

σ - π Conjugation in Benzyl Derivatives of Tin and Mercury as Probed by ^{119}Sn and ^{199}Hg Resonance

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Benzylic mercurials of the types RHgCl and R_2Hg incorporating a range of meta and para substituents have been synthesized and their ^{13}C and ^{199}Hg spectra recorded. The ^{199}Hg chemical shifts in both series are unusual in that electron-withdrawing substituents cause shifts to higher field (of the parent benzylmercurial) but correlate reasonably well with substituent constants. *o*-Methylbenzylmercuric chloride resonates at a surprisingly low-field position, and an explanation is advanced which is contrary to a previous one. ^{119}Sn shifts in meta- and para-substituted benzyltrimethylstannanes move to lower field with electron-withdrawing substituents but again correlate well with substituent constants. A limited series of 6- and 7-substituted 1-(trimethylstannyl)-4-methyl-1,4-ethano-1,2,3,4-tetrahydronaphthalenes, in which the benzylic C-Sn bond is constrained to the nodal plane of the π system, have been synthesized and the ^{13}C and ^{119}Sn shifts obtained.

Introduction

The interaction of a polarized carbon-metal σ bond with an adjacent π system (carbon-metal hyperconjugation or σ - π conjugation) can be manifested by impressive changes in chemical reactivity¹ or spectroscopic parameters,² provided the alignment of the interacting orbital systems is appropriate. We have been concerned primarily with comparisons of ^{13}C chemical shifts and ^{13}C -metal coupling constants in organotin and -mercury systems that may and cannot engage in such interactions; the differences can be remarkable, but fully in accord with a conjugative description. σ - π carbon-metal conjugation would seem to be amenable to study by metal NMR shifts which are sensitive to general environmental changes and subtle electronic alterations.³⁻⁶ Although the paramagnetic term (σ_p) for nuclear shielding is relatively more important for heavier nuclei, deep understanding of the factors involved, and how they vary from metal to metal, has not been achieved.⁶⁻⁸ Examination of a carefully selected series of compounds, however, incorporating tactical structural and/or electronic changes, can provide data allowing general conclusions that would assist the theoretical approach. In this way, we have sought to determine the response of ^{199}Hg ⁹⁻¹² and ^{119}Sn ⁵ resonances to substituent

Table I. ^1H Chemical Shifts and ^{199}Hg - ^1H Couplings in Benzylmercurials^a

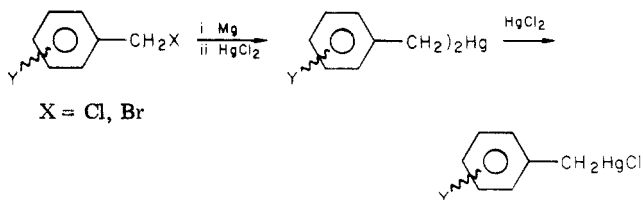
Y =	δ_{CH_2}	J^b	δ_{CH_3}	J^b	δ_{CH_2}	J^b	δ_{CH_3}	J^b
H	3.14	248			2.37	130		
<i>o</i> -CH ₃	3.24	256	2.40	27	2.40	130	2.36	13
<i>m</i> -CH ₃	3.25	252	2.31	14	2.45	136	2.31	7
<i>p</i> -CH ₃	3.26	248	2.32	42	2.40	131	2.31	19
<i>m</i> -F	3.24	265			2.47	134		
<i>p</i> -F	3.24	248			2.43	129		
<i>m</i> -Cl	3.30	250			^c			
<i>p</i> -Cl	3.22	254			2.44	132		
<i>m</i> -CF ₃	3.30	290			2.47	140		

^a For CDCl_3 solutions relative to Me_4Si . ^b Coupling to ^{199}Hg in hertz. ^c Small quantity was converted to the chloride.

changes in a selected series of benzylic derivatives and to rationalize any trends within the framework of ideas concerning σ - π conjugation and nuclear shielding.

Results and Discussion

Benzylmercury Compounds. The benzylmercuric chlorides were prepared in a standard way by cleaving the corresponding dibenzylmercurials with mercuric chloride in tetrahydrofuran. The dibenzylmercurials, in turn, were obtained from reaction of excess Grignard reagent with mercuric chloride. This approach ensured that only



chloride ligand was present, as contamination with bromide, for example (from starting benzyl bromide), could have a very large effect on ^{199}Hg shifts. Both series of compounds were characterized by their melting points, analyses, and initially by their ^1H NMR spectra. For the dibenzylmercurials, the CH_2 resonance is at ca. δ 2.40 flanked by ^{199}Hg satellites with $J = 130$ Hz for the parent and 140 Hz for the *m*-CF₃ derivative. ^{199}Hg coupling to methyl groups (for ortho, meta, and para derivatives) is also ob-

(1) See, for example, W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Am. Chem. Soc.*, **92**, 829 (1970), and references therein.

(2) See, for example, (a) W. Adcock, B. D. Gupta, W. Kitching, and D. Doddrell, *J. Organomet. Chem.*, **102**, 297 (1975); (b) A. R. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, *ibid.*, **20**, 49 (1969); (c) C. G. Pitt, *ibid.*, **23**, 35 (1970); (d) A. Schweig, U. Weidner and G. Manuel, *ibid.*, **67**, C4 (1974), and references therein.

