

THE EXCHANGE REACTION OF TETRAMETHYL-DIPHOSPHINE, -DIARSINE, -DISTIBINE AND -DIBISMUTHINE

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Summary

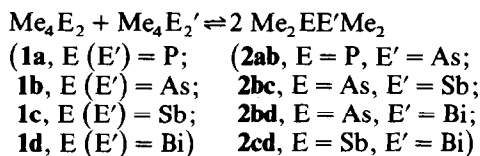
Tetramethyldiphosphine and tetramethyldiarsine undergo an exchange reaction to give (dimethylarsino)dimethylphosphine. The equilibrium constant at 25°C in benzene is found to be 0.26. Similarly, mixtures of tetramethyldistibine with tetramethyldiarsine or tetramethyldibismuthine are partially converted to (dimethylarsino)dimethylstibine or (dimethylbismuthino)dimethylstibine, respectively. The thermochromic arsinostibine, 1-(2,5-dimethylarsolo)-2,5-dimethylstibole, has been prepared by a similar reaction.

Introduction

A variety of distibines [1–9] and dibismuthines [10–13] show dramatic thermochromic effects on melting. For example, tetramethyldistibine forms red crystals which melt reversibly to a pale yellow oil [1,2]. The crystal structure of Me_4Sb_2 shows that the Sb atoms are aligned in linear chains with very close intermolecular $\text{Sb} \cdots \text{Sb}$ contacts [2]. Apparently the solid phase color is associated with extended bonding along the $\text{Sb}-\text{Sb} \cdots \text{Sb}-\text{Sb}$ chains [2,4,14]. Similar structures have been found for other thermochromic distibines [4,6] and a thermochromic dibismuthine [12]. There is a close analogy of optical properties of solid distibines with the corresponding dibismuthines [10], although in no case do the corresponding diarsines show thermochromic properties [15,16]. In order to extend our studies of thermochromic properties of compounds of the Group V elements, we became interested in preparing mixed tetraorganodipnictogens of the type $\text{R}_2\text{EE}'\text{R}_2$ where E and E' are different pnictogen atoms.

Several mixed diorganoarsino(diorganophosphines) have previously been obtained by the exchange reaction of the corresponding symmetrical tetraorganodi-

pnictogens [17–19]. Since all of the tetramethyldipnictogens are available, we have explored the following exchange reaction:



Results and discussion

We find that the tetramethyldipnictogens (Me_4E_2 , E = As, Sb, Bi) undergo rapid exchange reactions at 25°C both in solution and as neat liquids. The ^1H NMR spectra of the mixtures of the tetramethyldipnictogens in benzene- d_6 show signals for both the parent compounds and mixed compounds. A typical spectrum, that of a mixture of tetramethyldibismuthine and tetramethyldistibine, is shown in Fig. 1. The assignments of the proton NMR signals for (dimethylstibino)dimethylbismuthine and (dimethylarsino)dimethylbismuthine may be made since the methyl protons attached to bismuth are broadened by partial quadrupolar coupling to ^{209}Bi . For (dimethylarsino)dimethylstibine assignment may be made on the basis of deuterium labelling. Thus exchange between tetramethyldiarsine and tetramethyldistibine- d_{12} , which had been prepared by standard methods from iodomethane- d_3 [20], gave (dimethylarsino)dimethylstibine- d_6 . There was no evidence of proton–deuterium exchange because signals for methyl protons attached to antimony were not observed.

