁸ The ¹H NMR and ¹³C NMR spectra (C₇D₈) 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 tetramethyldiphosphine¹⁰ 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



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 I₂ occurs instantly at 25 °C with the formation of (C-H₃)₂BiI, (CH₃)BiI₂, BiI₃, 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} ditellurides¹⁵ 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.

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Registry No. **1a**, 82783-70-8; trimethylbismuthine, 593-91-9; 1,2-dichloroethane, 107-06-2; I₂, 7553-56-2.

(11) On the basis of a diatomic model, the force constants are BiBi, 1.88 × 10⁶ dyn cm⁻¹; SbSb, 2.31 × 10⁶ dyn cm⁻¹; AsAs, 2.80 × 10⁶ dyn cm⁻¹; PP, 3.01 × 10⁶ dyn cm⁻¹.

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 (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.
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Synthesis Gas Incorporation Into Acylmanganese Pentacarbonyls

John H. Freudenberger and Milton Orchin*

Department of Chemistry, University of Cincinnati
Cincinnati, Ohio 45221

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Summary: Hexane solutions of Ph(CH₂)_xC(O)Mn(CO)₅ (x = 1 or 2) treated with 2400 psi of CO/H₂ at 70 °C gave Ph(CH₂)_{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 $\xrightarrow{\text{H}_2/\text{CO}}$ RCH₂OMn(CO)₄ $\xrightarrow{2\text{CO}}$ RCH₂OC(O)Mn(CO)₅. In contrast, the same reactions carried out in sulfolane yielded only the aldehydes, Ph-(CH₂)_xCHO. Speculation on a mechanism consistent with these results is presented.