Organometallics **1983,** *2,* 1859–1866

removed under vacuum below 0 °C. This gave an orange solid residue to which 8.5 mg (0.0309 mmol) of $(C_6H_5)_3SiCH_3$ standard was added. The mixture was extracted with $CDCl_3$, $(CH_3)_4Si$ was added, and the ^1H NMR yields given in the results section were obtained. The ^1H NMR resonances utilized were as followed: **16**, δ 5.79;[12] (SS,RR)-$(\eta$-$C_5H_5)Re(NO)(PPh_3)(CH(OCH_3)C_6H_5)$, δ 4.89 and 2.67;[7b] (SR,RS)-$(\eta$-$C_5H_5)Re(NO)(PPh_3)(CH(OCH_3)C_6H_5)$, δ 4.65 and 2.55;[7b] $(\eta$-$C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ δ 4.73.[7b]
na

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support ofthis research. FT NMR spectra were recorded on spectrometers obtained via NSF departmental instrumentation grants. We are grateful to V. K. Wong and W. G. Hattan for assistance with this study. W.E.B. and J.H.M. thank the Regents of the University of California for fellowships; J.H.M. also thanks the Chevron Corp. for a fellowship.

Registry No. **1**, 82293-79-6; (–)-(*R*)-**1**, 82336-22-9; (+)-(*S*)-**1**, 87480-09-9; **2**, 82582-46-5; (–)-(*R*)-**2**, 87412-37-1; (+)-(*S*)-**2**, 87480-06-6; **3**, 82582-47-6; **4**, 87412-24-6; **5**, 76770-59-7; (–)-(*S*)-**5**, 87480-05-5; (+)-(*R*)-**5**, 87480-04-4; **6**, 82582-48-7; **7**, 87412-25-7; (–)-(*R*)-**7**, 87480-07-7; (+)-(*S*)-**7**, 87480-08-8; **8**, 87412-26-8; **9**, 87412-27-9; **10**, 87412-28-0; (–)-(*R*)-**11**, 82336-34-3; (+)-(*S*)-**11**, 82336-35-4; **12**, 87412-29-1; **13**, 71763-28-5; (–)-(*R*)-**13**, 82336-32-1; (+)-(*S*)-**13**, 82336-33-2; **14**, 87412-30-4; **15**, 87412-32-6; **16**, 76770-58-6; **17**, 87412-34-8; **18**, 87412-36-0; (SS,RR)-$(\eta$-$C_5H_5)Re(NO)(PPh_3)(CH(OCH_3)C_6H_5)$, 76770-56-4; (SR,RS)-$(\eta$-$C_5H_5)Re(NO)(PPh_3)(CH(OCH_3)C_6H_5)$, 76821-65-3.

Preparation and Properties of Dibismuthines

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Tetramethyldibismuthine, **1**, tetraisopropenyldibismuthine, **15**, 1,1′-bibismolane, **16**, and tetrakis(2-methyl-1-propenyl)dibismuthine, **17**, have been prepared from the reaction of the corresponding tertiary bismuthines with sodium in liquid ammonia followed by treatment with 1,2-dichloroethane. Tetraphenyldibismuthine, **4**, was prepared by an analogous route from diphenylbismuth chloride. While all the dibismuthines are red in solution, **1**, **15**, and **16** freeze to blue solids. Compounds **4** and **17** form red solids. The Raman, UV, and mass spectra of the dibismuthines are discussed. The dibismuthines thermally decompose to form bismuth metal and corresponding tertiary bismuthine. The reactions of tetramethyldibismuthine with iodine, bromotrichloromethane, benzyl bromide, hydrochloric acid, and butyllithium have been explored. The reactions afford products in which the Bi–Bi bond has been cleaved.

Introduction

Although tetramethyldibismuthine, **1**, was reported in 1935,[1] the intervening years have seen little sustained interest in compounds containing bismuth–bismuth bonds.[2–4] This situation changed abruptly in 1982 with reports of the synthesis of tetrakis(trimethylsilyl)dibismuthine, **2**,[5] tetraethyldibismuthine, **3**,[6] and a reinvestigation of tetramethyldibismuthine.[7] More recently, tetraphenyldibismuthine, **4**,[8] and a series of tetraalkyldibismuthines, **5**, **6**, and **7**,[9] have been characterized.

$\underset{\mathbf{1}}{Me_4Bi_2}$ $\underset{\mathbf{2}}{(Me_3Si)_4Bi_2}$ $\underset{\mathbf{3}}{Et_4Bi_2}$

$\underset{\mathbf{4}}{Ph_4Bi_2}$ R_4Bi_2
5, R = Pr
6, R = Bu
7, R = *i*-Pr

The major reason for this renaissance of interest in dibismuthine chemistry has been the hope that dibismuthines might show the same dramatic thermochromic effects which have been observed for distibines. For example, the distibine tetramethylbistibolyl, **8**, forms blue crystals which melt reversibly to a yellow oil. A crystal structure of **8** shows that the Sb atoms are aligned in linear chains with very short "intermolecular" Sb···Sb contacts.[10] Apparently the solid-phase color is associated with this extended bonding along the Sb–Sb···Sb–Sb chains.[11] Similar thermochromic effects are found for tetramethyldistibine, **9**,[1] tetrakis(trimethylsilyl)distibine, **10**,[12,13] tetraisopropenyldistibine, **11**,[14] and bistibolane, **12**.[15] Crystal structures show that **9**[16] and **10**[13] have intermolecular association similar to that of **8**. On the other hand, distibines such as tetraphenyldistibine, **13**,[17] and tetra-

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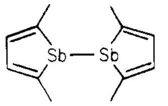
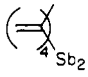
isobutenyldistibine, **14**,[14] do not show thermochromic effects. Probably the bulky substituents of **13**[13] and **14**[14] prevent the close intermolecular Sb···Sb interactions.


8

Me_4Sb_2
9

$(Me_3Si)_4Sb_2$
10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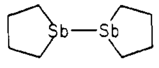
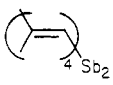
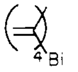

12

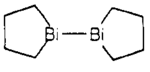
Ph_4Sb_2
13


14

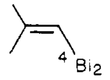
Preliminary results indicate that tetramethyldibismuthine,[7] tetrakis(trimethylsilyl)dibismuthine,[5] and probably tetraethyldibismuthine[6] are thermochromic, although it is less certain whether the tetraalkyldibismuthines **5**, **6**, and **7** are.[9] In order to systematically compare dibismuthines with distibines, we decided to prepare compounds **1**, **15**, **16**, **4**, and **17**. These dibismuthines represent a variety of structural types. Compounds **1**, **15**, and **16** are analogues of the thermochromic distibines while **4** and **17** are analogues of nonthermochromic distibines. We have made a preliminary report on **1**[7] while during the course of our work the Calderazzo group reported on **4**.[8] We now wish to report in detail on the synthesis and spectra of these dibismuthines. Since little other chemical data are available, we have also undertaken a detailed comparison of the chemical properties of **1** with those of tetramethyldistibine and tetramethyldiarsine.

Me_4Bi_2
1


15


16

Ph_4Bi_2
4


17

Results and Discussion

Synthesis. In 1935 Paneth reported that the reaction between methyl radicals and a heated bismuth mirror gave a trace of tetramethyldibismuthine.[1] Although the Paneth synthesis is interesting from a historial prospective, it did not appear to be a promising preparative method. On the other hand, a variety of distibines have been prepared in high yields by using the coupling reactions of sodium diorganostibides.[19] We find that this method also works well for preparing dibismuthines.

Like most tertiary bismuthines, trimethylbismuthine is readily available from the reaction of the appropriate Grignard reagent with bismuth trichloride.[20] The reaction of trimethylbismuthine with sodium in liquid ammonia gave an intensely red solution of sodium dimethylbimuthide. Treatment with 1,2-dichloroethane afforded a 70% yield of tetramethyldibismuthine as a viscous red oil. This liquid freezes reversibly at −12.5 °C to violet-blue crystals. Purification is most conveniently accomplished by recrystallization from cold (−20 °C) pentane. In the same manner, triisopropenylbismuthine gave a 67% yield of tetraisopropenyldibismuthine as blue crystals, mp 13.5 °C, while tetraisobutenyldibismuthine was obtained in 80% yield as red crystals, mp 29 °C.