(3) G. E. Maciel in "NMR of Nuclei Other than Protons", T. Axenrod and G. A. Webb, Eds., Wiley, New York, 1974, Chapter 23.

(4) P. R. Wells in "Determination of Organic Structures by Physical Methods", Vol. 4, F. C. Nachod and J. J. Zuckerman, Eds., Academic Press, New York, 1971, Chapter 5.

(5) For ^{119}Sn shifts see, H. J. Kroth, H. Schumann, H. G. Kuivila, C. D. Schaeffer, and J. J. Zuckerman, *J. Am. Chem. Soc.*, **97**, 1754 (1975). For ^{29}Si shifts see C. R. Ernst, L. Spialter, G. R. Buell, and D. L. Wilhite, *ibid.*, **96**, 5375 (1974).

(6) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

(7) J. R. Van Wazer in "Determination of Organic Structures by Physical Methods", Vol. 4, F. C. Nachod and J. J. Zuckerman, Eds., Academic Press, New York, 1971, p 335.

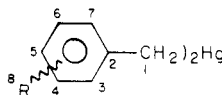
(8) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

(9) M. A. Sens, N. K. Wilson, P. D. Ellis, and J. D. Odom, *J. Magn. Reson.*, **19**, 323 (1975).

(10) R. E. Dessy, T. J. Flaut, H. H. Jaffé, and G. F. Reynolds, *J. Chem. Phys.*, **30**, 1422 (1959).

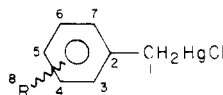
(11) M. Borzo and G. E. Maciel, *J. Magn. Reson.*, **19**, 279 (1975).

(12) P. F. Barron, D. Doddrell, and W. Kitching, *J. Organomet. Chem.*, **139**, 361 (1977).

Table II. ^{13}C NMR Chemical Shifts and Couplings of Bis(substituted benzyl) Mercury Compounds^a

R	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
H	46.0 (633.4)	144.2 (72.6)	127.5 (54.1)	128.1 (23.6)	124.5 (29.2)	128.1 (23.6)	127.5 (54.1)	
<i>p</i> -Me	46.2 (627.4)	141.1 (73.2)	127.7 (54.9)	129.0 (24.4)	132.4 (30.5)	129.0 (24.4)	127.7 (54.9)	20.7 (9.8)
<i>m</i> -F	45.7 (647.0), nr	147.1, nr [7.3]	109.6 (54.9) [20.8]	162.7, nr [244.1]	114.0 (34.0) [20.8]	129.3 (25.4) [8.5]	123.2 (53.7) [2.4]	
<i>p</i> -F	45.8 (637.2), nr	139.7 (75.7) [2.4]	128.8 (50.0) [7.3]	114.8 (24.4) [20.8]	159.7, nr [241.7]	114.8 (24.4) [20.8]	128.8 (50.0) [7.3]	
<i>p</i> -Cl	46.6 (635.9)	139.6 (73.9)	128.1 (53.4)	129.6 (24.8)	131.4 (31.1)	129.6 (24.8)	128.1 (53.4)	
<i>m</i> -CF ₃	45.6 (650.6), nr	145.4 (75.7), nr	123.9 (54.9) [3.7]	130.0, nr [30.5]	119.6 (31.7) [3.7]	128.4 (26.9), nr	130.8 (54.9), nr	124.2, nr [272.2]

^a Recorded in 60% CDCl₃ and 40% CH₂Cl₂ solvent. Chemical shifts in parts per million referenced to center of CDCl₃ triplet as 77.0 ppm. ^{13}C - ^{199}Hg couplings (hertz) in parentheses and ^{13}C - ^{19}F couplings in brackets. nr = couplings not resolved.

Table III. ^{13}C NMR Chemical Shifts and Couplings of Substituted Benzylmercury Chlorides^a

R	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
H	36.0 (1429)	139.2 (156.8)	128.3 (105.0)	128.4 (51.3)	125.2 (63.5)	128.4 (51.3)	128.3 (105.0)	
<i>o</i> -Me	34.4 (1369)	137.6 (161.9)	134.1 (92.8)	130.0 (58.6)	125.8 (65.9)	126.1 (54.9)	128.7 (103.7)	20.0 (20.8)
<i>p</i> -Me	36.2 (1421)	135.7 (157.3)	128.4 (105.0)	129.4 (50.1)	135.2 (64.0)	129.4 (50.1)	128.4 (105.0)	20.9 (23.2)
<i>m</i> -F	35.5 (1455), nr	142.0 (148.9) [7.3]	112.0 (106.8) [20.8]	162.6, nr [245.4]	115.0 (66.0) [22.0]	129.9 (53.7) [8.5]	124.0 (107.4) [2.4]	
<i>p</i> -F	35.0 (1445), nr	134.9 (149.0) [2.4]	129.6 (96.0) [8.5]	115.1 (50.0) [22.0]	160.6, nr [244.6]	115.1 (50.0) [22.0]	129.6 (96.0) [8.5]	
<i>p</i> -Cl	35.2 (1407)	130.8 (150.2)	129.5 (103.8)	128.4 (53.6)	137.8 (64.7)	128.4 (53.6)	129.5 (103.8)	
<i>m</i> -CF ₃ ^b	32.2 (1460), nr	142.4 (165.4), nr	124.1 (110.8) [3.7]	129.8, nr [31.7]	120.6 (67.1) [3.7]	128.2 (51.3), nr	131.0 (111.6), nr	^c