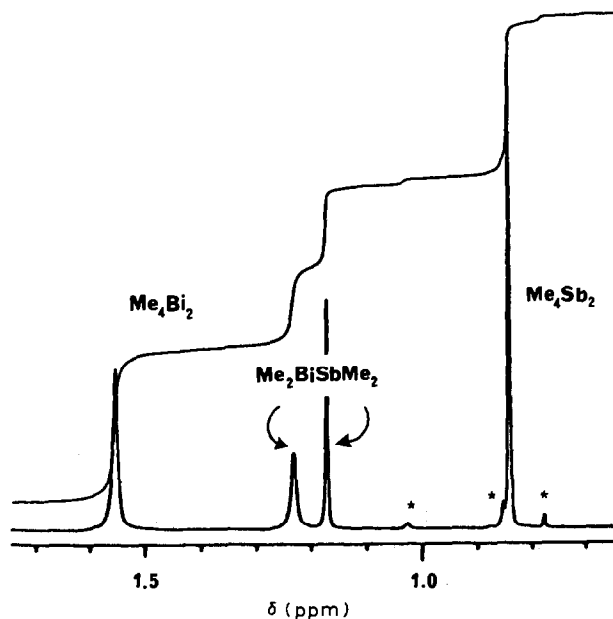
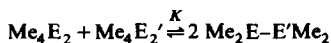


Fig. 1. ^1H NMR spectrum (in benzene- d_6) of a mixture of Me_4Bi_2 , Me_4Sb_2 and $\text{Me}_2\text{BiSbMe}_2$. Unidentified impurities are indicated by (*).

TABLE 1

PROTON NMR DATA (δ in ppm) AND EQUILIBRIUM CONSTANTS FOR THE EXCHANGE REACTIONS OF THE TETRAMETHYLDIPNICTOGENS (Solvent is benzene- d_6)



E	E'	Me_4E_2	$\text{Me}_4\text{E}'_2$	$\text{Me}_2\text{E}-\text{E}'\text{Me}_2$	$\text{Me}_2\text{E}-\text{E}'\text{Me}_2$	K
P	As	0.92 (t, J 7.0 Hz) ^a	0.96 (s)	1.00 (d, J 4.15 Hz)	0.90 (d, J 8.31 Hz)	0.26
Bi	Sb	1.55 (br s)	0.84 (s)	1.23 (br s)	1.17 (s)	1.2
Sb	As	0.84 (s)	0.96 (s)	0.76 (s)	1.03 (s)	0.9
Bi	As	1.55 (br s)	0.96 (s)	1.42 (br s)	1.14 (s)	9×10^{-3}

^a $^2J(\text{PH})$ 2.90, $^3J(\text{PH})$ 11.25 Hz, ref. 21.

The mixed compound formed from the exchange reaction of tetramethyldiphosphine with tetramethyldiarsine was detected both by ^1H and ^{31}P NMR spectroscopy. The proton NMR spectrum of $\text{Me}_2\text{PAsMe}_2$ consists of doublets at δ 1.00 ($J(\text{PH})$ 4.15 Hz) due to PMe_2 and δ 0.90 ($J(\text{PH})$ 8.31 Hz) due to AsMe_2 . Assignment was made on the basis that $^3J(\text{PH})$ values are usually larger than $^2J(\text{PH})$ values for similar compounds [21]. The ^{31}P NMR signal for $\text{Me}_2\text{PAsMe}_2$ was observed as a symmetrical 15-line multiplet (with 4.15 Hz spacing) at δ -56.18. The anticipated X portion of the XA_6B_6 -spectrum (J_{AX} 8.3, J_{BX} 4.15 Hz) should consist of 19 observable lines. While the outer four low intensity lines were not observed, the intensities of the remaining 15 lines precisely matched the calculated spectrum.

The relative concentration of each species was determined from the integration of the proton signals. The equilibrium constants were calculated using the following expression:

$$K = \frac{[\text{Me}_2\text{EE}'\text{Me}_2]^2}{[\text{Me}_4\text{E}_2][\text{Me}_4\text{E}'_2]} \quad (2)$$

The data are summarized in Table 1.

There was no evidence of an exchange reaction of tetramethyldiphosphine with either tetramethyldistibine or tetramethyldibismuthine. Even after heating samples of Me_4Sb_2 and Me_4P_2 to 80°C for 4 h or allowing them to stand at 25°C for 6 days, no new signals were observed in the ^1H NMR spectrum. In the case of mixtures of Me_4Bi_2 and Me_4P_2 , the samples could not be heated since the dibismuthine decomposes rapidly above 25°C [10]. We estimate that concentration greater than 2% of the mixed tetramethyldipnictogens could have been observed. Thus assuming that equilibrium had been reached, the equilibrium constants must be less than 9×10^{-3} . Our failure to observe (dimethylphosphino)dimethylstibine is consistent with the report of the lack of formation of the corresponding tetraphenyl compound [19].