The reaction of 1-phenylbismolane with sodium in liquid ammonia takes place with preferential cleavage of the phenyl rather than the tetramethylene moiety since subsequent treatment with 1,2-dichloroethane gave a good yield of the 1,1′-bibismolane.[21] Interestingly, the reaction of triphenylbismuthine with sodium in liquid ammonia gave a red solution suggesting the formation of sodium diphenylbismuthide. However, on subsequent treatment with 1,2-dichloroethane, no tetraphenyldibismuthine was obtained. On the other hand, the similar reaction of diphenylbismuth chloride with sodium in liquid ammonia gave a reasonable yield of the red crystalline tetraphenyldibismuthine. In 1940, Gilman had obtained (but did not isolate) this dibismuthine by this same route.[2a] More recently this procedure was repeated by Calderazzo.[8]

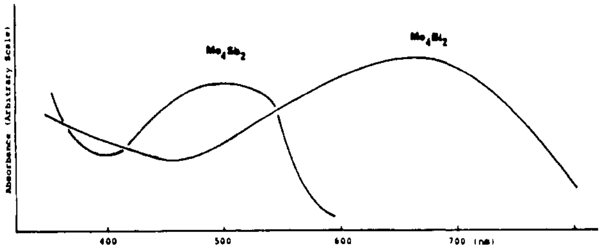
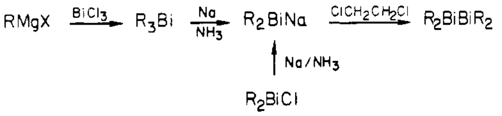


Figure 1. The diffuse reflectance spectra of tetramethyldistibine, **9**, and tetramethyldibismuthine, **1**. The vertical scale is arbitrary.


$$\begin{tikzcd} RMgX \arrow[r, "BiCl_3"] & R_3Bi \arrow[r, "Na", "NH_3"'] & R_2BiNa \arrow[r, "ClCH_2CH_2Cl"] & R_2BiBiR_2 \\ & & R_2BiCl \arrow[u, "Na/NH_3"'] & \end{tikzcd}$$

Dibismuthines **1**, **15**, and **17** are heavy red liquids. The density of tetramethyldibismuthine at 20 °C is 2.85 g/cm^3. Tetramethyldibismuthine and tetraisopropenyldibismuthine freeze to blue-violet crystals, while tetraisobutenyldibismuthine forms red crystals. 1,1-Bibismolane and tetraphenyldibismuthine, respectively, form blue and red crystals. All the dibismuthines are soluble in hydrocarbon solvents giving red solutions in pentane or toluene. Thus dibismuthines **1**, **15**, and **16** are thermochromic while **4** and **17** are not.

UV–Visible Spectra. The solution UV spectra of **1**, **15**, **16**, and **17** show maxima near 270 nm, while tetraphenyldibismuthine has maxima at 310 and 362 nm. The most characteristic feature of the visible spectra is a low intensity featureless tail extending out to ~700 nm. Presumably this tail corresponds to the red color of the dibismuthine.

The colors of the solid dibismuthine have been characterized by their diffuse reflectance spectra. The reflectance spectrum of **1** illustrated in Figure 1 shows a very broad absorption maximum centered at 670 nm. Thermochromic dibismuthines **15** and **16** show similar spectra with broad maxima centered at 575 and 580 nm, respectively. These maxima are 300–400 nm red-shifted from their solution maxima. For comparison, the nonthermochromic **17** shows a reflectance maximum at ~300 nm which is close to its solution maximum.

We have found a complete match of thermochromic properties for dibismuthines with the corresponding distibines. Thus, dibismuthines **1**, **2**, **3**, **15**, and **16** are thermochromic as are the analogous distibines **9**, **18**, **10**, **11**, and **12**. Nonthermochromic dibismuthines **4** and **17** correspond to the nonthermochromic distibines **13** and **14**. Since distibines **8**[10] and **19**[14] are known to be thermochromic, it seems likely that the unknown tetramethylbibismolyl, **20**, and tetravinyldibismuthine, **21**, will also

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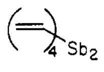
Table I. A Comparison of the Diffuse Reflectance Absorption Maxima (nm) of Dibismuthines with the Corresponding Distibines

R_4E_2	Bi	Sb	Δ(Bi–Sb)
R = CH_3	665	530	135
R = isopropenyl	575	475	100
R_2 = $(CH_2)_4$	580	490	90
R_2 = $((CH_3)_2C_4H_2)$		605	

show thermochromic properties. To date we have been unable to prepare these materials.

Et_4Sb_2
18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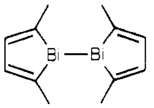
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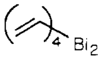
21

Figure 1 illustrates a comparison of the reflectance spectra of the thermochromic tetramethyldibismuthine and tetramethyldistibine. The absorption maximum of the dibismuthine is considerably broader and is red-shifted ~135 nm from the distibine maximum. The tetraisopropenyldibismuthine and bibismolane show similar red shifts compared to **11** and **12** (see Table I). On this basis, tetramethylbibismolyl, **20**, should have maximum absorption close to 800 nm.

The close analogy of the optical properties of solid dibismuthines with those of the corresponding distibines strongly suggests similar solid-phase structures. We confidently predict that the bismuth atoms of the thermochromic dibismuthines are aligned in linear chains with close intermolecular metal contacts. The solid-phase color is probably due to electronic excitation along this Bi–Bi···Bi–Bi chain.

Mass Spectra. The mass spectra have been determined on samples volutized from a heated solid probe by using electron-impact ionization (70 eV). The spectra of **1**, **15**, **16**, and **17** show very similar fragmentation patterns summarized in Table II. These dibismuthines show weak but easily observable molecular ions followed by weak peaks for sequential loss of carbon groups. Fragmentation to R_2Bi^+, RBi^+, and Bi^+ are much more intense. However, these fragments are also important in the mass spectra of the corresponding tertiary bismuthines, which are themselves thermolysis products of dibismuthines.

Under these conditions, tetraphenyldibismuthine shows no molecular ions. In fact, its spectrum is identical with that shown by triphenylbismuthine.

Raman Spectra. Raman spectroscopy is a most useful and convenient method for characterizing the dibismuthines. The five dibismuthines we have studied show intense polarized bands near 110 cm^{-1} (see Table III). That these bands are insensitive to the nature of the substituents suggests that they are due largely to localized Bi–Bi vibrations. For comparison the symmetrical stretching frequency of Bi_4 has been found to be 152 cm^{-1}.[22]

It is interesting to compare the Bi–Bi stretching frequency of tetramethyldibismuthine with the corresponding bands of other tetramethyldipictnogen compounds. The 110 cm^{-1} band of solid **1** corresponds to 179 cm^{-1} Sb–Sb band of tetramethyldistibine,[23,24] the 271 cm^{-1} As–As band of tetramethyldiarsine,[25] and the 455 cm^{-1} P–P band of tetramethyldiphosphine.[26] This shift to lower frequency for the heavier dipictnogen bands exceeds that expected for increasing mass and is consistent with a progressive weakening of the vibrational force constants.[27] A very similar trend has been noted for the group 4 series, hexamethyldisilicon, -germanium, -tin, and -lead.[28]

The Raman spectra of the liquid samples of tetramethyldiarsine, -diphosphine, and -distibine show new bands not present in the spectra of solid samples.[23-26] Analyses of the vibrational spectra of these compounds indicates that all three crystallize in the trans rotomer conformation (C_{2h} symmetry). The new bands suggest that a second, probably a gauche (C_2 symmetry) conformer, is also present in the liquid. By comparison, tetramethylhydrazine appears to populate exclusively the gauche conformation in both liquid and solid phases.[29] The Raman spectrum of **1** is virtually identical in solid and liquid phase. Excluding the possibility that the gauche has the same bands as the trans conformer, one concludes that only a single (presumably trans) conformer is populated in both phases. If this conclusion is correct, the heavier hydrazine analogues show an increasing preference for the trans over gauche conformers.[30]

Chemical Characterization. The dibismuthines are all highly sensitive to oxygen but may be conveniently handled by using drybox or Schlenk-ware techniques. They are unreactive toward water, mild acids, and bases. Tetramethyldibismuthine decomposes thermally at 25 °C with nearly quantitative formation of trimethylbismuthine and bismuth metal. In a dilute solution in benzene, it shows a half-life of approximately 6 h. 1,1′-Bibismolane decomposes at a similar rate to bismuth metal and uncharacterized apparently polymeric bismuthines. The other alkyldibismuthines (**3**, **5**, **6**, and **7**) have a similar stability. Qualitatively, the tetravinyldibismuthines are much more stable. Dilute benzene solutions of **15** and **17** survive for more than a week at 25 °C. Each yields decomposition products of the corresponding tertiary bismuthine and bismuth metal. Tetraphenyldibismuthine is the most stable of the five dibismuthines. Crystals of **4** may be stored at room temperature. On heating to about 100 °C, it darkens with formation of triphenylbismuthine and bismuth metal:

$$R_4Bi_2 \xrightarrow[\Delta]{} R_3Bi + Bi$$

The thermal decomposition reactions are analogous to reactions reported for distibines and diarsines.[31] Tetramethyldistibine undergoes qualitative formation of antimony metal and trimethylstibine only at 160–200 °C.[32] Diarsines are even more robust. Tetraphenyldiarsine yields arsenic and triphenylarsine at 300 °C[33] while tetramethyldiarsine gives arsenic and polyarsenomethane.[34]

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(27) With the assumption of a diatomic model, the stretching constants are calculated to be as follows: BiBi, 0.74 × 10^5 dyn cm^{-1}; SbSb, 1.15 × 10^5 dyn cm^{-1}; AsAs, 1.62 × 10^5 dyn cm^{-1}; PP, 1.87 × 10^5 dyn cm^{-1}. The values quoted in ref 7, footnote 11, are in error.