^a Recorded in 60% CDCl₃ and 40% CH₂Cl₂ solvent. Chemical shifts in parts per million referenced to center of CDCl₃ triplet as 77.0 ppm. ^{13}C - ^{199}Hg couplings (hertz) in parentheses and ^{13}C - ^{19}F couplings in brackets. ^b Recorded with 3 drops of pyridine, due to solubility problems. ^c Not observed due to poor solubility of compound.

served. The spectra of the benzylmercuric chlorides are similar, with CH₂ at ca. δ 3.20, but in the *m*-CF₃ derivative $J_{\text{CH}_2\text{-Hg}}$ is substantially increased to 290 Hz (248 Hz in the parent) and presumably associated with electron withdrawal from the C-Hg bond and increased nuclear charge at mercury. The coupling of ^{199}Hg to methyl groups is in the sequence $J_{p\text{-CH}_3} > J_{o\text{-CH}_3} > J_{m\text{-CH}_3}$, as expected for a conjugative interaction. The full assembly of ^1H data is located in Table I.

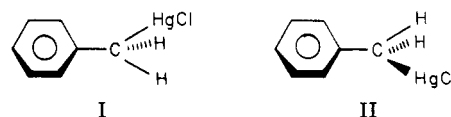
Carbon-13 Spectra. The ^{13}C chemical shifts and ^{13}C - ^{199}Hg and ^{13}C - ^{19}F coupling constants are shown in Table II for the dibenzylmercurials and Table III for the benzylmercuric chlorides. Assignments of signals were made on the basis of chemical shifts, signal intensities, relative magnitudes of ^{13}C - ^{199}Hg ¹³ and ^{13}C - ^{19}F couplings,¹⁴ and substituent effects.

The chemical shifts of the benzylic carbon (C₁) are relatively constant throughout a series, but in both, *m*-CF₃, a strong electron-withdrawing group ($\sigma = 0.42$), induces an upfield shift of C₁. This is consistent with our previous report¹⁵ that in substituted ethylbenzenes, the CH₂ shift is *inversely* dependent on σ_1 . In *o*-methylbenzylmercuric chloride, C₁ is shielded by 1.6 ppm, and we shall return

to this aspect later. C₁ in the disubstituted series is ca. 10 ppm to lower field than C₁ in the benzylmercuric chlorides, similar to the results for phenylmercuric chloride (151 ppm) and diphenylmercury (170 ppm).¹⁶

The ^{13}C - ^{199}Hg couplings show substantial variations in both series, and in the disubstituted series the couplings to all carbons are about one-half of those to the corresponding carbons in the benzylmercuric chlorides. (This reduction in coupling is paralleled by a large shift of the ^{199}Hg resonance to lower field). Regarding 1J (i.e., to C₁), this coupling does not fluctuate greatly and is largest in both series for *m*-CF₃. *o*-Methylbenzylmercuric chloride is unusual in that 1J is the smallest (and significantly smaller than for *p*-CH₃) and implies an ortho effect.

Couplings to ring carbons are substantial, and greater to ortho and para positions than to meta, consistent with predominant π transmission, as would operate in I but not II.²



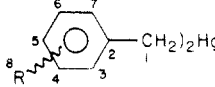
The coupling to the ortho carbon (C₇) (remote from the meta substituent at C₄) is close to 100 Hz irrespective of substituent. Normal vicinal coupling to C₇ (which operates

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

(14) W. Adcock, B. D. Gupta, T. C. Khor, D. Doddrell, and W. Kitching, *J. Org. Chem.*, **41**, 751 (1976).

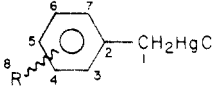
(15) W. Adcock, W. Kitching, V. Alberts, G. Wickham, P. Barron, and D. Doddrell, *Org. Magn. Reson.*, **10**, 47 (1977).

(16) N. K. Wilson, R. D. Zahr, and P. D. Ellis, *J. Magn. Reson.*, **21**, 437 (1976); F. J. Weigert and J. D. Roberts, *Inorg. Chem.*, **12**, 313 (1973).

Table IV. ^{199}Hg NMR Chemical Shifts of Substituted Dibenzylmercurial Compounds^a


R	chemical shift, ppm	$J(^{199}\text{Hg}-^{19}\text{F})$, Hz
H	0.0	
<i>m</i> -Me	6.3	
<i>p</i> -Me	10.0	
<i>m</i> -F	-27.1	19.5 (t)
<i>p</i> -F	3.2	43.9 (t)
<i>p</i> -Cl	-21.2	
<i>m</i> -CF ₃	-31.4	7.3 (sept) ^b

^a Positive values are to lower field of dibenzylmercury. Chemical shifts in parts per million referenced to the unsubstituted parent compound. Recorded in 60% CDCl₃ and 40% CH₂Cl₂ solvent. ^b Coupling constant obtained with 3 drops of pyridine.

