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THE EXCHANGE REACTION OF TETRAMETHYLDIPNICTOGENS WITH DIMETHYLDICHALCOGENIDES

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Summary

Tetramethyldipnictogens Me_4E_2 (E = P, As, Sb, Bi) undergo exchange reactions with dimethyldichalcogenides Me_2A_2 (A = S, Se, Te) to produce the corresponding (dimethylpnicto)methylchalcogenides Me_2EAMe. These compounds have been characterized by NMR, Raman and mass spectroscopy.

Introduction

In the course of a study of element–element bonding of tetraorganodipnictogens R_4E_2 (E = P, As, Sb, Bi) [1–3] we became interested in obtaining related compounds containing hetero element–element bonds. In a previous paper we reported that interpnictogen compounds $Me_2EE'Me_2$ could be prepared by the exchange reaction of the corresponding tetramethyldipnictogens (eq. 1) [4].

$$\underset{(\mathbf{1})}{Me_4E_2} + \underset{(\mathbf{1'})}{Me_4E_2'} \rightleftharpoons \underset{(\mathbf{2})}{2\ Me_2EE'Me_2} \qquad (1)$$

(E′ ≠ E **a**, E = P;
b, E = As;
c, E = Sb;
d, E = Bi)

$$\underset{(\mathbf{1})}{Me_4E_2} + Me_2A_2 \rightleftharpoons 2\ Me_2EAMe \qquad (2)$$

(**1**) (**3**, A = S; **4**, A = Se; **5**, A = Te) (**6**, A = S; **7**, A = Se; **8**, A = Te)

(Diorganopnicto)organochalcogenides R_2EAR may be prepared by a similar reaction of R_4E_2 and R_2A_2 (A = S, Se, Te). Grobe and coworkers have reported on a systematic investigation of the exchange reaction of diphosphines and diarsines with dichalcogenides [5–7]. More recently several (diorganoarsino)organotellurides R_2AsTeR' [8], (diorganostibino)organotellurides R_2SbTeR' [9,10] and a (diorgano-

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bismuthino)organotelluride R_2BiTeR' [11] have been prepared via the exchange reaction of a ditelluride with the corresponding tetraorganodipnictogens.

On the other hand, a number of (diorganopnicto)organosulfides have been obtained by displacement reactions [12–15]. Since samples of all of the tetramethyldipnictogens were available to us, we have explored their exchange with all of the dimethyldichalcogenides **3–5**. This has allowed us to explore the generality of the reaction and to obtain spectroscopic characterization of the (dimethylpnicto)methylchalcogenides **6–8** which had not previously been reported.

Results and discussion

Exchanges with dimethylditelluride

We find that the tetramethyldipnictogens (Me_4E_2, E = P, As, Sb, Bi) undergo rapid exchange with dimethylditelluride at 25°C in solution or as neat liquids. The ^1H NMR spectra of mixtures of either tetramethyldiphosphine or tetramethyldiarsine with dimethylditelluride in benzene-d_6 show signals for both the parent compounds and mixed compounds **8a** and **8b**, respectively. The relative concentration of each species was determined by integration of the proton signals. The equilibrium constants were calculated using the following expression:

$$K = [Me_2EAMe]^2/[Me_4E_2][Me_2A_2] \quad (3)$$

The equilibrium constants at 25°C are 63 and 3×10^{-2} for formation of **8b** and **8a**, respectively.

On the other hand, mixtures of either tetramethyldistibine or tetramethyldibismuthine with dimethylditelluride were completely converted to (dimethylstibino)methyltelluride (**8c**) or (dimethylbismuthino)methyltelluride (**8d**), respectively. Based upon our estimated levels of detection of starting materials, the equilibrium constants must exceed 10^3.

NMR spectra

The proton NMR data for **8a–8d** are summarized in Table 1. Data for **8b** are consistent with those reported by Grobe [5]. Relative assignments may be made easily since the signals for the methyl groups attached to the pnictogen atom are twice as intense as those for the methyl groups attached to tellurium. This assignment is consistent with the ^{125}TeH coupling constants. For **8a**, **8b** and **8c**, the ^2J(TeH) is approximately 21 Hz, only slightly smaller than the 23.6 Hz shown for Te_2Me_2 [16]. On the other hand, the smaller ^3J(TeH) values for Me_2ETeMe increase in the series E = Sb < As < P. The proton signals for **8d** were so broad that the J(TeH) values could not be determined.