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(31) The reaction is also very similar to the thermal decomposition of hexamethyldilead. See: Arnold, D. P.; Wells, P. R. *J. Organomet. Chem.* **1976**, *111*, 269, 285. Puddephatt, R. J.; Thistlewaite, G. H. *Ibid.* **1972**, *40*, 143. Cooper, J.; Hudson, A.; Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1056.

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Table II. Mass Spectra of Organodibismuthines R_4Bi_2 [a]

	R			R	
ion	CH_3	isopropenyl	$R_2 = (CH_2)_4$	C_6H_5	2-methyl-1-propenyl
R_4Bi_2	478 (2.6)	582 (1.3)	530 (4.2)		638 (0.1)
R_3Bi_2	463 (3.7)	541 (5.4)		649 (0.8)	583 (0.1)
R_2Bi_2	448 (2.0)	500 (0.4)	474 (2.8)		528 (0.1)
RBi_2	434 (3.4)	459 (9.8)			473 (0.2)
Bi_2H		419 (2.9)	419 (1.5)		419 (0.1)
Bi_2	418 (4.9)	419 (5.3)	418 (18.8)		418 (0.5)
R_2Bi	239 (79.3)	291 (25.3)	254 (58.9)	363 (25)	319 (40.8)
RBi	224 (62.3)	250 (44.6)		286 (63.8)	264 (99.8)
Bi	209 (100)	209 (100)	209 (100)	209 (100)	209 (100)
R_2-H		81 (2.5)	55 (18.3)		109 (60)

[a] The *m/e* values are given followed by the relative intensities in parentheses.

Table III. γ_{BiBi} (cm^{-1}) from the Raman Spectra of R_4Bi_2 in Solid and Liquid Phases

	γ_{BiBi}	
R_4Bi_2	liquid	solid
$R = CH_3$	111	109
R = isopropenyl	116	111
$R_2 = (CH_2)_4$	110	111
R = 2-methyl-1-propenyl	108	111
$R = C_6H_5$		103

These thermal decompositions appear to take place via a free radical mechanism. The decomposition of tetramethyldibismuthine in benzene is slow in the dark but takes place rapidly on ultraviolet irradiation. Interestingly, the thermal decompositions take place very much more rapidly in carbon tetrachloride or chloroform. Even the relatively stable tetraphenyldibismuthine rapidly darkens in chloroform at 25 °C. This result appears to be analogous to the reaction of dialkylmercury compounds with carbon tetrachloride.[35] It was found that di-*tert*-butylmercury in carbon tetrachloride was able to initiate other free radical reactions apparently through the direct production of charge-transfer radicals.

We wish to propose the following very tentative mechanism for decomposition of tetramethyldibismuthine.

$$Me_4Bi_2 \xrightarrow[(\text{or } \Delta)]{h\nu} 2Me_2Bi\cdot \quad (1)$$

$$Me_2Bi\cdot + Me_4Bi_2 \rightarrow 2Me_3Bi + Bi^0 \quad (2)$$

If this mechanism pertains, it is fairly surprising that $ClBiMe_2$ was not observed in either CCl_4 or $CHCl_3$. This suggests that abstraction of Cl from CCl_4 by $Me_2Bi\cdot$ (eq 3) is slower than reaction of $Me_2Bi\cdot$ with Me_4Bi_2 (eq 2).

$$Me_2Bi\cdot + CCl_4 \nrightarrow Me_2BiCl + \cdot CCl_3 \quad (3)$$

In order to try to divert dimethylbismuth radicals by processes similar to (3), we have explored the thermal decomposition of tetramethyldibismuthine in the presence of the more reactive bromotrichloromethane. On addition of tetramethyldibismuthine to a tetrahydrofuran solution of bromotrichloromethane, a mirror of bismuth metal was deposited almost instantly. The major products were now dimethylbismuth bromide and a second compound we identified by its mass spectrum as dimethyl(trichloromethyl)bismuthine. Because of its lability, we have been unable to purify this material. Smaller quantities of trimethylbismuthine and the radical termination products hexachloroethane and tetrachloroethylene were also found.

Analogously the reaction of tetramethyldibismuthine with benzyl bromide in benzene quickly gave bismuth metal and trimethylbismuthine. Smaller quantities of dimethylbismuth bromide and benzyldimethylbismuthine were also isolated. The benzyldimethylbismuthine was identical with an authentic sample prepared from benzylmagnesium chloride and dimethylbismuth bromide. See eq 4–8.

$$Me_2Bi\cdot + BrCCl_3 \rightarrow Me_2BiBr + \cdot CCl_3 \quad (4)$$

$$\cdot CCl_3 + Me_4Bi_2 \rightarrow Me_2BiCCl_3 + MeBi\cdot \quad (5)$$

or

$$Me_2Bi\cdot + BzBr \rightarrow Me_2BiBr + Bz\cdot \quad (6)$$

$$Bz\cdot + Me_4Bi_2 \rightarrow BzBiMe_2 + Me_2Bi\cdot \quad (7)$$

$$Ph_3CBr + Me_2Bi\cdot \rightarrow Ph_3C\cdot + Me_2BiBr \quad (8)$$

Unfortunately, we have been unable to detect $Me_2Bi\cdot$ directly by ESR spectroscopy. However, when triphenylmethyl bromide was added to tetramethyldibismuthine in isooctane, we observed the ESR detectable triphenylmethyl-free radical as well as dimethylbismuth bromide. We presume they are formed as in eq 8.[36]

For comparison, we have examined the corresponding reactions of tetramethyldistibine and tetramethyldiarsine with benzyl bromide and bromotrichloromethane.[37] These reactions are much cleaner and take place more slowly than the dibismuthine reactions. Benzyl bromide reacted with tetramethyldistibine in benzene at 25 °C to give exclusively dimethylantimony bromide and benzyldimethylstibine. In a similar manner the reaction of bromotrichloromethane with tetramethyldistibine in tetrahydrofuran at 25 °C gave dimethylantimony bromide and (trichloromethyl)dimethylstibine. Again, tetramethyldiarsine gave analogous products on reactions with benzyl bromide in benzene at 150 °C and bromotrichloromethane in tetrahydrofuran at 150 °C. Under these conditions, we found no free Sb or As and no trimethylpictnogen. If these reactions are taking place by radical mechanisms analogous to eq 4–7,[38] this implies that the steps analogous to eq 4 and 6 are much faster than steps 2.

$$Me_4E_2 + BzBr \xrightarrow[\Delta]{} Me_2EBz + Me_2EBr$$

$$Me_4E_2 + BrCCl_3 \xrightarrow[\Delta]{} Me_2ECCl_3 + Me_2EBr$$

$$E = As, Sb$$

In order to be able to place dibismuthine chemistry in context, we have examined several other reactions that have been reported for diarsines and distibines. The reactions of tetramethyldiarsine and tetramethyldistibine

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[34] Dehn, W. M.; Williams, E. *Am. Chem. J.* **1908**, *40*, 103.

[35] Nugent, W. A.; Kochi, J. K. *J. Organomet. Chem.* **1977**, *124*, 371.

[36] For a similar result with $Mn_2(CO)_{10}$ see: Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065.

[37] For analogous reactions of diarsine compounds see: Cullen, W. R.; Hota, N. K. *Can. J. Chem.* **1964**, *42*, 1123. Cullen, W. R. *Ibid.* **1960**, *38*, 439.