Table V. ^{199}Hg NMR Chemical Shifts of Substituted Benzylmercuric Chlorides^a


R	chemical shift, ppm	$J(^{199}\text{Hg}-^{19}\text{F})$, Hz
H	0.0	
<i>o</i> -Me	26.9	
<i>m</i> -Me	-3.3	
<i>p</i> -Me	-0.4	
<i>m</i> -F	-6.2	36.6 (d)
<i>p</i> -F	-2.9	97.7 (d)
<i>p</i> -Cl	-8.4	
<i>m</i> -CF ₃	-9.2	14.7 (q) ^b

^a Positive values are to lower field of benzylmercuric chloride. Chemical shifts in parts per million referenced to the unsubstituted parent compound. Recorded in 60% CDCl₃ and 40% CH₂Cl₂ solvent. ^b Coupling constant obtained with 3 drops of pyridine.

through a saturated framework) will be favored for conformation II,¹⁷ and such vicinal ^{199}Hg - ^{13}C coupling is strongly dihedral angle dependent and large, e.g., 200–300 Hz for the favored 180° angle as present in II.¹⁷ The difference in coupling to C₅ and C₇ is ca. 40 Hz for all benzylmercuric chlorides and indicates that II is unimportant. This agrees with vibrational spectra for benzylmercuric chloride¹⁸ and other data.¹⁹

^{199}Hg Spectra. Substituent effects on ^{199}Hg chemical shifts in both series of compounds are shown in Tables IV and V.

In the benzylmercuric chloride series, we confirm the report²⁰ that *m*- and *p*-CH₃ have minor effects on the ^{199}Hg shifts, but more powerful substituents do, and *electron-withdrawing* groups (e.g., *m*-CF₃) shift the ^{199}Hg signal higher field.

A linear trend ($r^2 = 0.77$) between the ^{199}Hg shifts and σ constants is realized for the benzylmercuric chlorides and shown in Figure 1. A better correlation ($r^2 = 0.95$) is

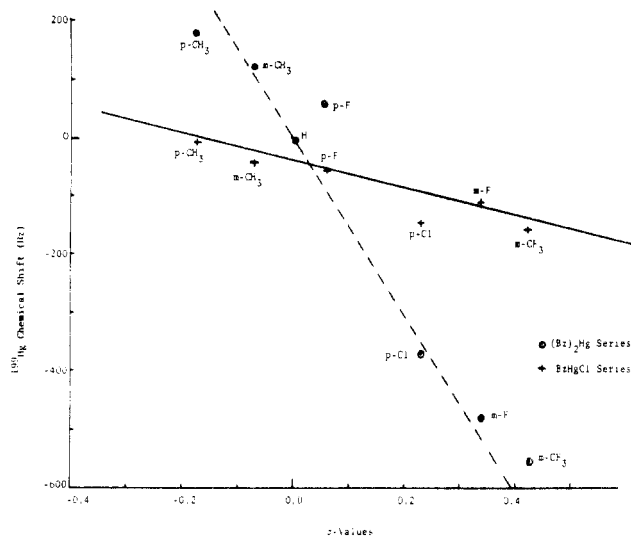


Figure 1. ^{199}Hg chemical shifts (in hertz, relative to the shift of benzylmercuric chloride or dibenzylmercury as the case may be) are plotted against σ constants of the substituent groups. Correlation parameters are given in the text, but it is clear that groups with more positive σ constants (e.g., *m*-CF₃) cause shifts to higher field of the parent. (σ constants from C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, **90**, 4328 (1968), and P. R. Wells, "Linear Free Energy Relationships", Academic Press, New York, 1968.

obtained for the dibenzyl series, which provides a greater range of shifts (Figure 1). Interesting comparisons follow from the recognition that in benzylmercurials the ^{199}Hg nucleus is β to the ring as is $^{13}\text{CH}_3$ in ethylbenzenes and ^{19}F in arylmethyl fluorides. Both of these nuclides display "inverse" or "abnormal" dependence on substituent character^{15,21} (i.e., low-field shift resulting from electron donation and vice versa) and ^{199}Hg may be another example. However for ^{199}Hg , this result is not peculiar to the benzyl system, as Sens⁹ and others^{11,12} have reported measurements which show that the more covalent mercurials resonate at lower field and more ionic at higher field. (Some considerations⁵ could indicate this behavior is unexceptional for nuclides dominated by the paramagnetic term). However, if substituent effects are feeble, other factors, such as differential solvation, could conceivably produce different trends in ^{199}Hg shifts for the same series of compounds. In Tables IV and V values of ^{199}Hg - ^{19}F couplings are also listed, and for the *m*- and *p*-F derivatives, such couplings are about twice as large in the benzylmercuric chlorides. Note that ^{199}Hg - ^{19}F coupling is much greater for the *p*-F isomer (cf. 43.9 Hz with 19.5 Hz in Table IV) as anticipated for σ - π transmission.

Having established the nature of the connection between electron-density changes in the benzylic C-Hg bond and the ^{199}Hg chemical shifts, we can discuss the low-field resonance for *o*-methylbenzylmercuric chloride (+26.9 ppm) and the greater shift for 2,4,6-trimethylbenzylmercuric chloride (+50 ppm). Strelenko²⁰ interpreted these low-field shifts in terms of *o*-CH₃ groups increasingly displacing (by steric interaction) the HgCl group from the aromatic ring plane (A), thus increasing the population of the out-of-plane rotamer (B) in which σ - π interaction is promoted. This analysis requires that in benzylmercuric chloride itself a quite significant population of the in-plane rotamer (A) must be present, a requirement not supported

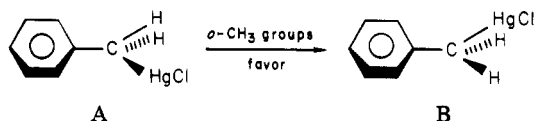
(17) W. Kitching, D. Praeger, D. Doddrell, F. A. L. Anet, and J. Krane, *Tetrahedron Lett.*, 759 (1975).

