558 J. Org. Chem. 1981, 46, 558-563

toluenesulfonamide, 75934-57-5; (*S*)-(+)-*sec*-butyl 4-toluenesulfonate, 50896-54-3; isobutylene, 115-11-7; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; ethyl *N*-(triphenylmethyl)glycinate, 18514-46-0; ethyl glycolate, 623-50-7; triphenylmethane, 519-73-3; triphenylcarbinol, 76-84-6; ethyl *N*-nitrocarbamate, 626-37-9; *N*-isobutyl-*N*-nitrosohydroxylamine potassium salt, 75934-58-6; isobutyl tosylate, 4873-56-7; *N*-benzyl-*N*-nitrosohydroxylamine ammonium salt, 75934-59-7.

Nuclear Magnetic Resonance Studies of Some 2-(Group 4B)-Substituted 1,3-Dithianes

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Received July 10, 1980

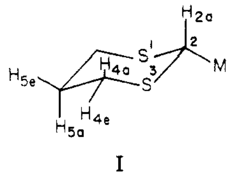
A number of 1,3-dithianes substituted with trimethylsilyl, stannyl, and plumbyl groups at the 2-position have been synthesized and their ^{1}H and ^{13}C NMR spectra obtained. Examination of chemical shifts, low-temperature spectra, and metal–^{13}C coupling constants in certain 2,2-disubstituted 1,3-dithianes lead to the conclusion that these metalloidal groups have a much greater equatorial preference (at C-2) in 1,3-dithiane than in cyclohexane. For example, trimethylplumbyl, with an *A* value of 0.7 kcal/mol in cyclohexane, has an *A* value at C-2 in 1,3-dithiane in excess of 2 kcal/mol, whereas for simple alkyl groups, comparable *A* values are found for both systems. These results are related to the very large equatorial preference (>6 kcal/mol) of a 2-lithio group in 1,3-dithiane. Inter alia it is shown that electrophilic substitution by trimethyltin chloride on 5-*tert*-butyl-2-lithio-1,3-dithiane proceeds with overall retention of configuration.

We have reported conformational *A* values for various metal and metalloidal groups attached to the cyclohexane ring,[1-3] utilizing both direct (low-temperature ^{13}C NMR) and indirect methods. Various investigations have reported *A* values for a number of substituents in heterocyclic ring systems,[4] and data are now available for the 1,3-dithiane system.[5-11] The general conclusion was that for 2-substituted 1,3-dithianes the *A* values for alkyl and phenyl groups were very similar to those for the corresponding cyclohexanes. It seemed a worthwhile exercise, therefore, to examine a number of 2-metallo-1,3-dithianes from the viewpoint of conformational preference so that comparisons with the cyclohexane system could be made. This was particularly interesting, in view of the studies of Eliel[12-14] which demonstrated that a 2-lithio group had a very large equatorial preference (*A* value >6 kcal/mol) in 1,3-dithiane, whereas comparably polar groups (e.g., MgX and Mg) in cyclohexane[15] lack such a large preference (*A* values from 0.50 to 0.80 kcal/mol depending on solvent etc.), and HgX actually has a slight axial preference[2,3] (*A* ≈ −0.2 kcal/mol). In this report, we discuss the NMR characteristics of various 2-M-1,3-dithianes, where M is a group 4B metal or metalloid, and draw conclusions regarding the magnitude of their conformational preference. While this work was in its early stages, Cane, Graham, and Vancea[16] reported the synthesis of some group 4B-substituted 1,3-dithianes and their iron tetracarbonyl complexes, but the major thrust of their work was in a different direction.

Results and Discussion

We initially prepared the series of 2-X-1,3-dithianes, where X = CH_3, C_6H_5, $Si(CH_3)_3$, $Ge(CH_3)_3$, $Sn(CH_3)_3$, and $Pb(CH_3)_3$, and recorded their ^{1}H and ^{13}C NMR spectra under ambient conditions. These data are shown in Table I.

The general features of the ^{1}H spectra of 2-substituted 1,3-dithianes have been discussed,[5,6,17,18] and accurate values of the various coupling constants are available. In the present context, we note the sharp appearance of the H_2 resonance ($W_{1/2}$ not greater than 1.5 Hz) for the compounds in Table I. This indicates quite strongly the predominantly equatorial nature of the substituent, because long-range couplings from $H_{4,6}$ or H_5 to $H_{2\mathrm{axial}}$ are known to be much smaller than the significant (1–2 Hz) H_{2e}–$H_{4,6e}$ or H_{5e}–H_{2e} couplings (see I).[5,19] The latter then cause equatorial protons H_{2e} to be much broader ($W_{1/2} \approx$ 4 Hz), which is not the case here.



I

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[3] P. R. Barron, D. Doddrell, and W. Kitching, *J. Organomet. Chem.*, **132**, 339 (1977).

[4] See, for example: (a) F. G. Riddell, *Qt. Rev. Chem. Soc.*, **21**, 364 (1967); (b) C. Romers, C. Altonia, H. R. Buys, and E. Havinga, *Top. Stereochem.*, **4** (1972).

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[16] D. J. Cane, W. A. G. Graham, and L. Vancea, *Can. J. Chem.*, **56**, 1538 (1978).

[17] H. R. Buys, *Recl. Trav. Chim. Pays-Bas*, **89**, 1244 (1970).