[38] Alternative heterolytic mechanisms have not been excluded.

with iodine are clean giving only the corresponding dimethyl pictnogen iodide:

$$Me_4As_2 + I_2 \rightarrow 2Me_2AsI$$ [39]

$$Me_4Sb_2 + I_2 \rightarrow 2Me_2SbI$$ [1]

In contrast the reaction of tetramethyldibismuthine is quite indiscriminate, yielding all the possible iodo- and methylbismuthines as well as bismuth metal:

$$I_2 + Me_2Bi_2 \rightarrow Bi^0 + BiMe_3 + BiMe_2I + BiMeI_2 + BiI_3$$

The formation of bismuth metal and trimethylbismuth suggests the intermediacy of $Me_2Bi\cdot$ radicals. However, the production of $BiMeI_2$ is somewhat puzzling since only a trace of methyl iodide was detected. It may be that the $BiMeI_2$ was formed by exchange reaction of $BiMe_3$ with BiI_3 (itself formed from Bi^0 and I_2). Mixing $BiMe_3$ and BiI_3 very rapidly forms a mixture of the methylbismuth iodides:

$$BiMe_3 + BiI_3 \rightleftharpoons MeBiI_2 + Me_2BiI$$

Reaction with HCl. Burg has shown that the reaction of tetramethyldistibine with an excess of HCl gave hydrogen gas and dimethylantimony chloride.[32] We have repeated this reaction at −78 °C. An equivalent of HCl in CS_2 gives a mixture of dimethylantimony chloride and dimethylstibine. The latter product is known to react with excess HCl to give hydrogen and dimethylantimony chloride.[32]

$$Me_4Sb_2 \xrightarrow{HCl} Me_2SbCl + Me_2SbH \xrightarrow{HCl} H_2 + Me_2SbCl$$

The reaction of tetramethyldibismuthine with HCl gives hydrogen gas, bismuth metal, trimethylbismuthine, and dimethylbismuth chloride. At −78 °C, a labile bismuth-containing intermediate, presumably dimethylbismuthine, can be detected. On warming hydrogen gas is produced. Dimethylbismuthine may be prepared independently by the $LiAlH_4$ reduction of dimethylbismuth bromide. As reported by Amberger, dimethylbismuthine decomposes to hydrogen, bismuth metal, and trimethylbismuthine.[40] However, we find this secondary bismuthine to be more labile than had been reported.

Thus we feel that the reaction of tetramethyldibismuthine with HCl takes the same initial step as does the distibine:

$$Me_4Bi_2 \xrightarrow{HCl} Me_2BiCl + Me_2BiH \rightarrow H_2 + Bi^0 + BiMe_3$$

Reactions with Butyllithium. The reaction of butyllithium with tetramethyldistibine affords largely butyldimethylstibine with smaller quantities of dibutylmethylstibine and tributylstibine. The latter two products are probably not primary products from the reaction of the distibine, since tertiary stibines undergo exchange with butyllithium.[41] Thus treating trimethylstibine with butyllithium gave butyldimethylstibine, dibutylmethylstibine, and tributylstibine. Whether these reactions occur through a direct displacement or via the intermediacy of an "ate" complex is problematical:

$$BuLi + Me_4Sb_2 \rightarrow Me_2SbLi + Me_2SbBu \xrightarrow{BuLi} MeLi + MeSbBu_2 \xrightarrow{BuLi} MeLi + SbBu_3$$

$$([BuMe_2Sb\text{–}SbMe_2]^-Li^+, \text{“ate” complex})$$

Tetramethyldibismuthine reacts in a similar fashion. The addition of butyllithium in hexane to tetramethyldibismuthine immediately gave a deep red solution suggesting formation of lithium dimethylbismuthide. The major product was butyldimethylbismuthine along with smaller quantities of trimethyl-, dibutylmethyl-, and tributylbismuthine. The same product mixture may be obtained by treating trimethylbismuthine with butyllithium.[42]

$$Me_4Bi_2 \xrightarrow{BuLi} Me_2BiLi + Me_2BiBu \xrightarrow{BuLi} MeLi + MeBiBu_2 \xrightarrow{BuLi} MeLi + Bu_3Bi$$

$$Me_3Bi \xrightarrow{BuLi} MeLi + BuMe_2Bi \xrightarrow{BuLi} MeLi + Bu_2MeBi \xrightarrow{BuLi} MeLi + Bu_3Bi$$

In summary, tetramethyldibismuthine is a very labile compound. It reacts with free radical, electrophilic, and nucleophilic reagents. The products invariably result from cleavage of the Bi–Bi band.

Experimental Section

General Remarks. Proton NMR spectra were run on either a Varian Associates T60A or a Bruker WM360 NMR spectrometer, and ^{13}C NMR spectra were recorded on a JEOL FX90Q spectrometer. Tetramethylsilane was used as an internal reference. IR spectra were obtained on a Beckman IR 4240 spectrophotometer calibrated with the polystyrene 1601.4 cm^{-1} absorption band. UV–visible spectra were obtained on a Varian Associates Cary 219 spectrophotometer, and solid reflectance data were determined on the same instrument using a Varian Associates in-cell space diffuse reflectance accessory. This was accomplished by placing the sample on a microscope slide topped with a coverslip, and the sample was frozen by clamping a piece of dry ice against it. Mass spectral determinations were made by using a Finnigan 4023 GC/MS with an electron ionization energy of 70 eV. The dibismuthines were ionized from a solid probe, and the various reaction mixtures were analyzed through separation by the GC/MS system. This was done by using a 6 ft × $^1/_4$ in. glass column packed with 5% SE-30 on Carbowax. An initial column temperature of 60 °C was increased at a rate of 10 °C/min to 200 °C under a helium flow of 20 mL/min. The injector temperature was maintained at 150 °C. Raman spectra were obtained on a Spex 1401 double spectrometer using the 6328-Å excitation line of a Spectra Physics Model 125 helium neon laser. The ESR spectra were recorded on a Bruker ER 200E-SRC spectrometer from samples in 4-mm polished quartz tubes. Gas chromatographic separations were performed by using an Antek 300 GC equipped with thermal conductivity detector. Most bismuth compounds showed extensive thermal decomposition on chromatography. Relative concentrations determined by GC were unreliable. Where possible, we quote concentrations determined from the ^1H NMR spectra.

All operations were performed under argon or nitrogen.

Elemental analyses were performed either by Galbraith Laboratories or Spang Microanalytical Laboratories. Because of their lability, it was not possible to obtain microanalyses of most of the bismuth compounds.

Triisopropenylbismuthine. The reaction of bismuth trichloride (7.9 g, 25 mmol) in 60 mL of tetrahydrofuran with isopropenylmagnesium bromide, which had been prepared from 2.4 g (100 mmol) of magnesium turnings and 12.1 g (100 mmol) of isopropenyl bromide in 50 mL of tetrahydrofuran, gave 6.5 g (78%) of triisopropenylbismuthine[43] as a clear, colorless, air-sensitive liquid: bp 35–37 °C (0.01 torr); ^1H NMR (C_7D_8) δ 2.43 (dd, J = 1.8, 1.3 Hz, CH_3), 5.64 (dq, J = 1.5, 1.3 Hz, H_{cis}), 6.91 (dq, J = 1.5, 1.8 Hz, H_{trans});[44] ^{13}C NMR (C_7D_8, 90.56 MHz) δ 29.3 (CH_3), 126.3 (C_β), 162.2 (br, C_α).

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[39] Montimer, C. T.; Skinner, H. A. *J. Chem. Soc.* **1952**, 4331.

[40] Amberger, E. *Chem. Ber.* **1961**, *94*, 1447.

[41] Woods, L. A.; Gilman, H. *Proc. Iowa Acad. Sci.* **1941**, *48*, 251.

[42] For a similar reaction see: Gilman, H.; Yale, H. L. *J. Am. Chem. Soc.* **1950**, *72*, 8.

[43] Borisov, A. E.; Osinova, M. A.; Nesmeyanov, A. N. *Izv. Akad. Nauk SSSR* **1963**, 1507.

[44] The relative assignment can be made since vinyl protons trans to bismuth have unusually low chemical shift values. Diephouse, T. R. Ph.D. Thesis, The University of Michigan, 1981.