(18) J. Mink and Yu. A. Pentin, *J. Organomet. Chem.*, **23**, 293 (1970).

(19) R. D. Bach, A. T. Weibal, W. Schmoners, and M. Glick, *J. Chem. Soc., Chem. Commun.*, 961 (1974).

(20) Yu. A. Strelenko, Yu. G. Bundel, F. H. Kasumov, V. I. Razenberg, O. A. Reutov, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, **159**, 133 (1978).

(21) For leading examples see: (a) W. Adcock and A. N. Abeywickrema, *Tetrahedron Lett.*, 1809 (1979); (b) J. Bromilow, R. T. C. Brownlee, and A. V. Page, *ibid.*, 3055 (1976); (c) W. Adcock, M. J. S. Dewar, R. Golden, and M. A. Zeb, *J. Am. Chem. Soc.*, **97**, 2198 (1975).

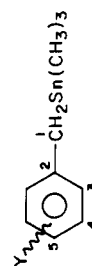


by vibrational spectroscopic data¹⁸ and crystal structure determinations,¹⁹ as well as our analysis of the C₇-¹⁹⁹Hg couplings. The assumption was made that "displacement of the mercury atom from the aromatic ring plane should facilitate σ - π conjugation, thus increasing the positive charge on the mercury atom and deshielding the ¹⁹⁹Hg nuclei"²⁰ (our emphasis). We have shown above that reduction in electron density in the C-Hg bond is associated with a high-field shift of the ¹⁹⁹Hg resonance, and, hence, had this conformational analysis been correct, shifts to higher field would have resulted, but did not.

A more appealing explanation is based on the operation of the familiar steric compression (γ) effect involving the *o*-CH₃ and CH₂Hg groups.²² This compressional polarization of C-H electron density toward carbon and into the C-Hg bond would be predicted to cause (a) mutual shielding of CH₃ and CH₂Hg, (b) reduction in $J_{\text{CH}_2\text{-Hg}}$ by reducing nuclear charge at mercury, and (c) a low-field shift of the ¹⁹⁹Hg nucleus by increased electron density at mercury. The observations are in accord with the above, but note the low value (1369 Hz) for $J_{\text{CH}_2\text{-Hg}}$ (the lowest in Table III) and the shielded nature of CH₂Hg (34.3 ppm) and *o*-CH₃ (20.0 ppm, Table III). The conclusion regarding the response of ¹⁹⁹Hg shifts to varying levels of σ - π interaction in benzylmercurials is supported by our studies²³ of α -chloromercuri ketones, and in arrangements permitting σ - π interaction (with $\pi_{\text{C=O}}$), the ¹⁹⁹Hg resonance is to higher field.

We have obtained also the ¹³C and ¹¹⁹Sn spectra of a wide range of benzyltrimethylstannanes which are relatively stable liquids. A problem in the study of benzyl derivatives concerns the preferred conformation of the CH₂M group with respect to the ring, and we reported^{2a} that for the parent benzyltrimethylstannane, the average dihedral angle (defined by the Sn-C₁-C₂ and ring planes) was approximately 60°. This was based on the close agreement between $^5J_{^{119}\text{Sn}-^{13}\text{C}}$ in benzyltrimethylstannane (14.8 Hz) and the conformationally rigid indanyltrimethylstannane (15.4 Hz) in which $\theta \approx 60^\circ$. Conformational mobility is indicated by some variable-temperature studies of the ¹³C, ¹¹⁹Sn, and ¹⁹F of benzyltrimethylstannane and the *p*-fluoro derivative which are described in Table VI.

The salient features of the data are (i) increased shielding²⁴ of the para carbon (C₅) and ortho carbon (C₃) at lower temperature, with the shift of the meta carbon (and internal benzene) being essentially constant, (ii) an increase in $^5J_{^{119}\text{Sn}-^{13}\text{C}}$ at lower temperature (from 14.6 to 15.3 Hz), such coupling established^{2a} as being heavily dependent on π transmission (the slight decreases in $^3J_{^{119}\text{Sn}-^{13}\text{C}}$ (to C_{3,7}) are almost certainly associated with the angular requirements for vicinal coupling²⁵ being lower in out-of-plane conformers), (iii) a substantial low-field shift of the ¹¹⁹Sn resonance at lower temperature, and (iv) increased

Table VI. NMR Shifts of Benzyltrimethylstannanes^achemical shift, δ , for carbon no.