[18] (a) J. Martin and J. B. Robert, *Org. Magn. Reson.*, **7**, 76 (1975). (b) E. L. Eliel, V. S. Rao, F. W. Vierhapper, and G. Z. Jvaristi, *Tetrahedron Lett.*, 4339 (1975)

[19] K. C. Ramey and J. Messick, *Tetrahedron Lett.*, 4423 (1965).

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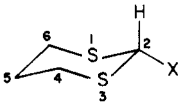
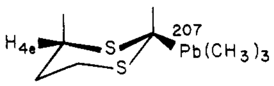
Table I. ^{13}C and ^{1}H NMR Data[a] for



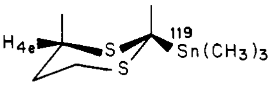
	^{1}H data				^{13}C data			
X	2	4,6	5	other	2	4,6	5	other
H	3.81	2.86 (m)	2.12 (m)		31.84	29.83	26.54	
CH_3	4.12 (q)	2.86 (m)	2.02 (m)	1.45 (d)	42.06	30.68 [+0.85][b]	25.24	21.27
C_6H_5	5.10 (s)	2.93 (m)	2.04 (m)	7.29 (m)	51.07	32.04 [+2.21][b]	25.10	139.05, 128.71, 128.42 (br), 127.71
$C(CH_3)_3$[c]					61.78	31.18 [+1.35][b]	25.97	35.67, 27.85
$Si(CH_3)_3$	3.70 (s)	2.80 (m)	2.08 (m)	0.16 (s)	34.19	30.95 [+1.12][b]	26.10	−3.23
$Ge(CH_3)_3$	3.85 (s)	2.79 (m)	2.12 (m)	0.32 (s)	33.40	31.26 [+1.43][b]	26.16	−3.54
$Sn(CH_3)_3$[d]	3.98 (s) (44)	2.80 (m)	2.14 (m)	0.24 (s) (57)	27.37 (257)	32.43 (28) [+2.60][b]	27.03	−10.19 (356, 338)
$Pb(CH_3)_3$[e]	4.26 (s) (30)	2.80 (m)	2.15 (m)	0.80 (s) (64)	28.54 (88)	33.69 (38) [+3.86][b]	27.11	−0.64 (261)

[a] In δ units relative to internal Me_4Si. [b] Values in brackets are the γ effect (relative to X = H). [c] From ref 22. [d] Values in parentheses are $^{119,117}Sn$ couplings, where resolved. [e] Values in parentheses are ^{207}Pb couplings.

The fact that $J_{H_{2e}-H_{4e}}$ is significant (~1–2 Hz) suggested that if $(CH_3)_3Sn$ and $(CH_3)_3Pb$ (both of which have magnetically active isotopes: $^{117,119}Sn$, $I = {}^1/_2$, each ~8% abundant; ^{207}Pb, $I = {}^1/_2$, ~21% abundant) were indeed equatorially disposed, as shown in I, significant coupling between H_{4e}–^{207}Pb and H_{4e}–$^{117,119}Sn$ should occur. In the 270-MHz ^{1}H NMR spectra of these derivatives (Figure 1) H_{4e} and H_{4a} are well-resolved and separated from the H_5 pair. H_{4e} is easily identified as the higher field half of the H_{4e}–H_{4a} system, as it experiences only one large coupling, viz., the geminal coupling to H_{4a}, and smaller couplings to H_{5e} and H_{5a}. H_{4a}, on the other hand, experiences large couplings to H_{4e} and H_{5a} and a smaller coupling to H_{5e}. Satellites associated with the presence of ^{207}Pb and $^{117,119}Sn$ are identified in high-quality spectra (at 100 and 270 MHz) about the H_{4e} resonance, and the coupling constants are shown in II and III.



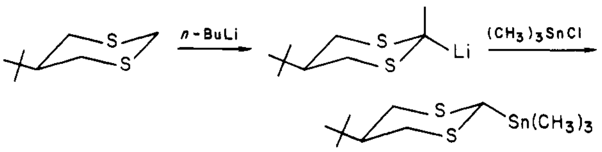
II, $^{4}J_{^{207}Pb-H_{4e}} \simeq 17$ Hz



III, $^{4}J_{^{119}Sn-H_{4e}} \simeq 12$ Hz

Coupling about H_{4a} is not identifiable and must be quite small in comparison. Given that long-range metal–proton coupling is also favored by a zig-zag array,[20] these large couplings again point to a predominantly equatorial disposition of these metal groups. (We could not positively identify coupling to H_{5e} as the $H_{5a,5e}$ pattern is far more complex, but it is clear that H_{5a} is to higher field than H_{5e}.)[21] It is interesting to observe that the ratio of metal–H_{4e} couplings (^{207}Pb, ^{119}Sn) of 17/12 is very similar to that (38/28) for metal–C_4 couplings (Table I).

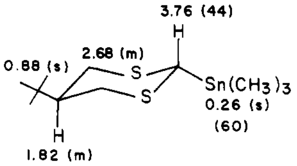
We have reported previously that *vicinal* coupling between $^{119,117}Sn$[23] or ^{207}Pb[1] and ^{199}Hg[24] and ^{13}C ($^{3}J_{^{13}C-M}$) have pronounced dihedral angle dependences of the Karplus form. For example, in cyclohexane, with an *equatorial* $Sn(CH_3)_3$, $^{3}J_{^{119}Sn-^{13}C}$ (to $C_{3,5}$; $\theta = 180°$) is ~65 Hz, while a much lower value (~10–12 Hz) is characteristic of an *axial* $Sn(CH_3)_3$ ($\theta = 60°$).[25] In the $(CH_3)_3Sn$ and $(CH_3)_3Pb$ derivatives of 1,3-dithiane (Table I), vicinal coupling to $C_{4,6}$ is observable, being 28 and 38 Hz, respectively. These couplings, according to the discussion above, are characteristic of *equatorial* $M(CH_3)_3$ groups and are clearly substantially attenuated by the intervening sulfur atom. (Corresponding values in cyclohexane are ~65 and ~121 Hz, respectively.)[23,25] To confirm these conclusions, we synthesized the conformationally homogeneous derivative by the route shown in eq 1.