The equilibrium constant for formation of (dimethylarsino)dimethylphosphine at 25°C is 0.26. This constant is very similar to the value of 0.37 found for the corresponding tetraphenyl compound in benzene at 30°C [19]. Similarly, the equilibrium constant for formation of $(\text{CF}_3)_2\text{PAs}(\text{CF}_3)_2$ from $(\text{CF}_3)_4\text{P}_2$ and $(\text{CF}_3)_4\text{As}_2$ is close to 1 [17]. Thus the equilibria seem only modestly sensitive to substituent effects.

At 25°C the equilibrium constants for formation of the mixed AsSb and SbBi compounds are close to unity, while formation of all other mixed compounds is less favored. All the equilibrium constants are smaller than the value of 4 expected on simple probability considerations. The equilibria must reflect the differences in bond strengths between the products and the starting materials. Thus it appears that only for near neighbors in the periodic table do the bond strengths of the mixed dipnictogens approach the mean of the corresponding symmetrical dipnictogens. Apparently the interpnictogen compounds provide a violation of Pauling's postulate that heteronuclear bonding is always stronger than homonuclear bonding [22]. This widely accepted postulate is the basis for the electronegativity scale [22,23]. However, the small range of electronegativity of P (2.19), As (2.18), Sb (2.05) and Bi (2.02) [24] may allow other factors to control the equilibria.

Raman spectra

Raman spectroscopy is extremely useful for characterization of compounds containing metal-metal bonds. Metal-metal stretching vibrations normally give rise to intense, easily identifiable Raman bands. Samples obtained by mixing Me_4Bi_2 and Me_4Sb_2 show two new bands at 128 and 163 cm^{-1} which we assign to the BiSb stretching frequencies of $\text{Me}_2\text{BiSbMe}_2$. Similarly, mixtures of Me_2Sb_2 and Me_4As_2 show new bands at 218 and 231 cm^{-1} which were assigned to Sb-As stretch. $\text{Me}_2\text{AsPMe}_2$ shows bands at 370 and 349 cm^{-1} assigned to the PAs stretch. For comparison it had previously been reported that $\text{Ph}_2\text{AsPPh}_2$ shows a PAs stretch at 375 cm^{-1} [25]. On the other hand, the low concentrations of $\text{Me}_2\text{BiAsMe}_2$ in mixtures of Me_4As_2 and Me_4Bi_2 prevented us from observing the Bi-As band.

As expected, the bands assigned to heterodipnictogen stretch occur at frequencies intermediate between the bands of the symmetrical tetramethyldipnictogens (see Table 2). Me_4P_2 [26], Me_4As_2 [27] and Me_4Sb_2 [28] show two bands for the

TABLE 2
 ν_{EE} (cm^{-1}) FROM RAMAN SPECTRA OF TETRAMETHYLDIPNICTOGEN COMPOUNDS

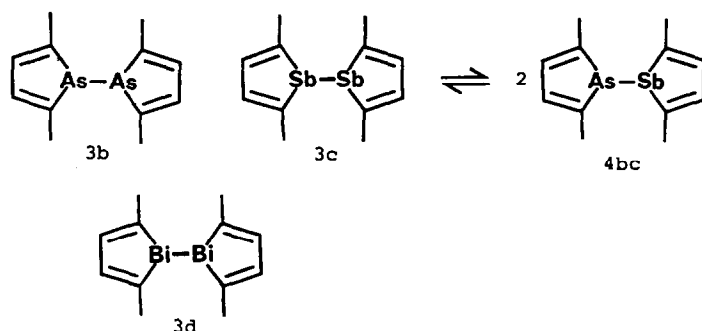
$\text{Me}_2\text{EE}'\text{Me}_2$	ν_{EE} (cm^{-1})	Assignment
Me_4P_2 (1a) ^a	455	PP <i>trans</i>
	429	PP <i>gauche</i>
$\text{Me}_2\text{PAsMe}_2$ (2ab)	370	PAs <i>trans</i>
	349	PAs <i>gauche</i>
Me_4As_2 (1b) ^b	272	AsAs <i>trans</i>
	254	AsAs <i>gauche</i>
$\text{Me}_2\text{SbAsMe}_2$ (2bc)	231	AsSb <i>trans</i>
	218	AsSb <i>gauche</i>
Me_4Sb_2 (1c) ^c	175	SbSb <i>trans</i>
	143	SbSb <i>gauche</i>
$\text{Me}_2\text{SbBiMe}_2$ (2cd)	163	SbBi <i>trans</i>
	128	SbBi <i>gauche</i>
Me_4Bi_2 (1d) ^d	109	BiBi