Y =	T, K	1	2	3	4	5	CH ₃	$\delta_{^{119}\text{Sn}}$	$\delta_{^{19}\text{F}}$
H	303	19.95 (290.5)	143.06	126.59 (22.6)	128.10 (13.4)	122.86 (14.6)	-10.39 (328.4)	+3.52	
H	201	19.27 (282.0)	142.99	126.18 (22.0)	127.88 (12.8)	122.37 (15.3)	-10.58 (331.0)	+4.24	
5-F	303	19.18 (293.1)	138.91 (40.3)	127.90 (22.0)	115.03 (13.2)	159.80 (14.7)	-10.16 (329.0)	3.50 [24.4]	-8.28 [24.4]
			[3.1]	[7.9]	[21.4]	[239.9]			
5-F	201	18.67 (285.0)	138.91 (38.5)	127.57 (21.4)	114.95 (13.4)	159.18	-10.21 (328.4)	4.12 [25.0]	-8.57 [24.7]
				[7.3]	[20.8]				
5-F	183								-8.64 [24.4]

^a ¹³C shifts are relative to internal Me₄Si, ¹¹⁹Sn shifts are relative to internal (CH₃)₄Sn, and ¹⁹F shifts are relative to internal fluorobenzene. Quantities in parentheses are ¹³C-¹¹⁹Sn couplings and in brackets are ¹³C-¹⁹F or ¹⁹F-¹¹⁹Sn couplings. Solvent CDCl₃.

(22) D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315 (1967); D. K. Dalling and D. M. Grant, *ibid.*, **89**, 6612 (1967); D. K. Dalling and D. M. Grant, *ibid.*, **94**, 5318 (1972). See also, N. K. Wilson and J. B. Stothers, *Top. Stereochem.*, **8**, 1 (1974).

(23) W. Kitching and G. M. Drew, manuscript in preparation.

(24) For appropriate comparisons see, D. Doddrell, M. Bullpitt, C. J. Moore, C. Fong, W. Kitching, W. Adcock, and B. D. Gupta, *Tetrahedron Lett.*, 665 (1973).

(25) 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).

shielding of the p - ^{19}F with lower temperature in (p -fluorobenzyl)trimethylstannane. Each of the above features requires a greater population at lower temperatures of that conformer able to engage in conjugative (σ - π) electron donation, i.e., the out-of-plane rotamer. (That decreased electron density in the benzyl-tin bond causes a low-field shift of the ^{119}Sn signal is established later.)

We sought additional evidence that the average dihedral angle in benzyltrimethylstannane was $\sim 60^\circ$ by examining variations in $^6J_{^{119}\text{Sn}-^{19}\text{F}}$ and using the relationship, $J(\theta) = J_{90} (\sin^2 \theta)$.²⁶ The rigid (5-fluoroindanyl)trimethylstannane has $^6J_{^{119}\text{Sn}-^{19}\text{F}}$ of 23.2 Hz, allowing an estimate of 6J for the out-of-plane rotamer ($\theta = 90^\circ$) of 30.9 Hz. In the p -fluorobenzyl derivative $^6J_{^{119}\text{Sn}-^{19}\text{F}}$ of ca. 25 Hz is observed and corresponds to an average θ of 62° . The above data suggest a free energy difference between the in-plane and out-of-plane rotamers of ca. 400 cal/mol.²⁷

Previously we had reported²⁴ continuous wave ^{13}C shifts for a few substituted benzyltrimethylstannanes and noted no substantial variation in the CH_2 shifts. Some shifts, and ^{13}C - ^{119}Sn couplings obtained under FT conditions are listed in Table VII.

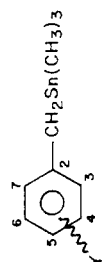
The ^{13}C chemical shifts of $\text{Sn}-\text{CH}_3$ are essentially independent of substituent; a greater variation in the values might have been expected. The variations in CH_2-Sn (C_1 in Table VII) are minor (except for the special 2- CH_3 case and perhaps p - OCH_3). The trend is that substituents with negative σ constants cause slight shielding at C_1 , but this shift has a lower sensitivity toward substituents with positive σ constants. These results resemble those reported¹⁵ for substituted ethylbenzenes, and the analysis given there is probably appropriate.

The slight variation in the three bond coupling (~ 22.5 Hz) to C_7 is indicative of similar averaged conformations for all benzyl derivatives. Coupling increases with resonance donors, e.g., for p - OCH_3 , $J = 23.4$, and decreases with electron withdrawers (e.g., m - CF_3 , 21.2 Hz) in line with a greater population of the out-of-plane rotamer for the latter. However, the changes are small and other substituent effects may cloud this picture. As in the case of the mercury systems, coupling to C_{para} (C_5 in Table VII) is greater than to C_{meta} , as appropriate for substantial π transmission. The one-bond ^{13}C - ^{119}Sn couplings show significant variations in the sense that $J_{^{13}\text{C}_{\text{CH}_2}-^{119}\text{Sn}}$ are larger for donor groups (e.g., p - OCH_3 , 304.8 Hz) and smaller for electron-withdrawing substituents (e.g., m - CF_3 , 273.3 Hz). $J_{^{13}\text{C}_{\text{CH}_3}-^{119}\text{Sn}}$ is not as sensitive but varies in the opposite sense, i.e., 325.3 Hz for p - OCH_3 but 334 Hz for m - CF_3 . $\sum^1 J$ about tin is approximately constant [i.e., $J_{\text{CH}_2-\text{Sn}} + (3 \times J_{\text{CH}_3-\text{Sn}})$] with a mean of 1276.1 Hz (standard error of mean 0.9).