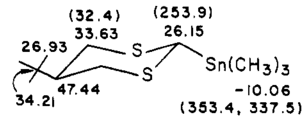
(1)

The extensive studies of Eliel[12-14] have demonstrated the very large equatorial preference of a 2-lithio group, and coupled with the presumed significant equatorial preference of the 5-*tert*-butyl group,[5] the diequatorial conformation above for the Li derivative is the only reasonable one. Quenching of 2-lithio-1,3-dithianes with a variety of electrophiles uniformly proceeds with retention[12-14] of configuration, and as there is no reason to attribute special behavior to $(CH_3)_3SnCl$, the expected product is *trans*-5-*tert*-butyl-2-(trimethylstannyl)-1,3-dithiane. ^{1}H and ^{13}C NMR examination of the product confirmed formation of the tin compound in a highly specific fasion—one isomer was formed.

The ^{1}H and ^{13}C NMR data are summarized in structures IV and V, with the shifts being given as δ values (values in parentheses are $^{119,117}Sn$ couplings).



IV



V

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(20) See, for example, D. N. Ford, W. Kitching, and P. R. Wells, *Aust. J. Chem.*, 22, 1157 (1969), and references therein.

(21) In ref 18a it is reported that H_{5a} is to lower field than H_{5e} in 2-phenyl-1,3-dithiane, but the reverse sequence appears to apply in the case of 2-*tert*-butyl-1,3-dithiane (footnote 12 in ref 22); see also ref 18b.

(22) E. L. Eliel, V. S. Rao, and F. G. Riddell, *J. Am. Chem. Soc.*, 98, 3583 (1976).

(23) D. Doddrell, I. Burfitt, W. Kitching, M. Bullpitt, C. Lee, R. J. Mynott, J. L. Considine, H. G. Kuivila, and R. H. Sarma, *J. Am. Chem. Soc.*, 96, 1640 (1974).

(24) W. Kitching, D. Praeger, D. Doddrell, F. A. L. Anet, and J. Krane, *Tetrahedron Lett.*, (1975).

(25) See W. Kitching, H. Olszowy, J. A. Waugh, and D. Doddrell, *J. Org. Chem.*, 43, 898 (1978).

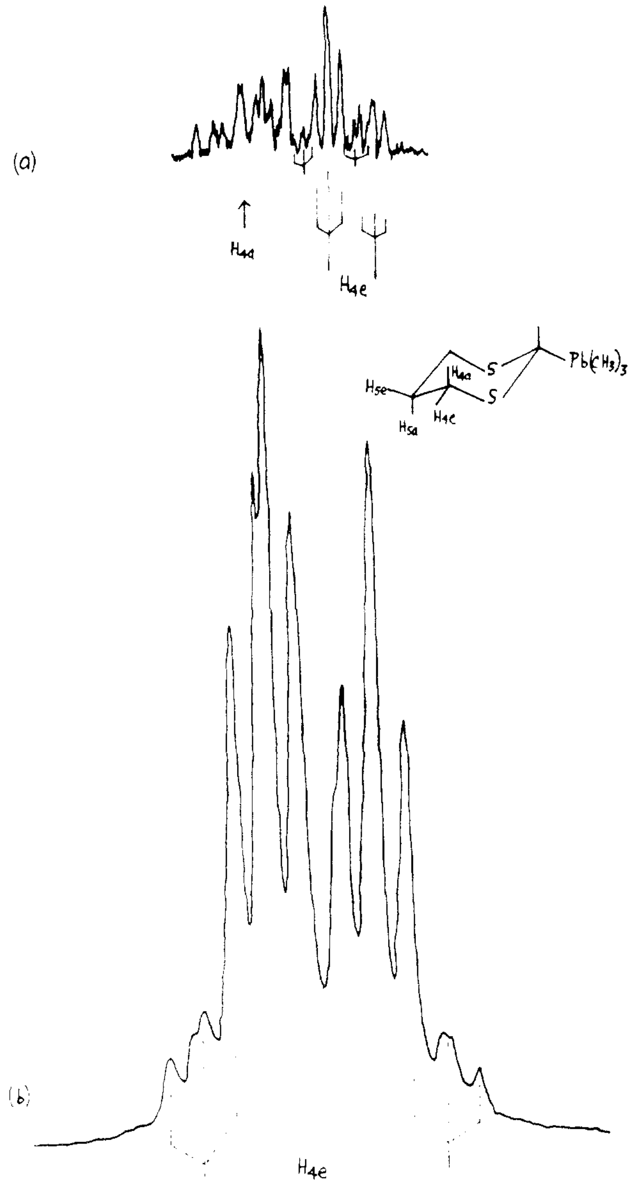
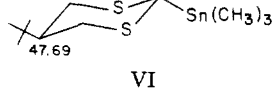


Figure 1. (a) H_{4a},H_{4e} region of the 100-MHz ^1H NMR spectrum of 2-(trimethylplumbyl)-1,3-dithiane. H_{4e}, experiencing one large (to H_{4a}) and two smaller couplings (to $H_{5a,5e}$), is clearly the higher field half of the H_{4a},H_{4e} AB system. The ^{207}Pb coupling about the more intense "triplet part" of H_{4e} is indicated. (b) The H_{4e} resonance at 270 MHz, now approaching first-order appearance (H_{4a} not shown), and the outside ^{207}Pb satellites about the pair of triplets are shown. (The other pair of ^{207}Pb satellites are submerged in the main H_{4e} absorption.)