The proton-noise decoupled ^{125}Te NMR spectra of **8a–8d** have been measured in benzene-d_6. Excess dimethylditelluride served as an internal reference at δ 63 ppm. The ^{125}Te chemical shift data of **8a–8d** and some related compounds are collected in Table 2.

The ^{125}Te NMR resonances occur over a large range. The chemical shift value of **8a** at 90 ppm is more than 350 ppm downfield from δ −277 ppm shown by **8d**. There is a progressive Te-shielding in the series Me_2ETeMe as E changes from phosphorus to bismuth. A similar trend is shown by p-tolyltellurium derivatives $TolTeER_2$ (E = P, Sb, Bi) [11,17], although differences in pnictogen substitution

TABLE 1

PROTON NMR DATA FOR THE (DIMETHYLPNICTO)METHYLCHALCOGENIDES, Me_2EAMe [a]

Compound	δ(Me_2EAMe) (ppm)	^3J(AH) (Hz) [b]	δ(Me_2EA*Me*) (ppm)	^2J(AH) (Hz) [b]	J(PH) (Hz)
Me_2PSMe (**6a**)	1.08 [c]	–	1.88 [c]	–	^2J(PH) 6.4; ^3J(PH) 9.8 [c]
Me_2AsSMe (**6b**)	1.05 [d]	–	1.97 [d]	–	–
Me_2SbSMe (**6c**)	0.81	–	2.03	–	–
Me_2PSeMe (**7a**)	1.21 [e]	8.2	1.78 [e]	10.5	^2J(PH) = ^3J(PH) = 7.0 [e]
$Me_2AsSeMe$ (**7b**)	1.14 [f]	6.5	1.85 [f]	8.5	–
$Me_2SbSeMe$ (**7c**)	0.90	3.7	1.85	9.9	–
$Me_2BiSeMe$ (**7d**)	1.28 (br s)	–	2.29 (br s)	–	–
Me_2PTeMe (**8a**)	1.41	16.6	1.67	21.0	^2J(PH) 7.3; ^3J(PH) 4.6
$Me_2AsTeMe$ (**8b**)	1.30 [g]	10.3	1.73 [g]	20.6	–
$Me_2SbTeMe$ (**8c**)	1.07	7.6	1.69	20.5	–
$Me_2BiTeMe$ (**8d**)	1.45 (br s) [h]	–	2.07 (br s) [h]	–	–

[a] The solvent is benzene-d_6 unless noted otherwise. Chemical shifts are relative to TMS. [b] A refers to ^{125}Te or ^{77}Se. [c] Literature values δ 1.25, 2.04; ^2J(PH) 6.5, ^3J(PH) 9.8. Ref. 15. [d] Literature values δ 1.25, 2.10. Ref. 14. [e] Literature values δ 1.25, 1.82; ^2J(PH) 7.2, ^3J(PH) 7.4. Ref. 5. [f] Literature values δ 1.23, 1.90. Ref. 5. [g] Literature values δ 1.47, 1.82. Ref. 5. [h] The solvent is toluene-d_8.

make the comparison tenuous. Very large substituent effects on the ^{125}Te chemical shift values have been found for dialkylditellurides [18,19].

(Dimethylphosphino)methyltelluride was also detected by ^{31}P NMR spectroscopy. The compound shows a signal at δ -33.4 ppm with easily observable satellites arising from ^{125}Te coupling (^1J(PTe) 397 Hz). The value of the TeP coupling constant is similar to that shown by other singly bonded TeP compounds [17].

Exchanges with dimethyldiselenide and dimethyldisulfide

In an identical manner we find that the tetramethyldipnictogens undergo rapid reaction with dimethyldiselenide to give the corresponding (dimethylpnicto)methyl-

TABLE 2

TELLURIUM-125 NMR CHEMICAL SHIFT VALUES FOR (DIORGANOPNICTO)ORGANOTELLURIDES R_2ETeR' (E = P, As, Sb, Bi) AND SELECTED DIORGANODITELLURIDES