^a Ref. 26. ^b Ref. 27. ^c Ref. 28. ^d Ref. 10.

metal–metal stretch. These bands have been assigned to *trans* and *gauche* conformers. On the other hand, the Raman spectrum of Me_4Bi_2 shows only a single band for the BiBi stretching vibration [10]. Thus the spectra of $\text{Me}_2\text{PAsMe}_2$, $\text{Me}_2\text{BiSbMe}_2$ and $\text{Me}_2\text{SbAsMe}_2$ suggest that each compound also populates both *trans* and *gauche* conformers.

Attempted separation

The mobility of the equilibria between the tetramethyldipnictogens has frustrated our attempts to obtain pure samples of the mixed compounds. For example, slow cooling of mixtures of Me_4As_2 , Me_4Sb_2 and $\text{Me}_2\text{AsSbMe}_2$ results in crystallization of red crystals of Me_4Sb_2 and a liquid phase which is enriched in Me_4As_2 . Rapid cooling affords an orange slush which apparently contains all three species. However, we have succeeded in obtaining a pure sample of an arsinostibine of a related series of compounds. Since these data bear on the original objective of our study, we record them here.



Mixing the thermochromic 2,2',5,5'-tetramethylbistibole (**3c**) [4] with the non-thermochromic 2,2',5,5'-tetramethylbiarsole **3b** [15] in tetrahydrofuran- d_8 gives a solution containing 1-(2,5-dimethylarsolo)-2,5-dimethylstibole (**4bc**). Integration of the ^1H NMR signals shows the equilibrium constant to be 6.6. Removal of the solvent affords a dark residue which on a slow sublimation gave three distinct crystalline solids: golden crystals of the biarsole, violet crystals of the bistibole and red crystals of the mixed compound **4bc**.

The crystalline **4bc** showed a strong Raman band at 204 cm^{-1} , assigned to the Sb–As stretch. Only very weak bands at 170 cm^{-1} for bistibole and 241 cm^{-1} for biarsole [15] were observed. The compound melted at $66\text{--}72^\circ\text{C}$ to a yellow liquid which on cooling to 25°C solidified to a violet solid. In the melt reequilibration had occurred to reform mixtures of **3c**, **3b** and **4bc**. The appearance of the violet color on solidification is due to the intense dominating color of the bistibole.

The diffuse reflectance spectrum of **4bc** shows a broad absorption maximum centered at 410 nm, which was distinctly different from that shown by **3b** at 350 nm and **3c** [9] at 605 nm. Solutions of **3b**, **3c** and **4bc** show only a low intensity shoulder at 346 nm (due to **3c**) [4] with end absorption to 420 nm. Thus there is a large red shift between solution and solid that is similar to that observed for **3c**. Thermochromic properties of distibines and dibismuthines have been associated with solid phase structures with close intermolecular contacts along chains of metal atoms [2,4,6,11]. The observation that arsinostibine **4bc** is thermochromic suggests that it also crystallizes with stacking along its Sb–As bond axis. Unfortunately, we have been

TABLE 3

COMPARISON OF THE DIFFUSE REFLECTIVE ABSORPTION MAXIMA OF 3b, 3c, 3d AND 4bc

Compound	λ_{\max} (nm)
2,2',5,5'-Tetramethylbiarsole (3b)	360 ^a
1-(2,5-Dimethylarsolo)-2,5-dimethylstibole (4bc)	410 ^a
2,2',5,5'-Tetramethylbistibole (3c)	605 ^b
2,2',5,5'-Tetramethylbismole (3d)	690 ^c

^a This work. ^b Ref. 9. ^c Ref. 13.

unable to obtain crystals of 4bc of crystallographic quality in order to confirm this prediction.