The close agreement in $^3J_{^{119}Sn-C_{4,6}}$ (32.4 Hz) and $\delta_{Sn(CH_3)_3}$ (−10.06) with the corresponding values in 2-(trimethylstannyl)-1,3-dithiane (28 Hz and δ −10.19) confirm a similar orientation of the metallo group, viz., equatorial. By use of published data[22] for 5-tert-butyl-1,3-dithiane, it is possible to calculate the ^{13}C shifts (shown in VI) for the 5-*tert*-butyl-2-trimethyltin derivative, assuming additivity.

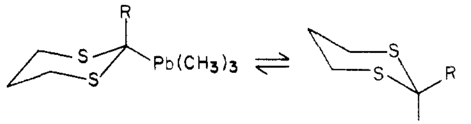


VI

The excellent agreement again demands like dispositions for the 2-trimethyltin groups. These data provide α and γ effects of the trimethyltin group (in the 5-*tert*-butyl system) of −5.1 and +2.61 ppm respectively (vide infra). γ effects of substituents can vary substantially depending on orientation with respect to the γ-carbon, the presence of free electron pairs on a heteroatom, or the possession of formal acceptor properties.[26,27] In the latter connection, we reported that the γ effects of $M(CH_3)_3$ (M = C, Si, Ge, Sn, Pb) in cyclohexyl derivatives were substantial for an antiperiplanar array (equatorial position) and increased down the group.[27] In Table I, it is clear the same trend is observed, with a maximum effect (+3.86 ppm) for $Pb(CH_3)_3$ [+3.06 ppm in *equatorial* c-HxPb(CH_3)$_3$]. The sulfur atoms appear to exert only a very minor effect on transmission of the γ effect, the nature of which is still unclear.[28]

Low-Temperature ^1H and ^{13}C NMR Spectra. $(CH_3)_3Pb$ has an *A* value in cyclohexane of +0.70 kcal/mol[1] (16 ± 2% of that of the axial conformer at −69 °C), and it seemed reasonable that if we were to observe the axial conformer of any of the group 4B derivatives of 1,3-dithiane, it would be for lead. This derivative has the additional attraction of exhibiting readily observable $^{207}Pb-^{13}C$ couplings, which could provide useful information as well. With CD_2Cl_2 as solvent, variable-temperature, 270-MHz ^1H NMR and 67.89-MHz ^{13}C NMR spectra of 2-(trimethyllead)- and 2-(trimethylstannyl)-1,3-dithiane were obtained down to 173 K, but no meaningful changes in any NMR parameters were noted. Kalff and Havinga[6] found that the methyl resonances of 2,2-dimethyl-1,3-dithiane were resolved at 193 K, providing $\Delta G^{\ddagger} \approx 10.3$ kcal/mol for chair–chair interconversion. Because of the high intensity of the ^{207}Pb satellites about the main resonance of the CH_3 groups (ca. 10% each) we estimated that 0.5% of the axial conformer would have been detected. The conclusion must be that the *A* values for $(CH_3)_3Sn$ and $(CH_3)_3Pb$ are very much larger than the corresponding values in cyclohexane, and a minimum value of 2.15 kcal/mol for the *A* values is obtained, compared with 1.06 ($Sn(CH_3)_3$) and 0.67 kcal/mol ($(CH_3)_3Pb$) in cyclohexane.

2,2-Disubstituted 1,3-Dithianes. Failure to observe directly the axial conformers of the group 4B derivatives suggested that examination of appropriate 2-substituted 2-$(CH_3)_3Sn$ or 2-$Pb(CH_3)_3$ compounds would be useful in confirming the high *A* values for these groups. This "counter-pose" approach depends on choosing groups whose *A* values are of considerable magnitude so that the equilibrium of eq 2 is not too one-sided.



(2)

For methyl and phenyl, *A* values at position 2 in 1,3-dithiane are 1.77 and 1.7 ± 0.3 kcal/mol, respectively,[5,6,8] The compounds prepared and examined are shown in Table II, with their ^1H and ^{13}C NMR data.

The data for 2-methyl-2-(trimethylstannyl)-1,3-dithiane is particularly illuminating. Compared with 2-(trimethylstannyl)-1,3-dithiane itself, we note that the δ_{CH_3-Sn} values are almost identical (−10.19 and −10.14 ppm) and in very close agreement with δ_{CH_3-Sn} values (−10.06 ppm) for *trans*-5-*tert*-butyl-2-(trimethylstannyl)-1,3-dithiane discussed above. Additionally, vicinal $^{119}Sn-^{13}C$ couplings

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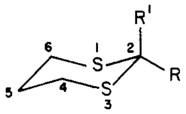
[26] E. L. Eliel, W. F. Bailey, L. D. Kopp, R. L. Willer, D. M. Grant, R. Bertrand, K. A. Christensen, D. K. Dallring, M. W. Duch, E. Wenkert, F. M. Schell, and D. W. Cochran, *J. Am. Chem. Soc.*, 97, 322 (1975).