Tris(2-methyl-1-propenyl)bismuthine. In the same manner the reaction of 7.9 g (25 mmol) of bismuth trichloride in 60 mL of tetrahydrofuran with 2-methyl-1-propenylmagnesium bromide,[45] generated from 13.5 g (100 mmol) of 1-bromo-2-methyl-1-propene[46] and 2.4 g (100 mmol) of magnesium turnings in 70 mL of tetrahydrofuran, gave 3.8 g (41%) of tris(2-methyl-1-propenyl)bismuthine as a pale yellow, air-sensitive liquid which can be distilled only with some decomposition: bp 84–86 °C (0.005 torr); ^{1}H NMR (C_7D_8) δ 1.75 (apparent br s, 9 H), 1.85 (apparent br s, 9 H), 7.55 (m, 3 H); ^{13}C NMR (C_7D_8, 90.56 MHz) δ_C 27.0 (CH_3), 28.8 (CH_3), 130.0 (br, C_α), 146.3 (C_β); IR (CCl_4) 2956 (s), 2920 (s), 2897 (s), 2840 (s), 2700 (w), 1592 (m), 1426 (s), 1362 (m), 1352 (m), 1245 (s), 1090 (s), 1040 (w) cm^{-1}; MS, *m/e* (relative intensity) 373 (0.8, M$^+$), 319 (12.8), 265 (5.0), 264 (90.7), 249 (2.2), 224 (1.7), 210 (1.3), 209 (99.8), 109 (100.0), 95 (80.5), 67 (87.1), 55 (75.1); UV–visible (cyclohexane) 270 sh (ϵ 3700), λ_{max} <220 nm.

1-Phenylbismolane. The reaction of 7.0 g (15 mmol) of phenylbismuth dibromide in 80 mL of ether with dibromo(μ-butane-1,4-diyl)dimagnesium, which had been prepared from 3.85 g (150 mmol) of magnesium turnings and 10.8 g (50 mmol) of 1,4-dibromobutane in 100 mL of ether, gave 2.6 g (49%) of 1-phenylbismolane as a clear, colorless, air-sensitive liquid: bp 78–80 °C (0.1 torr); ^{1}H NMR ($CDCl_3$) δ 7.6 (dd, *J* = 7, 2 Hz, H_o), 7.17 (m, H_m, H_p), 3.0–1.6 (m, C_4H_8); IR (film) 3050 (w), 2960 (w), 2920 (s), 2840 (s), 1570 (w), 1470 (w), 1440 (w), 1430 (w), 1230 (w), 1180 (w), 1090 (w), 1015 (w), 1000 (w), 720 (s), 630 (s) cm^{-1}; MS, *m/e* (relative intensity) 392 (2.7, M$^+$), 286 (63.9), 265 (3.6), 209 (100), 154 (2.1), 55 (26.6).

Tetramethyldibismuthine. Sodium metal (0.5 g, 22 mmol) was added piecewise to 2.9 g (11 mmol) of trimethylbismuthine[20] in 100 mL of liquid ammonia. The deep red solution was allowed to stir for 30 min after which 0.88 mL of 1,2-dichloroethane was added dropwise over 30 min. The flask was warmed to 0 °C. After the ammonia had evaporated, 50 mL of cold, deoxygenated pentane was added, the cold solution was filtered under nitrogen, and the pentane was removed. Three low-temperature recrystallizations, each from 1 mL of pentane, gave 2.6 g (70%) of pure tetramethyldibismuthine as a viscous red oil ($d_{20°C}$ = 2.85 g/cm^3) which freezes, mp −12.5 °C, to a blue irridescent solid. Tetramethyldibismuthine is thermally unstable, having a half-life of decomposition to trimethylbismuthine and bismuth metal in dilute benzene solution of approximately 6 h at 25 °C: ^{1}H NMR (C_7D_8) δ 1.62 (br s); ^{13}C NMR (C_7D_8, 90.56 MHz) δ_C −18.9; UV–visible (pentane) 220 (ϵ 37 000), 264 nm (7200), featureless tail to 700 nm; diffuse reflectance, maximum absorbance 665 nm.

Tetraisopropenyldibismuthine. In the same manner sodium metal (0.35 g, 15 mmol) was added piecewise to 2.5 g (7.5 mmol) of triisopropenylbismuthine in 100 mL of liquid ammonia. The deep red solution was allowed to stir for 30 min, after which 0.60 mL of 1,2-dichloroethane was added dropwise over 30 min. Recrystallization from pentane gave 1.45 g (67%) of pure tetraisopropenyldibismuthine as a viscous red liquid which freezes at 13.5 °C to a purple solid. Tetraisopropenyldibismuthine is much more thermally stable than tetramethyldibismuthine, decomposing to triisopropenylbismuthine and bismuth metal with a half-life in dilute benzene solution at 25 °C of about 2 weeks: ^{1}H NMR (C_7D_8) δ 2.75 (dd, *J* = 1.8, 1.2 Hz, CH_3), 5.87 (dq, *J* = 1.4, 1.2 Hz, H_{cis}), 7.14 (dq, *J* = 1.4, 1.8 Hz, H_{trans});[44] ^{13}C NMR (C_7D_8, 90.56 MHz) δ_C = 34.8 (CH_3), 129.6 (C_β), 148.6 (br, C_α); IR (CH_2Cl_2) 3040 (w), 2945 (s), 2895 (m), 2840 (w), 1594 (m), 1440 (m), 1428 (m), 1364 (w), 1157 (s), 902 (s) cm^{-1}; UV–visible (pentane) λ_{max} 230 (ϵ 15 000), 270 nm (6150), featureless tail to 700 nm; diffuse reflectance, maximum absorbance 575 nm.

Tetrakis(2-methyl-1-propenyl)dibismuthine. In the same manner sodium metal (0.27 g, 11.8 mmol) was added piecewise to 2.2 g (5.9 mmol) of tris(2-methyl-1-propenyl)bismuthine in 100 mL of liquid ammonia. The deep red solution was allowed to stir for 1 h after which 0.47 mL of 1,2-dichloroethane was added dropwise over 30 min. Recrystallization from pentane gave 1.55 g (82%) of pure tetrakis(2-methyl-1-propenyl)dibismuthine as a deep red solid that melts to a viscous red liquid, mp 29–29.5 °C. Tetrakis(2-methyl-1-propenyl)dibismuthine decomposes to tris(2-methyl-1-propenyl)bismuthine and bismuth metal with a half-life in dilute benzene solution at 25 °C of about 1 week: ^{1}H NMR (C_7D_8) δ 1.77 (apparent br s, 12 H), 1.99 (apparent br s, 12 H), 8.36 (apparent br s, 4 H); ^{13}C NMR (C_7D_8, 90.56 MHz) δ_C 27.8 (CH_3), 29.3 (CH_3), 146.1 (C_β), no C_α found; IR (CH_2Cl_2) 3040 (w), 2960 (s), 2930 (s), 2910 (s), 2850 (m), 1605 (m), 1440 (s), 1380 (w), 1370 (m), 1255 (m), 1108 (m) cm^{-1}; UV–visible (pentane) λ_{max} <220, 265 nm sh (ϵ 16 000); diffuse reflectance, maximum absorbance 300 nm.

Tetraphenyldibismuthine. Sodium metal (0.23 g, 10 mmol) was added piecewise to a well stirred mixture of 3.58 g (10 mmol) of diphenylbismuth chloride[47] in 100 mL of liquid ammonia. On warming to 0 °C, the ammonia evaporated from the green-black solution. The residue was taken up in 25 mL of toluene and filtered. After the addition of 10 mL of methanol, 1.55 g (45%) of tetraphenyldibismuthine was obtained as red air-sensitive crystals. These darkened on heating to 100 °C and decomposed at 124–126 °C. Chloroform solution of tetraphenyldibismuthine completely decomposed to triphenylbismuthine and bismuth metal after 20 h at 25 °C: ^{1}H NMR ($CDCl_3$) δ 7.87 (dd, *J* = 8, 1.7 Hz, H_o), 7.32–7.25 (m, H_m, H_p); ^{13}C NMR ($CDCl_3$) δ 140.4 (C_o), 130.7 (C_m), 127.2 (C_p), C_1 not observed; UV (pentane) λ_{max} 216 (20 500), 310 (2750), 362 nm (3900), tail to 400 nm; diffuse reflectance, absorbance 390, 450 nm. Anal. Calcd for $C_{24}H_{20}Bi_2$: C, 39.68; H, 2.79. Found: C, 39.91; H, 2.89.