It is interesting to compare the absorption maxima shown by the thermochromic solid 4bc, 3c [9] and 3d [13] (see Table 3). Hoffmann et al. have suggested that the solid phase color of 3c is due to an $\sigma \rightarrow \pi^*$ excitation [14]. One expects the lowest π^* orbitals of 4bc, 3c and 3d to be of similar energy. However, it is likely that energy of the σ bonds decrease in the order As-Sb, Sb-Sb and Bi-Bi. Thus the red shift in the series is consistent with decreasing band gap predicted from the Hoffmann model [14].

Experimental

General remarks

Proton and phosphorus NMR spectra were run on a Bruker WM 360 NMR spectrometer. Tetramethylsilane was used as an internal reference for the proton spectra while 85% H_3PO_4 was an external reference for the phosphorus spectra. UV-VIS 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. Raman spectra were obtained on a Spex 1401 double spectrometer using the 6328-Å excitation line of a Spectra Physics Model 126 helium neon laser.

All operations were performed under argon or nitrogen. Tetramethyldiphosphine and tetramethyldiarsine were obtained from Strem Chemical Corporation. Tetramethyldistibine [3,20], tetramethyldibismuthine [10], 2,2',5,5'-tetramethylbistibole [4] and 2,2',5,5'-tetramethylbiarsole [15] were prepared by literature methods.

Exchange reactions of tetramethyldipnictogens

Samples for proton and phosphorus NMR spectroscopy were prepared by placing 10 μ l for each of two tetramethyldipnictogens and 0.5 ml of benzene- d_6 in 5 mm NMR tubes. Samples for Raman spectra were prepared by sealing 10 μ l of each of two tetramethyldipnictogens in 1 mm glass capillaries. The relative equilibrium concentrations were determined from integration of the proton NMR signals. The equilibrium constants were calculated from eq. 2. Their values are estimated to be accurate to 10%. Where exchange was not detected, it was assumed that the mixed tetramethyldipnictogen would have different chemical shift values than the starting materials. The estimated minimum concentration of 2% of the mixed tetramethyldipnictogen was based upon the maximum intensities of peaks for the unknown impurities similar to those illustrated in Fig. 1.

Exchange reaction of 2,2',5,5'-tetramethylbistibole (3c) and 2,2',5,5'-tetramethylbiarsole (3b)

A NMR sample was prepared by making a solution of approximately equimolar amounts of the bistibole **3c** and biarsole **3b** in 0.5 ml of tetrahydrofuran-*d*₈. The ¹H NMR spectrum showed peaks due to **3b**, **3c**, and **4bc**. The relative concentrations were obtained from integration of the signals and the equilibrium constant was calculated to be 6.6.

¹H NMR (C₄D₈O): δ 2.01 (s, CH₃, **3b**), 2.05 (s, CH₃, **4bc**), 2.14 (s, CH₃', **4bc**), 2.16 (s, CH₃, **3c**), 6.47 (br s, CH, **3b**), 6.50 (br s, CH, **4bc**), 6.72 (br s, CH', **4bc** and CH, **3c**).

Equimolar amounts of the bistibole **3c** and biarsole **3b** were dissolved in a mixture of 1 ml of pentane and 1 ml of toluene. The solvent was removed and the residue was slowly sublimed at 40°C (0.005 torr). At the end of the sublimation, three different materials could be observed: gold, purple and red solids. The red crystals of **4bc** could be manually separated from the other material. The crystals melted, m.p. 66–71°C, to a yellow liquid which solidified upon cooling to a purple solid. Diffuse reflectance: λ_{max} 420–400 nm; Raman: solid, 204 cm⁻¹ (Sb–As stretch).

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