[27] W. Kitching, M. Marriott, W. Adcock, and D. Doddrell, *J. Org. Chem.*, 41, 1671 (1976).

[28] For a recent summary see J. P. Forrest and J. G. Webb, *Org. Magn. Reson.*, 12, 371 (1979).

Table II. ^1H and ^{13}C NMR Data[a,b] for

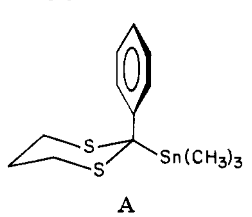


		^1H data			^{13}C data			
R	R'	4,6	5	other	2	4,6	5	other
$Sn(CH_3)_3$	CH_3	2.84	2.04	2.08 (CH_3), 0.25 ($Sn(CH_3)_3$) (55)	n.o.	24.00 (25.6)	27.59	25.87, −10.14 (323.1)
$Sn(CH_3)_3$	C_6H_5	2.67	2.02	7.24 (3 H), 7.87 (2 H), 0.18 (54)	42.15	25.65 (25.6)	25.65	143.77, 128.47 (9.2), 127.52 (14.0), 124.32,[d] −9.63 (341.8, 326.5)
$Si(CH_3)_3$	C_6H_5	2.65	1.99	7.25 (3 H), 7.90 (2 H), 0.16	47.51	25.09	25.14	140.41, 129.59, 128.22, 125.15,[d] −3.93 (53.7)[c]
$Si(CH_3)_3$	$Si(CH_3)_3$	2.71	1.97	0.28	31.02	26.26	24.68	0.46 (52.9)[c]
$Sn(CH_3)_3$	$Sn(CH_3)_3$	2.60	2.05	0.24[e]	21.37	30.22 (26.9)	26.04	−6.77 (323.9, 309.2)[f]

[a] Chemical shifts in δ units relative to Me_4Si. [b] Values in parentheses are $^{117,119}Sn$ couplings. [c] Coupling to ^{29}Si. [d] C_{para}. [e] From D. Seebach, I. Willert, A. K. Beck, and B. Grobel, *Helv. Chim. Acta*, **61**, 2510 (1978). [f] D. Seebach, private communication.

(to $C_{4,6}$) in the three compounds are comparable, viz. 25.6, 28, and 32.4 Hz, respectively, and both sets of data strongly suggest the same orientation for the $Sn(CH_3)_3$ group in all three compounds, i.e., equatorial. The chemical shift of $C_{4,6}$ is also revealing. The γ effect of axial 2-CH_3 in 1,3-dithiane is reported to be −7.2 or −9.4 ppm,[22] depending on the system, whereas the γ effect of an equatorial 2-CH_3 is +0.80 ppm.[22] The γ effect of equatorial $(CH_3)_3Sn$ in 1,3-dithiane is +2.60 ppm and of an axial $Sn(CH_3)_3$ in cyclohexane is ca. −1.00 ppm.[1] For the arrangement with CH_3 axial and $Sn(CH_3)_3$ equatorial, the shift of $C_{4,6}$ is calculated to be either 25.23 or 23.03 ppm (depending on the γ effect of the axial CH_3). These values agree reassuringly with the observed value of 24.00 ppm. For the alternate arrangement (CH_3 equatorial, $Sn(CH_3)_3$ axial) a value for $C_{4,6}$ of 29.13 ppm is obtained (with $\gamma_{ax\text{-}Sn(CH_3)_3} \approx -1.5$ ppm[29] and $\gamma_{eq\text{-}CH_3} = +0.80$ ppm). Clearly this represents inferior agreement. While we recognize that additivity of group effects (particularly with geminal groups) is imprecise, the above comparisons are most consistent with conformations with the $Sn(CH_3)_3$ group predominantly equatorial. Eliel has shown[5,22] that axial 2-CH_3 groups resonate (in the ^1H NMR spectrum) at lower field than equatorial 2-CH_3 groups, typical values being ca. 1.90 and 1.50 ppm, respectively. On comparison of the CH_3 ^1H shift in 2-methyl-1,3-dithiane (1.45 ppm) with that in 2-methyl-2-(trimethylstannyl)-1,3-dithiane (2.08 ppm), it is clear that the latter value is appropriate for an axial C–CH_3 group.

Examination of the data for the 2-phenyl-2-trimethylstannyl derivative favors conformation A, rather than the alternative with $(CH_3)_3Sn$ axial.



A

Thus the vicinal $^{119}Sn–C_{4,6}$ coupling (25.6 Hz), while slightly smaller than for the parent (28 Hz), is consistent with an equatorial $Sn(CH_3)_3$. The chemical shifts of C_2 (42.15 ppm) and $C_{4,6}$ (25.65 ppm) are far more appropriate for an axial phenyl. Thus an equatorial phenyl has an γ effect of +2.30 ppm,[22] which combined with (the approximate) γ effect of axial $Sn(CH_3)_3$ (∼−2.00 ppm)[29] leads to a calculated chemical shift of ca. 30.1 ppm for $C_{4,6}$, widely at variance with the observed 25.65 ppm. However, this is just what is expected for conformation A, which is also strongly favored by the pattern of ^1H absorptions of the phenyl groups. Kalff and Havinga[6] have examined a number of 2-phenyl-1,3-dithianes (CS_2 solvent) and concluded that an equatorial phenyl group gives rise to a relatively sharp absorption at ∼7.00 ppm whereas an axial phenyl is characterized by lower field resonances at ∼7.3 ppm (meta plus para) and 7.9 ppm (ortho). (A relatively narrow resonance is observed for 2-phenyl-1,3-dithiane.) The data in Table II indicate that in 2-phenyl-2-(trimethylsilyl)- and 2-phenyl-2-(trimethylstannyl)-1,3-dithianes, the metallo groups are predominantly equatorial. The crystal structure of 2-methyl-2-(triphenylsilyl)-1,3-dithiane has been reported, and the $(C_6H_5)_3Si$ group occupies the equatorial position.[30]