The ^{119}Sn shifts of these (arylmethyl)trimethylstannanes are all to lower field of $(\text{CH}_3)_4\text{Sn}$ (as anticipated⁵ for introduction of the phenyl group) and the total range of shifts is ca. 6.00 ppm which is similar to that reported for a group of meta- and para-substituted phenyltrimethylstannanes.⁵ The SCS values and σ constants are listed in Table VIII, and more positive ^{119}Sn SCS are associated with the substituents with more positive σ constants (Figure 2). (Linear regression analysis yields $r^2 = 0.95$ with the exclusion of o - CH_3 which will be discussed separately.) Thus electron withdrawal from the $\text{C}-\text{Sn}$ bond results in a low-field shift of the ^{119}Sn resonance, a result opposite to that found for the benzylic mercurials. The negative

(26) For leading references and an application to the fluoromethyl group see W. Adcock and A. N. Abeywickrema, *Aust. J. Chem.*, **33**, 181 (1980).

(27) The out-of-plane rotamer is predicted to be more favored (by 400 cal/mol) than the in-plane rotamer for benzyl fluoride. See R. T. C. Brownlee and D. J. Craik, *Tetrahedron Lett.*, 1681 (1980).

Table VII. ^{13}C NMR Data for Benzyltrimethylstannanes^a

Y =	carbon no.							other
	1	2	3	4	5	6	7	
H	20.16 (290.9)	143.14 (39.6)	126.73 (22.7)	128.28 (13.2)	123.04 (15.4)	128.28 (13.2)	126.73 (22.7)	-10.08 (328.2)
<i>p</i> - OCH_3	18.73 (304.8)	134.89 (39.6)	127.55 (23.4)	113.80 (13.2)	155.89 (14.7)	113.80 (13.2)	127.55 (23.4)	-10.17 (325.3)
<i>p</i> - CH_3	19.52 (298.2)	139.72 (38.1)	126.67 (23.5)	128.95 (13.2)	132.26 (16.1)	128.95 (13.2)	126.67 (23.5)	-10.14 (326.8)
<i>p</i> - C_6H_5	19.90 (286.5)	135.85 (38.1)	128.60 (24.9)	127.14 (nr)	141.15 (15.1)	127.14 (nr)	128.60 (24.9)	-9.99 (328.2)
<i>p</i> -F	19.08 (293.1)	138.63 (40.3)	127.72 (22.0)	114.96 (13.2)	159.66 (14.7)	114.96 (13.2)	127.72 (22.0)	-10.17 (329.0)
<i>m</i> - OCH_3	20.31 (287.9)	144.08 (38.1)	112.31 (22.7)	159.61 (13.2)	108.42 (14.7)	129.16 (12.5)	119.39 (22.0)	-10.05 (329.0)
<i>p</i> -Cl	19.61 (282.8)	141.76 (38.1)	127.90 (22.0)	128.28 (13.2)	128.45 (nr)	128.28 (13.2)	127.90 (22.0)	-10.08 (331.2)
<i>m</i> -F	20.27 (275.8)	146.08 (39.8)	113.23 (22.0)	163.00 (13.7)	109.81 (14.7)	129.56 (13.8)	122.34 (22.8)	-10.05 (332.6)
<i>m</i> -Cl	20.08 (276.2)	145.54 (37.4)	124.86 (22.0)	133.98 (14.6)	123.16 (14.7)	129.45 (13.2)	126.52 (22.7)	-9.99 (332.6)
<i>m</i> - CF_3	20.25 (273.3)	144.45 (37.4)	119.83 (nr)	130.60 (nr)	123.17 (nr)	128.63 (12.6)	129.92 (21.2)	-10.11 (334.1)
<i>o</i> - CH_3	18.17 (289.4)	141.50 (41.0)	133.25 (22.7)	129.83 (13.9)	123.28 (15.4)	125.88 (13.8)	127.20 (22.0)	-9.56 (325.3)
								20.13 (4.4)

^a Recorded for CDCl_3 solvent with chemical shifts in parts per million referenced to center of CDCl_3 triplet as 77.00 ppm. ^{13}C - ^{119}Sn couplings (hertz) in parentheses and ^{13}C - ^{19}F couplings in brackets.

Table VIII. ^{119}Sn Chemical Shifts of Benzyl- and (Naphthylmethyl)stannanes, $\text{X-ArCH}_2\text{Sn}(\text{CH}_3)_3$

Ar	X	^{119}Sn chemical shift ^a	^{119}Sn SCS ^b	σ ^c
benzyl	H	3.57 ^d	0.00	0.00
benzyl	<i>p</i> -OCH ₃	1.51	-2.06	-0.27
benzyl	<i>p</i> -CH ₃	1.77	-1.80	-0.17
benzyl	<i>p</i> -F	3.47 ^e	-0.1	+0.06
	<i>m</i> -OCH ₃	3.99	+0.42	+0.12
benzyl	<i>p</i> -C ₆ H ₅	4.04	+0.47	-0.01
benzyl	<i>p</i> -Cl	4.81	+1.24	+0.23
benzyl	<i>m</i> -F	6.00 ^f	+2.43	+0.34
benzyl	<i>m</i> -Cl	6.49	+2.92	+0.37
benzyl	<i>m</i> -CF ₃	7.44 ^g	+3.87	+0.43
benzyl	<i>o</i> -CH ₃	3.80	+0.23	
2-naphthyl	H	4.88	0.00	
2-naphthyl	6-CH ₃	4.30	-0.58	
1-naphthyl	H	9.97	0.00	

^a For CDCl₃ solutions (~0.25 M) relative to internal (CH₃)₃Sn. Positive shifts to lower field. ^b The difference in chemical shifts of the substituted and parent stannanes. ^c From the compilations in C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, **90**, 4328 (1968), and P. R. Wells, "Linear Free Energy Relationships", Academic Press, New York, 1968. ^d Reported (ref 5) as +4.00 ppm. ^e $J_{^{119}\text{Sn}-^{19}\text{F}} = 24.4$ Hz. ^f $J_{^{119}\text{Sn}-^{19}\text{F}} = 10.4$ Hz. ^g $J_{^{119}\text{Sn}-^{19}\text{F}} = 3.7$ Hz.