1,1′-Bibismolane. Sodium metal (0.31 g, 13.4 mmol) was added piecewise to 2.3 g (6.7 mmol) of 1-phenylbismolane in 100 mL of liquid ammonia. The deep red solution was allowed to stir for 20 min, after which 0.31 g (6.7 mmol) of ammonium chloride was added. Five minutes later 1.5 mL of 1,2-dichloroethane in 5 mL of ether was added dropwise over 10 min. On warming to 0 °C, the ammonia evaporated and the residue was extracted with 50 mL of pentane. After filtration, three recrystallizations gave 1.0 g (58%) of pure 1,1′-bibismolane. The purple solid dibismuthine melts at 46–47 °C to a red liquid. Solutions in pentane are dark red: ^{1}H NMR (C_7D_8) δ 3.38 (m, 2 H), 3.00 (m, 2 H), 2.66 (m, 2 H), 2.35 (m, 2 H); ^{13}C NMR (C_6D_6) δ 40.5 (C_β), 17.78 (br, C_α); UV (pentane) 220 (ϵ 37 000), 264 nm sh (7200), tail to >450 nm; diffuse reflectance, maximum absorbance 580 nm.

Reactions of Tetramethyldibismuthine. General Data. Because tetramethyldibismuthine is very thermally unstable as a neat material (decomposition is noticeable after 1 min at 25 °C), it was not possible to introduce a sample into an inert-atmosphere box. Therefore, the reaction mixtures were prepared in the inert-atmosphere box, the tubes or flasks were sealed with a rubber septum, and the tetramethyldibismuthine was added later by using a cold microliter syringe.

Reaction of Tetramethyldibismuthine with Iodine. An NMR tube was charged with 0.1 g of iodine crystals and 0.5 mL of benzene-d_6 at 25 °C. When 25 μL of tetramethyldibismuthine was added, an immediate reaction occurred which gave a green liquid consisting of trimethylbismuthine, dimethylbismuth iodide, methylbismuth diiodide, and bismuth triiodide along with a bismuth mirror. An authentic sample of the methylbismuth iodides was prepared by treating trimethylbismuthine with 0.5 equiv of bismuth triiodide in benzene-d_6. The ^{1}H NMR spectra of the two samples were identical: ^{1}H NMR (C_6D_6) δ 1.03 (br s, Me_3Bi, 26%), 1.46 (s, Me_2BiI, 27%), 1.58 (s, $MeBiI_2$, 47%).

The same reaction occurred when 25 mg of iodine was added to 10 μL of tetramethyldibismuthine in toluene-d_8 at −78 °C: ^{1}H NMR (C_7D_8) δ 1.01 (br s, Me_3Bi, 57%), 1.40 (s, Me_2BiI, 6%), 1.57 (br s, $MeBiI_2$, 36%). Only a trace (<0.1%) of methyl iodide (δ 1.47) could be detected. Under these conditions, methyl iodide does not react with either trimethylbismuthine or the methylbismuth iodides over a period of 3 days.

Reaction of Tetramethyldibismuthine with Triphenylmethyl Bromide. An NMR tube was charged with 0.05 g of triphenylmethyl bromide and 0.5 mL of benzene-d_6. When 25 μL of tetramethyldibismuthine was added, an immediate reaction occurred to yield trimethylbismuthine, dimethylbismuth bromide, and a bismuth mirror. For comparison, an authentic sample of methylbismuth bromides was prepared by treating trimethylbismuthine with bismuth tribromide in benzene-d_6: ^{1}H NMR

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(45) Poyser, J. P.; de Reinach Hirtzbach, F.; Ourisson, G. *Tetrahedron* **1974**, *30*, 977.

(46) Braude, E. A.; Evans, E. A. *J. Chem. Soc.* **1955**, 3324.

(47) Gilman, H.; Yablunky, H. L. *J. Am. Chem. Soc.* **1941**, *63*, 207.

(C_6D_6) δ 1.03 (br s, Me_3Bi), 1.35 (s, Me_2BiBr).

A solution of 0.05 g of triphenylmethyl bromide, 25 mL of tetramethyldibismuthine, and 0.5 mL of dry isooctane was prepared. This solution was filtered into an ESR tube to remove any bismuth metal which might inhibit the recording of an ESR spectrum. A strong resonance was found which precisely matched the spectrum of the triphenylmethyl radical.[48] When solutions of either tetramethyldibismuthine or triphenylmethyl bromide alone in isooctane were scanned, no resonance was observed.

Reaction of Tetramethyldibismuthine with Carbon Tetrachloride. An NMR tube was charged with 0.5 mL of carbon tetrachloride. When 25 μL of tetramethyldibismuthine was added, an instantaneous reaction occurred to yield only trimethylbismuthine and a bismuth mirror as shown by the ^{1}H NMR spectrum.

Reaction of Tetramethyldibismuthine with Benzyl Bromide. An NMR tube was charged with 12 μL of benzyl bromide and 0.5 mL of benzene-d_6. When 25 μL of tetramethyldibismuthine was added, a fast reaction occurred which yielded trimethylbismuthine (40.8%), dimethylbismuth bromide (31.3%), benzyldimethylbismuthine (28.0%), and bismuth metal. The proton NMR spectrum was consistent with that for an authentic sample of benzyldimethylbismuthine.

Benzyldimethylbismuthine. Dimethylbismuth bromide was generated by the dropwise addition of 1.36 g (8.5 mmol) of bromine to 2.15 g (8.5 mmol) of trimethylbismuthine in 15 mL of tetrahydrofuran at 0 °C. Upon warming to room temperature, this solution was added directly to benzylmagnesium chloride, generated from 1.5 g (12 mmol) of benzyl chloride and 0.3 g (12 mmol) of magnesium turnings in 20 mL of diethyl ether. The reaction mixture was allowed to reflux for 1 h. The solution was then cooled to 0 °C, and the reaction was quenched with 25 mL of aqueous ammonium chloride. The mixture was filtered under nitrogen, the layers were separated, and the ether phase was dried over anhydrous magnesium sulfate. Following removal of the solvent, distillation of the residue gave 1.45 g (52%) of pure benzyldimethylbismuthine as a pale green liquid: bp 64–65 °C (0.1 torr); ^{1}H NMR (C_6D_6) δ 0.85 (s, 6 H), 2.87 (s, 2 H), 6.8 (m, 5 H); MS, *m/e* (relative intensity) 330 (2.6, M$^+$), 315 (15.7), 239 (16.5), 224 (8.3), 209 (46.2), 105 (11.2), 92 (26.8), 91 (100.0), 89 (16.8), 79 (10.0), 77 (10.1), 65 (52.4), 63 (16.9), 51 (12.2).

Reaction of Tetramethyldistibine with Benzyl Bromide. A tube was charged with 12 μL of benzyl bromide, 25 μL of tetramethyldistibine,[19] and 0.5 mL of benzene-d_6. The reaction proceeded rapidly at room temperature and was complete in 10 min to yield dimethylantimony bromide (64%) and benzyldimethylstibine (36%) and no trace of benzyl bromide. The proton NMR was consistent with that for an authentic sample of benzyldimethylstibine.

Benzyldimethylstibine. Dimethylantimony chloride[49] was generated through the dropwise addition of 0.41 g (3 mmol) of sulfuryl chloride in 5 mL of methylene chloride to 0.9 g (3 mmol) of tetramethyldistibine in 20 mL of methylene chloride at −78 °C. Upon warming to 25 °C, the methylene chloride was removed and 20 mL of tetrahydrofuran was added. This solution was added directly to benzylmagnesium chloride, generated from 1.3 g (10 mmol) of benzyl chloride and 0.24 g (10 mmol) of magnesium turnings in 20 mL of diethyl ether. The reaction mixture was allowed to reflux for 2 h, the solution was cooled to 0 °C, and the reaction was quenched with aqueous ammonium chloride. The mixture was filtered under nitrogen, the layers were separated, and the ether phase was dried over anhydrous magnesium sulfate. Following removal of the solvent, distillation of the residue gave 0.95 g (65%) of pure benzyldimethylstibine as a clear, colorless liquid: bp 56 °C (0.2 torr); ^{1}H NMR (C_6D_6) δ 0.5 (s, 6 H), 2.64 (s, 2 H), 6.9 (m, 5 H); MS, *m/e* (relative intensity) 244 (16.4, M$^+$), 242 (28.5), 229 (17.4), 227 (24.4), 153 (17.6), 151 (22.2), 138 (10.6), 136 (12.2), 123 (9.2), 121 (10.5), 106 (68.8), 91 (100.0), 79 (29.4), 77 (27.9), 65 (85.8), 51 (31.6). Anal. Calcd for $C_9H_{13}Sb$: C, 44.49; H, 5.39. Found: C, 44.29; H, 5.45.