Several aspects of the data pertaining to the 2,2-bis(trimethylsilyl and -stannyl) derivatives (Table II) are of interest, as these compounds necessarily have an axial $Si(CH_3)_3$ or $Sn(CH_3)_3$ group. In the silicon case, it is clear that the γ effect (at $C_{4,6}$) of the axial group is ca. −4.7 ppm [after correction for the slight (+1.12 ppm) positive γ effect of the equatorial $Si(CH_3)_3$] and for axial $Sn(CH_3)_3$ is ca −2.2 ppm, again after correction. These values appear very reasonable. The value of the (vicinal) $^{117,119}Sn$ coupling to $C_{4,6}$ in the 2,2-bis(trimethylstannyl) compound is 26.9 Hz, in close agreement with that measured for the 2-trimethylstannyl, 2-methyl-2-trimethylstannyl, and 2-phenyl-2-trimethylstannyl derivatives, concluded on several grounds to have the $Sn(CH_3)_3$ predominantly equatorial. This agreement indicates that the vicinal coupling from an axial $^{117,119}Sn(CH_3)_3$ must be quite small, and if the ratio of vicinal couplings for an equatorial vs. axial

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(29) Estimated from the corresponding value in cyclohexane by assuming a slightly increased value as found for an axial CH_3 in the two systems.

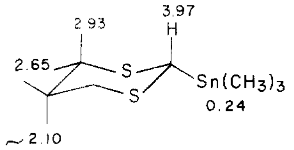
(30) R. F. Bryan, F. A. Carey, O. Hernandez, and I. F. Taylor, *J. Org. Chem.*, **43**, 85 (1978).

(31) J. M. Lehn and G. Wipff, *J. Am. Chem. Soc.*, **98**, 7498 (1976), and references therein.

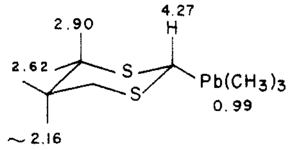
(32) R. Amstutz, D. Seebach, P. Seiler, B. Schweizer, and J. D. Dunitz, *Angew. Chem., Int. Ed. Engl.*, **19**, 53 (1980); D. Seebach, private communication.

$Sn(CH_3)_3$ in cyclohexane is any guide,[33] the coupling would be of the order of $^1/_6$–$^1/_7$ of that for the equatorially disposed $Sn(CH_3)_3$, i.e., *ca* 4 Hz.

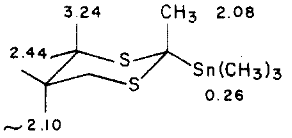
We did prepare the unstable (tertiary) 2-methyl-2-(trimethylplumbyl)-1,3-dithiane, which decomposed to tetramethyllead on attempted distillation. However, several conclusions are possible from the ^1H NMR spectrum (of the crude undistilled material), particularly when comparisons are made with the corresponding tin derivatives (see VII–X).



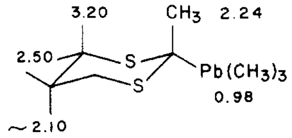
VII



VIII



IX



X

Accepting that 2-methyl-2-(trimethylstannyl)-1,3-dithiane has overwhelmingly the conformation drawn above (vide supra), one can see that the introduction of an axial $2\text{-}CH_3$ into the parent stannane causes a downfield shift of $H_{4,6}$ (axial) of 0.3 ppm ("steric deshielding") and an upfield shift of $H_{4,6}$ (equatorial) of 0.20 ppm, consistent with the large (^{13}C) γ effect of an axial $2\text{-}CH_3$ (−7.2 or −9.4 ppm).[22] The close similarity in $H_{4,6}$ (axial) and $H_{4,6}$ (equatorial) shifts for the 2-methyl-2-stannyl- and 2-methyl-2-plumbyl-1,3-dithianes strongly indicates very similar conformational situations, as the γ effect of $Pb(CH_3)_3$ would be anticipated to be much smaller than that of methyl.[1] The ^1H shifts are appropriate for axially disposed $2\text{-}CH_3$ groups[5,22] in both derivatives.