Compound	δ (ppm)	^1J(PTe) (Hz)
MeTeTeMe (**5**)	63	–
$MeTePMe_2$ (**8a**)	90	397
$MeTeAsMe_2$ (**8b**)	34	–
$MeTeSbMe_2$ (**8c**)	-271	–
$MeTeBiMe_2$ (**8d**)	-277	–
TolTeTeTol	432.2 [a]	–
$TolTeP(t\text{-}Bu)_2$	241.4 [b]	556 [c]
$TolTeP(i\text{-}Pr)_2$	197.4 [b]	553 [c]
$TolTeSbMe_2$	137.2 [b]	–
$TolTeBi(n\text{-}Pr)_2$	47.2 [b]	–

[a] Ref. 19. Solvent is $CHCl_3$. [b] Ref. 10. Adjusted to standard Me_2Te $\delta = 0$. [c] Ref. 17.

selenides 7. The ^1H NMR spectra of the reaction mixtures of each of the tetramethyldipnictogens with dimethyldiselenide in benzene-d_6 indicate complete conversion to 7. Based upon our estimated limits of detection of starting material the equilibrium constants must be $> 10^3$ for formation of **7a**–**7d**.

The ^1H NMR data are collected in Table 1. The chemical shift values of **7a** and **7b** are essentially identical to those previously reported by Grobe [5]. The ^{77}Se–^1H coupling constants of **7a**, **7b** and **7c** follow a trend similar to that observed for ^{125}Te–H coupling constants of **8**. Thus, the $^2J(^{77}SeH)_2$ are slightly smaller than that of dimethyldiselenide ($^2J(^{77}SeH)$ 11.9 Hz) [20] and they show only small variation in the series. On the other hand, the smaller $^3J(^{77}SeH)$ values increase in the series Me_2ESeMe, E = Sb < As < P.

We also find that tetramethyldiphosphine, tetramethyldiarsine and tetramethyldistibine undergo exchange reactions with dimethyldisulfide to produce the corresponding (dimethylpnicto)methylsulfides **6**. The equilibrium constants at 25°C are 28, 77 and 200 for the formation of **6a**, **6b** and **6c**, respectively. We were not able to detect exchange with tetramethyldibismuthine. However, since (diorganobismuthino)organosulfides have been prepared by displacement reactions, the equilibria are likely to be highly favorable [11]. Compounds **6a** [15] and **6b** [14] have previously been reported. Proton NMR spectral data are collected in Table 1.

Raman spectra

We have found Raman spectroscopy to be an extremely useful method for characterizing the (dimethylpnicto)methylchalcogenides **6**–**8**. Metal–metal (or heavy element–heavy element) stretching vibrations normally give rise to intense and easily identifiable Raman peaks. For each of the compounds Me_2EAMe we observe strong bands assigned to the E–A stretch at frequencies intermediate between the E–E bands of the corresponding tetramethyldipnictogen and the A–A bands of the corresponding dimethyldichalcogenide. However, in the case of bismuth compounds **7d** and **8d** we were unable to observe the BiA bands. Apparently the deeply colored bismuth compounds were destroyed by the laser exciting radiation. The Raman data are collected in Table 3.

Spectral assignments listed in Table 3 are consistent with the relatively few data available for compounds containing E–A bonds. Previous assignments for the PS, AsS and AsSe stretching frequencies of **6a** [15], **6b** [14] and **7b** [14] agree within 10 cm^{-1} with the present data. Raman spectra for a series of bis(diorganostiba)telluranes [9] -selenanes [9] and -sulfides [21] $(R_2Sb)_2E$ have been reported by Breunig and coworkers. Interestingly the assignments for bands from SbS (335 cm^{-1}), SbSe (225 cm^{-1}) and SbTe (180 cm^{-1}) vibrations are identical to those found for **6c**, **7c** and **8c**, respectively. A series of triorganopnicto-chalcogenides R_3EA including compounds R_3SbS, R_3SbSe and R_3PTe have been examined by Zingaro [22]. In each case the band assigned to E=A stretch occurs at higher frequency than the corresponding EA band for the Me_2EAMe. This shift is consistent with the expected multiple bond character of EA bonds of compounds R_3EA.