Reaction of Tetramethyldiarsine with Benzyl Bromide. A tube was charged with 12 μL of benzyl bromide, 25 μL of tetramethyldiarsine,[50] and 0.5 mL of benzene-d_6 and sealed. No reaction occurred at room temperature after 2 h. The tube was heated to 150 °C for 1 h to yield dimethylarsenic bromide (31.8%), benzyldimethylarsine (37.4%), and unreacted tetramethyldiarsine (30.8%) but no trace of benzyl bromide. The proton NMR was consistent with an authentic sample of benzyldimethylarsine: ^{1}H NMR (C_6D_6) δ 1.3 (s, Me_2AsBr).

Benzyldimethylarsine. This arsine was prepared in the same manner as benzyldimethylstibine. Dimethylarsenic chloride, prepared from 0.41 g (2 mmol) of tetramethyldiarsine and 0.27 g (2 mmol) of sulfuryl chloride, was added to benzylmagnesium chloride, generated from 0.63 g (5 mmol) of benzyl chloride and 0.12 g (5 mmol) of magnesium turnings in ether. Distillation of the residue gave 0.4 g (51%) of pure benzyldimethylarsine as a clear, colorless liquid: bp 122 °C (10 torr); ^{1}H NMR (C_6D_6) δ 0.72 (s, 6 H), 2.64 (s, 2 H), 7.0 (m, 5 H); MS, *m/e* (relative intensity) 196 (82, M$^+$), 181 (15.7), 105 (41.9), 91 (100.0), 79 (59.5), 77 (52.9), 75 (8.3), 65 (88.2), 51 (62.1). Anal. Calcd for $C_9H_{13}As$: C, 55.12; H, 6.68. Found: C, 54.97; H, 6.59.

Reaction of Tetramethyldibismuthine with Bromotrichloromethane. An NMR tube was charged with a solution of 10 μL of bromotrichloromethane in 0.5 mL of tetrahydrofuran-d_8. When 25 μL of tetramethyldibismuthine was added, a fast reaction occurred with the formation of a bismuth mirror. GC/MS analysis of the reaction mixture indicated the presence of trimethylbismuthine (retention time, 9.4 min), dimethylbismuth bromide (retention time, 17.1 min), tetrachloroethylene (retention time, 10.5 min; 3.0%), and hexachloroethane (retention time, 18.3 min; 1.6%). The identity of these products was established by a comparison of GC retention times, mass spectra, and where appropriate ^{1}H NMR spectra to those of an authentic material. A component (retention time, 19.0 min) was identified as dimethyl(trichloromethyl)bismuthine based on its mass and NMR spectra: MS, *m/e* (relative intensity) 360 (0.3, M$^+$), 358 (1.1), 356 (1.1), 330 (0.01), 328 (0.1), 326 (0.1), 305 (0.6), 303 (0.7), 295 (0.1), 293 (0.8), 291 (1.3), 261 (4.7), 259 (14.7), 239 (81.6), 224 (31.0), 209 (100.0), 121 (2.2), 119 (6.3), 117 (6.6), 101 (1.0), 99 (6.9), 97 (10.8); ^{1}H NMR (C_4D_8O) δ 1.09 (br s, Me_3Bi, 3.7%), 1.28 (s, Me_2BiCCl_3, 39.5%), 1.63 (s, Me_2BiBr, 56.6%).

Reaction of Tetramethyldistibine with Bromotrichloromethane. An NMR tube was charged with 10 μL of bromotrichloromethane and 25 μL of tetramethyldistibine in 0.5 mL of tetrahydrofuran-d_8. A slow reaction occurred which was complete after 3 h at 25 °C. GC/MS analysis of the reaction mixture indicated the presence of the following compounds: dimethylantimony bromide (retention time, 15.6 min; 37.8%), dimethyl(trichloromethyl)stibine (retention time, 19.2 min; 20.9%), and tetramethyldistibine (retention time, 30.9 min; 41.4%): ^{1}H NMR (C_4D_8O) δ 0.96 (s, Me_4Sb_2, 21.5%), 1.06 (s, Me_2SbCCl_3, 13.9%), 1.33 (s, Me_2SbBr, 64.6%). The identity of dimethylantimony bromide and tetramethyldistibine was established by a comparison of its GC retention time, ^{1}H NMR spectra, and mass spectra to those of authentic material. The dimethyltrichloromethylstibine was identified from its mass spectrum: *m/e* (relative intensity) 276 (0.1, M$^+$), 274 (1.2), 272 (5.0), 270 (8.3), 268 (4.9), 259 (0.2), 257 (0.8), 255 (1.3), 253 (0.8), 244 (0.1), 242 (0.4), 240 (0.7), 238 (0.4), 199 (0.1), 197 (2.0), 195 (14.7), 193 (35.2), 191 (25.3), 175 (4.9), 173 (22.4), 171 (21.4), 153 (70.8), 151 (100.0), 138 (20.8), 136 (31.8), 123 (24.1), 121 (28.8), 119 (6.1), 117 (6.3), 101 (0.2), 99 (1.3), 97 (2.0).

Reaction of Tetramethyldiarsine with Bromotrichloromethane. A solution of 10 μL of bromotrichloromethane and 25 μL of tetramethyldiarsine in 0.5 mL of tetrahydrofuran-d_8 was sealed in an NMR tube. No reaction had occurred after 24 h at 25 °C. After the mixture was heated to 100 °C for 4 h, there was very little change in the ^{1}H NMR spectrum. Heating to 150 °C for 2 h completed the reaction. GC/MS analysis of the reaction mixture indicated the presence of dimethylarsenic bromide (retention time, 14.5 min; 6.4%), dimethyl(trichloromethyl)arsine (retention time, 17.2 min; 69.2%) and tetramethyldiarsine (retention time, 24.0 min; 24.4%). The dimethylarsenic bromide and tetramethyldiarsine showed identical ^{1}H NMR and mass

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spectra to those of authentic material. The dimethyl(trichloromethyl)arsine was identified on the basis of its mass and NMR spectra: *m/e* (relative intensity) 228 (1.2), 226 (11.0), 224 (34.2), 222 (35.5), 213 (0.2), 211 (2.4), 209 (7.7), 207 (8.0), 196 (0.3), 194 (0.9), 192 (1.0), 151 (4.8), 149 (15.6), 147 (71.7), 145 (86.0), 123 (2.2), 121 (5.0), 119 (14.8), 117 (15.5), 105 (100.0), 91 (8.5), 90 (32.8), 89 (70.2), 88 (25.1), 75 (20.9); ^{1}H NMR (C_4D_8O) δ 1.18 (s, Me_2AsCCl_3, 22.2%), 1.29 (s, Me_4As_2, 14.8%), 1.72 (br s, Me_2AsBr, 63.0%).

Reaction of Tetramethyldibismuthine with Anhydrous Hydrogen Chloride. A solution of 0.05 M hydrogen chloride in carbon disulfide was prepared by bubbling HCl gas into a sample of carbon disulfide followed by titration of the solution with standard base. An NMR tube was charged with 0.5 mL of carbon disulfide, 0.05 mL of methylene-d_2 chloride, and 25 μL (0.03 mmol) of tetramethyldibismuthine. The mixture was cooled to −78 °C, and 0.5 mL (0.025 mmol of HCl) of 0.05 M HCl/CS_2 solution was added via syringe. An immediate reaction occurred. Proton NMR analysis of the reaction mixture indicated the presence of trimethylbismuthine, dimethylbismuth chloride, the unstable dimethylbismuthine, and a bismuth mirror: ^{1}H NMR (CS_2/CD_2Cl_2, −70 °C) δ 1.13 (br s, Me_3Bi, 4.0%), 1.26 (br s, Me_2BiH, 7.3%), 1.66 (br s, Me_2BiCl, 88.7%), 210 (br s, Me_2BiH). The signals for trimethylbismuthine and dimethylbismuth chloride were identical with those shown by authentic samples.