The above discussion indicates that $M(CH_3)_3$ (M = Si, Ge, Sn, Pb) exhibits a large preference ($A > 2.0$ kcal/mol) for the equatorial orientation at position 2 in 1,3-dithiane. This preference is much greater than that in cyclohexane, and the question naturally arises as to why this preference is so pronounced. In the highly polar (if not ionic) 2-lithio-1,3-dithianes, Eliel originally suggested[12] that the lithium ion was held in the equatorial position by the cooperative effect of the carbanion and one of the unshared electron pairs of each of the two sulfur atoms. Further investigations, however, tended to support the hypothesis that the equatorial orientation of the carbanion was more stable for stereoelectronic reasons. The calculations of Lehn and Wipff suggest that a carbanion flanked by two sulfurs is 9 kcal/mol more stable in the equatorial-like position.[31]

Information on the solid-state structure of 2-lithio-2-methyl-1,3-dithiane–tetramethylethylenediamine has recently been provided by Seebach and Dunitz.[32] A dimeric structure in which pairs of dithiane molecules are double bridged by equatorial lithium atoms was established, with the lithium interacting approximately equally with the carbanionoid carbon of one ring and a sulfur of the other. In addition to the anomeric effect favoring the equatorial disposition for lithium, it was concluded that steric factors were probably of comparable importance, and as in the above example, methyl is the smallest group, and would thus adopt the axial position. Although C–Si, –Ge, –Sn, and –Pb bonds are somewhat polar, extrapolation of these results[32] and data for free carbanions[13,14] to these essentially covalent systems must be somewhat tenuous. It may be profitable to note that 2-substituents such as the electronegative chloro or benzoyloxy strongly prefer the axial position,[9,10] and this anomeric effect[4,33,39] is related to a desire to maximize favorable back-bonding interactions. Electropositive groups, e.g., $(CH_3)_3Sn$, could then prefer the equatorial position, because the "reversed" dipole effect could be stabilized by some effect associated with the sulfur atoms, just as it destabilizes the equatorial position for electronegative groups (e.g., Cl). Whatever the details of the effect, it is clearly very significant. The polar nature of the C–Si and C–Sn bonds may be responsible for the significant shielding (~3–4 ppm) of C_{para} in the $2\text{-Ph-}2\text{-}M(CH_3)_3$ derivatives (see Table II). Alternatively, these derivatives may be regarded as benzylic derivatives of Si or Sn, and in conformation A, carbon–metal σ–π donor interactions would be anticipated[34] with shielding of C_{para}.

Experimental Section

Compounds. 1,3-Dithiane was commercially available and was converted into the 2-substituted derivatives by a standard procedure of lithiation (*n*-butyllithium in hexane) followed by quenching with the appropriate organic or organometal halide.[35]

The following are prepared in this general way and had physical properties in satisfactory agreement with published data. The spectral characterization is discussed in the text.

2-Methyl-1,3-dithiane: bp 88 °C (18 mm) [lit.[36] bp 84 °C (17 mm)].

2-(Trimethylsilyl)-1,3-dithiane: bp 70–72 °C (0.5 mm) [lit.[35] bp 54.5 °C (0.17 mm)]. **2-(Trimethylgermyl)-1,3-dithiane**: bp 90 °C (1.5 mm) [lit.[16] bp 89 °C (1.4 mm)]. **2-(Trimethylstannyl)-1,3-dithiane**: bp 80 °C (0.6 mm) [lit.[16] bp 98 °C (1.5 mm)] **2-(Trimethylplumbyl)-1,3-dithiane**: bp 87 °C (0.4 mm) [lit.[16,37] bp 112 °C (0.4 mm)]. **2-Phenyl-2-(trimethylsilyl)-1,3-dithiane**: mp 94.5–95 °C (lit.[35] mp 94.4–94.8 °C). **2-Methyl-2-(trimethylstannyl)-1,3-dithiane**: bp 89–91 °C (0.4 mm) [lit.[38] bp (bath temperature) 130 °C (0.4 mm)]. **2-Phenyl-2-(trimethylstannyl)-1,3-dithiane**: mp 68–69 °C. Anal. Calcd: C, 43.49; H, 5.58. Found: C, 44.28; H, 5.72. **5-*tert*-Butyl-2-(trimethylstannyl)-1,3-dithiane**: mp 73.5–74.5 °C. Anal. Calcd C, 38.97; H, 7.29. Found: C, 38.97; H, 7.09.

Spectra. ^1H NMR spectra were recorded on JEOL JNM MH-100, Varian EM-360, or JEOL PS-100 spectrometers or the 270-MHz Bruker spectrometer at the National NMR center, Canberra. The spectra were recorded for $CDCl_3$ solutions and referenced to residual $CHCl_3$ (δ 7.27) or Me_4Si.

^{13}C spectra were recorded on the JEOL FX-100 (25.05 MHz) or Bruker spectrometers (67.89 MHz). The spectra pertain to $CDCl_3$ solutions (center of triplet at 77.00 ppm) or CD_2Cl_2 solutions for low-temperature measurements.

Acknowledgment. The authors are grateful to the Australian Research Grants Committee for partial funding of this research and for providing access to the high-field NMR spectrometer at the National NMR Center, Canberra (Director, Dr. Alan Jones). We are indebted to Professor Ernest Eliel for donation of several 1,3-dithiane

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(33) See, for example, E. L. Eliel and C. A. Giza, *J. Org. Chem.*, 33, 3754 (1968).

(34) W. Adcock, B. D. Gupta, W. Kitching, D. Doddrell, and M. Geckle, *J. Am. Chem. Soc.*, 96, 7360 (1974).

(35) See E. J. Corey, D. Seebach, and R. Freedman, *J. Am. Chem. Soc.* 89, 434 (1967).

(36) D. Seebach, *Synthesis*, 17 (1969).

(37) Although there appears to be a significant difference in boiling points, elemental analysis of our product is satisfactory. Calcd for $C_7H_{16}PbS_2$: C, 22.63; H, 4.31. Found: C, 22.93; H, 4.38.

(38) D. Seebach, I. Willert, and A. K. Bech, *Helv. Chim. Acta*, 61, 2510 (1978).