The fundamental EA stretching frequencies for all of compounds Me_2EAMe can be accurately estimated using Gordy's empirical equation (eq. 4) [23]. This equation expresses the force constant (k) for an isolated EA vibration in terms of the Pauling electronegativities (χ_A, χ_E) [24] and the EA bond distance (d), estimated from the sum of the Pauling covalent radii [25]. Substituting k and the reduced mass μ of

TABLE 3

SUMMARY OF THE ELEMENT-ELEMENT STRETCHING VIBRATIONS OF THE (DIMETHYLPNICTO)METHYLCHALCOGENIDES (Me_2EAMe), THE DIMETHYLDICHALOGENIDES (Me_2A_2) AND THE TETRAMETHYLDIPNICTOGENS (Me_4E_2) FROM THE RAMAN SPECTRA. A COMPARISON WITH FREQUENCIES CALCULATED USING GORDY'S RULE

Compound	Observed ν (cm^{-1})	Calcd. ν (cm^{-1})	Difference (cm^{-1})	Assignment
Me_4P_2 (**1a**)	455, 425 [a]	452	−3	P–P
Me_4As_2 (**1b**)	272, 254 [b]	266	−6	As–As
Me_4Sb_2 (**1c**)	175, 143 [c]	185	+10	Sb–Sb
Me_2S_2 (**3**)	505 [d]	517	+12	S–S
Me_2Se_2 (**4**)	286 [e]	273	−13	Se–Se
Me_2Te_2 (**5**)	188 [f]	195	+7	Te–Te
Me_2PSMe (**6a**)	470 [g]	483	+13	P–S
Me_2AsSMe (**6b**)	386, 372 [h]	382	−4	As–S
Me_2SbSMe (**6c**)	335	338	+3	Sb–S
Me_2PSeMe (**7a**)	383, 368	382	−1	P–Se
$Me_2AsSeMe$ (**7b**)	277, 261 [i]	289	+12	As–Se
$Me_2SbSeMe$ (**7c**)	233, 225	236	+3	Sb–Se
Me_2PTeMe (**8a**)	334	328	−6	P–Te
$Me_2AsTeMe$ (**8b**)	233	239	+6	As–Te
$Me_2SbTeMe$ (**8c**)	179	190	+11	Sb–Te

[a] Ref. 25. [b] Ref. 26. [c] Ref. 27. [d] "Sadtler Standard Raman Spectra," Sadtler Research Laboratories, Philadelphia, Pennsylvania (1976) 4084R. [e] W.H. Green and A.B. Harvey, J. Chem. Phys., 49 (1968) 3586. [f] C.W. Sink and A.B. Harvey, J. Mol. Struct., 4 (1969) 203. [g] Literature value 478 cm^{-1}. Ref. 15. [h] IR value 382 cm^{-1}. Ref. 14. [i] IR value 280 cm^{-1} (?). Ref. 14.

atoms A and E into the equation of the harmonic oscillator (eq. 5) gives the calculated frequencies tabulated in Table 3. The estimated values are very close to the experimental values. The average difference is only ± 7 cm^{-1} while the largest deviation is only 13 cm^{-1}. This agreement provides a considerable level of confidence in our assignments.

$$k = 1.67\left(\chi_A \chi_E / d^2\right)^{3/4} + 0.30 \tag{4}$$

$$\nu\ (cm^{-1}) = 1307\left(k/\mu\right)^{1/2} \tag{5}$$

Compounds **7a**, **7b**, **7c** and **6b** apppear to each show two EA bands. The tetramethyldipnictogens **1a** [25], **1b** [26], and **1c** [27] also each show two bands for the E–E stretching frequencies. These bands have been assigned to *trans* and *gauche* conformers. It may be that compounds **7** and **6b** populate similar conformers.

Mass spectra

Finally, the (dimethylpnicto)methylchalcogenides **6a–c**, **7a–c** and **8b–c** have been characterized by mass spectroscopy. Owing to their lability the mass spectra of **7d** and **8d** could not be recorded. The major fragmentation patterns are summarized in Table 4. Each compound shows easily identifiable molecular ions Me_2EAMe^+ and characteristic daughter ions of Me_2EA^+, $MeEA^+$, EA^+, Me_2E^+, E^+, MeA^+ and A^+.