Reaction of Tetramethyldistibine with Anhydrous Hydrogen Chloride. An NMR tube was charged with 0.5 mL of carbon disulfide, 0.05 mL of methylene-d_2 chloride and 5 μL (0.03 mmol) of tetramethyldistibine. The mixture was cooled to −78 °C, and 0.5 mL (0.025 mmol of HCl) of 0.05 M HCl/CS_2 solution was added via syringe. An immediate reaction occurred. ^{1}H NMR spectra of the reaction mixture indicated the presence of dimethylantimony chloride and the unstable dimethylstibine in the ratio of 60:40: ^{1}H NMR (CS_2/CD_2Cl_2, −70 °C) δ 0.87 (d, $J = 5.9$ Hz, Me_2SbH), 1.43 (s, Me_2SbCl), 2.13 (hept, $J = 5.9$ Hz, Me_2SbH). The signals assigned to dimethylstibine were identical with those of an authentic material prepared by the reduction of dimethylchlorostibine.[32]

Reaction of Tetramethyldibismuthine with *n*-Butyllithium. A 5-mL flask was capped with a septum, flushed with argon, charged with 20 μL (0.12 mmol) of tetramethyldibismuthine, and cooled to −78 °C. The flask was then charged with 62.5 μL (0.1 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. As the mixture was slowly warmed to room temperature, a fast reaction occurred which gave a deep red solution and a deposit of bismuth metal. GC/MS analysis of the reaction mixture indicated the presence of the following compounds: trimethylbismuthine (retention time, 9.0 min; 5.9%); *n*-butyldimethylbismuthine (retention time, 16.3 min; 48.1%) (MS, *m/e* (relative intensity) 296 (36.6, M^+), 282 (4.8), 281 (80.6), 267 (1.2), 266 (3.1), 265 (3.4), 240 (2.1), 239 (79.4), 225 (61.6), 224 (54.2), 210 (8.1), 209 (97.1), 57 (100.0), 55 (9.1), 41 (99.5)); di-*n*-butylmethylbismuthine (retention time, 21.5 min; 14.2%) (MS, *m/e* relative intensity) 338 (11.6, M^+), 323 (8.4), 296 (1.6), 282 (2.2), 281 (35.8), 267 (11.3), 266 (4.3), 265 (4.4), 240 (0.1), 239 (4.1), 225 (54.3), 224 (17.0), 210 (6.6), 209 (88.4), 57 (100.0), 55 (6.7), 41 (84.4)); tri-*n*-butylbismuthine (retention time, 28.3 min; 31.8%) (MS, *m/e* (relative intensity) 380 (8.4, M^+), 324 (2.7), 323 (28.2), 268 (3.0), 267 (63.3), 266 (10.3), 265 (4.8), 210 (8.7), 209 (100.0), 57 (94.6), 55 (8.7), 41 (92.9)). Samples of the bismuthines were collected from the GC for ^{1}H NMR analysis: Me_2BiBu (C_6D_6), δ 0.88 (apparent t, 3 H), 1.02 (s, 6 H), 1.28, m; 1.77, m, 6 H); $MeBiBu_2$ (C_6D_6), δ 0.90 (apparent t, 6 H), 1.02 (s, 3 H), (1.29, m; 1.82, m, 12 H); Bu_3Bi (C_6D_6), δ 0.81 (apparent t, 9 H), (0.89, m; 1.26, m, 18 H).

Reaction of Trimethylbismuthine with *n*-Butyllithium. A 10-mL round-bottomed flask was flushed with argon and charged with trimethylbismuthine (2.3 g, 9 mmol), 2 mL of tetrahydrofuran, and 6.25 mL (10 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. The reaction mixture was analyzed by GC and showed the bismuthines in the following product ratio: Me_3Bi, 2.8%; Me_2BiBu, 51.1%; $MeBiBu_2$, 38.4%; Bu_3Bi, 7.6%.

Reaction of Tetramethyldistibine with *n*-Butyllithium. A 5-mL flask was capped with a septum, flushed with argon, and charged with 25 μL (0.16 mmol) of tetramethyldistibine. The flask was then charged with 0.1 mL (0.16 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. In less than 2 min, the solution had turned dark brown. GC/MS analysis of the reaction mixture indicated the presence of the following compounds: butyldimethylstibine (retention time, 14.8 min; 66.1%) (MS, *m/e* (relative intensity) 210 (42.7, M^+), 208 (55.9), 195 (10.9), 193 (15.2), 181 (2.5), 179 (3.8), 167 (2.4), 165 (3.6), 154 (31.6), 153 (45.2), 152 (42.5), 151 (63.5), 139 (31.7), 138 (34.2), 137 (49.5), 136 (46.6), 135 (9.5), 124 (5.3), 123 (17.9), 122 (7.1), 121 (19.8), 57 (66.4), 55 (23.8), 41 (100.0)); dibutylmethylstibine (retention time, 20.3 min; 24.1%) (MS, *m/e* (relative intensity) 252 (23.6, M^+), 250 (31.7), 196 (7.1), 195 (27.3), 194 (10.1), 193 (38.0), 181 (9.8), 179 (22.9), 177 (13.5), 167 (5.9), 165 (8.6), 153 (24.3), 151 (35.9), 319 (71.4), 138 (60.4), 137 (100.0), 136 (78.9), 135 (5.8), 124 (4.8), 123 (18.6), 122 (6.4), 121 (22.1), 57 (70.4), 55 (58.7), 41 (94.2)); tributylstibine (retention time, 25.9 min; 9.9%) MS, *m/e* (relative intensity) 294 (8.1, M^+), 292 (10.7), 237 (2.6), 235 (3.4), 182 (2.5), 181 (53.5), 180 (18.3), 179 (100.0), 178 (20.2), 177 (39.8), 153 (2.7), 151 (10.0), 149 (8.8), 139 (5.6), 138 (5.4), 137 (8.7), 136 (7.1), 125 (2.1), 124 (2.5), 123 (6.5), 122 (3.4), 121 (4.8), 57 (46.9), 55 (65.7), 41 (45.4). Samples of the stibines were collected from the GC for ^{1}H NMR spectra and elemental analyses. Me_2SbBu ^{1}H NMR (C_6D_6) δ 0.62 (s, 6 H), 0.87 (apparent t, 3 H), (1.27, m; 1.41, 7, 6 H). Anal. Calcd for $C_6H_{15}Sb$: C, 34.49; H, 7.24. Found: C, 34.60; H, 7.32. $MeSbBu_2$: ^{1}H NMR (C_6D_6) δ 0.64 (s, 3 H), 0.86 (apparent t, 6 H), (1.32, m; 1.45, m, 12 H). Anal. Calcd for $C_9H_{21}Sb$: C, 43.06; H, 8.43. Found: C, 42.85; H, 8.54. Bu_3Sb: ^{1}H NMR (C_6D_6) δ 0.90 (apparent t, 9 H), (1.38, m; 1.55, m, 18 H). Anal. Calcd for $C_{12}H_{27}Sb$: C, 49.18; H, 9.29. Found: C, 49.27; H, 9.15.

Reaction of Trimethylstibine with *n*-Butyllithium. A 5-mL round-bottomed flask was flushed with argon and charged with trimethylstibine (0.7 g, 4.2 mmol) and 2.5 mL (4 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. A slow reaction occurred which had reached completion after 12 h. The reaction mixture was analyzed by GC and showed the stibines in the following product ratio: Me_2SbBu, 73.3%; $MeSbBu_2$, 24.1%; Bu_3Sb, 2.6%.

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Registry No. **1**, 82783-70-8; **4**, 7065-21-6; **7**, 85824-63-1; **15**, 87432-60-8; **16**, 87432-61-9; **17**, 87450-34-8; bismuth trichloride, 7787-60-2; isopropenyl bromide, 557-93-7; tris(2-methyl-1-propenyl)bismuthine, 87432-62-0; 2-methyl-1-propenyl bromide, 3017-69-4; 1-phenylbismolane, 87432-63-1; phenylbismuth dibromide, 39110-02-6; 1,4-dibromobutane, 110-52-1; trimethylbismuthine, 593-91-9; diphenylbismuthine chloride, 5153-28-6; iodine, 7553-56-2; triphenylmethyl bromide, 596-43-0; carbon tetrachloride, 56-23-5; benzyl bromide, 100-39-0; benzyldimethylbismuthine, 87432-64-2; dimethylbismuth bromide, 7529-35-3; benzyl chloride, 100-44-7; tetramethyldistibine, 41422-43-9; benzyldimethylstibine, 87432-65-3; dimethylantimony chloride, 18380-68-2; sulfuryl chloride, 7791-25-5; tetramethyldiarsine, 471-35-2; benzyldimethylarsine, 36678-76-9; dimethylarsenic chloride, 557-89-1; bromotrichloromethane, 75-62-7; dimethyl(trichloromethyl)bismuthine, 87432-66-4; dimethyl(trichloromethyl)stibine, 87432-67-5; dimethyl(trichloromethyl)arsine, 87432-68-6; hydrogen chloride, 7647-01-0; *n*-butyllithium, 109-72-8; *n*-butyldimethylbismuthine, 87432-69-7; di-*n*-butylmethylbismuthine, 87432-70-0; tri-*n*-butylbismuthine, 3692-81-7; butyldimethylstibine, 87432-71-1; dibutylmethylstibine, 87432-72-2; tributylstibine, 2155-73-9; bismuth, 7440-69-9.