(39) G. A. Jeffrey and J. H. Yates, *J. Am. Chem. Soc.*, 101, 820 (1979).

samples and to Professor Seebach for the ^{13}C data for 2,2-bis(trimethylstannyl)-1,3-dithiane.

Registry No. 1,3-Dithiane, 505-23-7; 2-methyl-1,3-dithiane, 6007-26-7; 2-phenyl-1,3-dithiane, 5425-44-5; 2-(1,1-dimethylethyl)-1,3-dithiane, 6007-21-2; 2-(trimethylsilyl)-1,3-dithiane, 13411-42-2; 2-(trimethylgeranyl)-1,3-dithiane, 73119-27-4; 2-(trimethylstannyl)-1,3-dithiane, 68971-93-7; 2-(trimethylplumbyl)-1,3-dithiane, 75768-53-5; 2-methyl-2-(trimethylstannyl)-1,3-dithiane, 68971-99-3; 2-phenyl-2-(trimethylstannyl)-1,3-dithiane, 75768-54-6; 2-phenyl-2-(trimethylsilyl)-1,3-dithiane, 13411-45-5; 2,2-bis(trimethylsilyl)-1,3-dithiane, 13411-46-6; 2,2-bis(trimethylstannyl)-1,3-dithiane, 68971-97-1; *trans*-5-*tert*-butyl-2-(trimethylstannyl)-1,3-dithiane, 75768-55-7.

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^2H Nuclear Magnetic Resonance Study of the Stereochemistry of Reduction of Some Organomercurials

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Received July 10, 1980

The stereochemical courses of the replacement of mercury by deuterium in a range of organomercury halides or acetates, by employing as reducing systems sodium borodeuteride/tetrahydrofuran/aqueous base and 1–2% sodium amalgam/deuterium oxide/sodium deuterioxide, have been investigated by ^2H nuclear magnetic resonance spectroscopy. The following organomercurials were examined: *cis*- and *trans*-(4-methylcyclohexyl)mercuric acetate (or bromide), *cis*-(3-methylcyclohexyl)mercuric bromide, *cis*- and *trans*-(2-methoxycyclohexyl)- and -(2-methoxycyclopentyl)mercuric chlorides, *exo,endo*-(2-norbornyl)mercuric acetate, (5-acetoxy-*exo,exo*-tricyclo-[2.2.1.0^{2,6}]hept-3-yl)mercuric chloride [(5-acetoxy-3-nortricyclyl)mercuric chloride] and (*cis-exo*-2-acetoxynorborn-5-en-3-yl)mercuric chloride. The sodium borodeuteride reductions provide mixtures and unambiguous assignments of the ^2H spectra were possible either by synthesis of authentic deuterated compounds or on the basis of established ^1H chemical shifts. The signal intensities provide accurate measures of the preferred directions of abstraction by the radicals generally agreed to be involved in these borohydride reductions. In contrast, sodium amalgam reductions are completely stereospecific with retention at carbon, and no rearrangement was observed in the rearrangement-prone nontricyclyl–norbornenyl pair. These results support the idea that the ^2H-incorporating step is electrophilic cleavage of the C–Hg bond, probably in a subvalent organomercury species. The stereochemistries of the (deuterio)alkylcyclohexanes resulting from AIBN-initiated tributylstannane-*d* reductions of various alkylcyclohexyl bromides were also determined for comparison purposes.

The reduction of C–Hg bonds (eq 1) can be achieved

$$RHgX \xrightarrow{\text{reduce}} RH + Hg^0$$

with a variety of reagents.[1] However, sodium borohydride (usually in basic aqueous tetrahydrofuran) is attractive because of its technical ease and rapidity and represents the second stage of the oxymercuration–demercuration route to Markovnikov alcohols from alkenes.[2] In recent years increasing attention has been directed toward understanding the mechanism of this reduction, and the evidence is persuasive that free radicals (from an unstable RHgH) are involved.[3-9] The rearrangements accompanying reduction and the required stereolability of some intermediate are consistent with radical intervention. On the other hand, reduction of norbornyl[6,10] and dibenzobicyclo[2.2.2]octadienyl-type[6] mercurials with Na/Hg proceeds in a highly stereospecific fashion and has been recommended[6] as the method of choice for site specificity and stereospecificity of deuterium incorporation. Determinations of stereochemistry of ^2H incorporation have employed ^1H NMR spectroscopy, and adequate separation of resonances is necessary to permit evaluation.[6,7] The systems mentioned above, with some electronegative oxy function, normally provide adequately separated resonances. However, ^1H NMR analysis is more difficult to apply when the product is a simple cyclic hydrocarbon, e.g., reduction of alkylcyclohexyl mercurials, and yet these strain-free nonfunctionalized systems permit more generalized conclusions about stereochemistry and mechanisms. Infrared analysis has also been employed successfully in some cases,[7] but normally a C–^2H vibration characteristic of each pure isomer should be identified. Such vibrations for axial and equatorial C–^2H bonds have been employed for conclusions concerning the stereochemistry of deuterium incorporation.[11] We have found this approach tedious and sometimes unrewarding, and we

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(1) For a general discussion see F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials", McGraw-Hill, New York, 1968, Chapter 6.

(2) H. C. Brown and P. Geoghegan, *J. Am. Chem. Soc.*, **89**, 1522 (1967); S. Bentham, P. Chamberlain, and G. H. Whitham, *Chem. Commun.*, 1528 (1970).

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