TABLE 4

MASS SPECTRA OF (DIMETHYLPNICTO)METHYLCHALCOGENIDES (Me_2EAMe) [a]

Ion	Me_2PSMe [b] (6a)	Me_2AsSMe (6b)	Me_2SbSMe [c] (6c)	Me_2PSeMe [d] (7a)	$Me_2AsSeMe$ [d] (7b)	$Me_2SbSeMe$ [c,d] (7c)	$Me_2AsTeMe$ [e] (8b)	$Me_2SbTeMe$ [c,e] (8c)
Me_3EA	108(83)	152(52)	200(37)	158(100)	202(47)	250(37)	250(4)	298(42)
Me_2EA	93(100)	137(100)	185(100)	143(26)	187(100)	235(100)	235(5)	283(58)
MeEA	78(10)	122(19)	170(54)	128(12)	172(43)	220(63)	220(2)	268(26)
EA	63(24)	107(37)	155(53) [f]	113(48)	157(73)	205(70)	205(2)	253(35)
Me_2E	61(16)	105(17)	153(25) [f]	61(33)	105(22)	153(40)	105(38)	153(62)
MeE	46(19)	90(16)	138(39)	47(7)	90(22)	138(51)	90(21)	138(72)
E	–	75(7)	123(50)	–	75(10)	123(70)	75(17)	123(100)
MeA	47(21)	47(22)	47(22)	97(10)	97(58)	97(83)	145(40)	145(78)
A	–	–	–	82(9)	82(18)	82(16)	130(21)	130(39)
Other	65(86)	121(23)	137(32)					
major	45(63)	109(65)	61(24)	76(89)	89(46)	137(34)	89(100)	137(61)
ions		89(35)	46(15)	45(36)				
			45(55)					

[a] The m/e values are followed by the relative intensities in parentheses. [b] Similar to published spectrum. Ref. 15. [c] The m/e are given for ^{123}Sb only, while the relative intensities are for ($^{123}Sb+^{121}Sb$). [d] The m/e are given for ^{82}Se only, while the relative intensities are for ($^{82}Se+^{80}Se+^{78}Se+^{77}Se+^{76}Se$). [e] The m/e are given for ^{130}Te only, while the relative intensities are for ($^{130}Te+^{128}Te+^{126}Te+^{125}Te+^{124}Te$). [f] Overlapping envelopes of peaks.

Experimental

General remarks

The proton, phosphorus and tellurium-125 NMR spectra were recorded using a Bruker WM-360 NMR spectrometer. Tetramethylsilane was used as an internal reference for the proton spectra, while 85% H_3PO_4 was used as an external reference for the phosphorus spectrum. For the tellurium-125 NMR spectra, dimethylditelluride was used as an internal reference at δ 63 ppm relative to an external sample of dimethyltelluride at δ 0 ppm. The tellurium chemical shifts are estimated to be ± 1 ppm.

Mass spectral determinations were made by using a Finnigan 4023 GC/MS with an electron ionization energy of 70 eV. 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. 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.

All operations were performed under argon or nitrogen. Tetramethyldiphosphine and tetramethyldiarsine were obtained from Strem Chemical Co., dimethyldisulfide was obtained from Aldrich Chemical Co. and dimethyldiselenide was obtained from Alfa Chemical Co. Tetramethyldistibine [28], tetramethyldibismuthine [1] and dimethylditelluride [29] were prepared by literature methods.

Exchange reactions of the tetramethyldipnictogens with the dimethyldichalcogenides

Samples for proton NMR spectroscopy were prepared by placing 10 μl of each of the tetramethyldipnictogen and the dimethyldichalcogenide and 0.5 ml of benzene-d_6 in 5 mm NMR tubes. These samples were also used for the GC/MS analyses. The relative equilibrium concentrations were determined from integration of the proton NMR signals. The equilibrium constants were calculated from eq. 3. Their values are estimated to be accurate to 10%. It is estimated that concentrations of starting materials $> 1\%$ could be detected. Where conversion to product was essentially complete, a small concentration of one of the starting materials was detected. The minimum equilibrium constants of 10^3–10^4 are based upon these concentrations.

Samples from the tellurium NMR spectra of **8b**, **8c** and **8d** were prepared by placing 70 μl of dimethylditelluride, 50 μl of the tetramethyldipnictogen and 1.5 ml of benzene-d_6 in 10 mm NMR tubes. The sample for the tellurium NMR spectrum of **8a** was prepared from 10 μl dimethylditelluride, 50 μl dimethyldiphosphine and 500 μl of benzene-d_6, while the sample for the ^{31}P NMR spectrum was prepared from 50 μl of dimethylditelluride, 10 μl of dimethyldiphosphine, and 500 μl of benzene-d_6. Samples for Raman spectra were prepared by sealing 10 μl each of a tetramethyldipnictogen and a dimethyldichalcogenide in 1 mm glass capillary tubes.

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