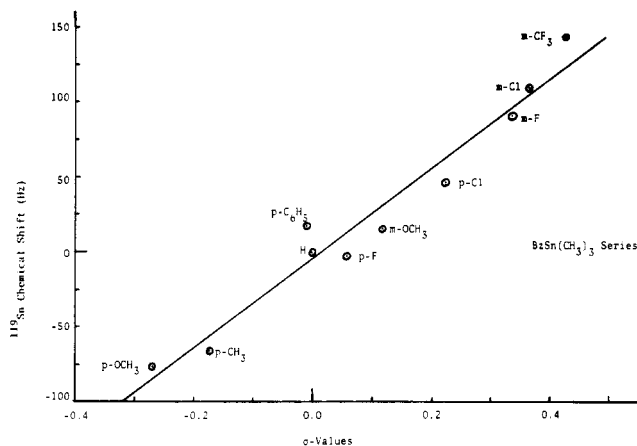


Figure 2. ^{119}Sn chemical shifts (in hertz, relative to the shift of benzyltrimethylstannane) are plotted against the σ constants of the substituent groups ($r^2 = 0.95$). Groups with more positive σ constants cause shifts to lower field of the parent, the reverse trend to that for the ^{199}Hg data in Figure 1.

SCS observed (Table VIII) for the 6-methyl group in the 2-naphthyl system is therefore consistent, and the value of -0.58 ppm (cf. with -1.80 ppm for *p*-CH₃ in the benzyl system) is roughly what is expected for the benzyl \rightarrow 2-naphthyl change, if conjugation is dominant.²⁸ To provide further insight into the nature of the dependence of ^{119}Sn shifts on substituent characteristics, we have conducted dual substituent parameter (DSP) analysis²⁹ of the data and the results are shown in eq 1 for *p*-benzyltrimethylstannanes and in eq 2 for *m*-benzyltrimethylstannanes. This dissection must be regarded as semiquantitative only, in view of the nonideal basis set of substituents.

$$^{119}\text{Sn SCS} = 6.11\sigma_I + 9.14\sigma_{R^0} \quad (1)$$

$$\text{SD} = 0.36; f = 0.24$$

(28) See W. Kitching, W. Adcock, S. Q. A. Rizvi, and A. J. Smith, *J. Organomet. Chem.*, **42**, 373 (1972); M. Bullpitt, W. Kitching, D. Doddrell, and W. Adcock, *J. Org. Chem.*, **41**, 760 (1976).

(29) See S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10**, 1 (1973).

$$^{119}\text{Sn SCS} = 8.09\sigma_I + 4.32\sigma_{R^0} \quad (2)$$

$$\text{SD} = 0.25; f = 0.09$$

^{119}Sn SCS exhibit positive dependences on both σ_I and σ_{R^0} , with the greater resonance susceptibility (ρ_R) in the para series. These correlations strongly support the concept of C-Sn-aryl σ - π interactions as being an important determinant of ^{119}Sn shifts in arylmethyl systems. In the ethylbenzenes, $^{13}\text{CH}_3$ SCS are negatively dependent¹⁵ on both σ_I and σ_{R^0} . The above results may be contrasted with those reported for *m*- (eq 3) and *p*-phenyltrimethylstannanes⁵ (eq 4), in which resonance susceptibility is quite low. These correlations confirm a very low level of π -interaction between the trimethyltin group and an aryl ring, but pronounced susceptibility to polar effects.

$$^{119}\text{Sn SCS} = 11.9\sigma_I + 2.95\sigma_{R^0} \quad (3)$$

$$^{119}\text{Sn SCS} = 10.2\sigma_I + 2.93\sigma_{R^0} \quad (4)$$

We had anticipated a systematic relationship between δ_{Sn} and the one-bond couplings $^1J_{^{13}\text{CH}_2-^{119}\text{Sn}}$ and $^1J_{^{13}\text{CH}_3-^{119}\text{Sn}}$, and linear regression analysis provided eq 5-7. $^1J_{\text{CH}_2-\text{Sn}}$

$$^1J_{\text{CH}_2-\text{Sn}} = (-5.2 \pm 0.4)\delta_{\text{Sn}} + (291 \pm 1) \quad (r^2 = 0.96) \quad (5)$$

$$^1J_{\text{CH}_3-\text{Sn}} = (+1.5 \pm 0.1)\delta_{\text{Sn}} + (329 \pm 0.3) \quad (r^2 = 0.94) \quad (6)$$

$$\sum ^1J = 1276.1 \pm 2.8 \quad (7)$$

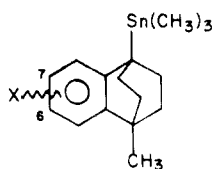
is inversely dependent on δ_{Sn} whereas $^1J_{\text{CH}_3-\text{Sn}}$ is directly proportional, but with a slope of +1.5 compared with -5.2 for $^1J_{\text{CH}_2-\text{Sn}}$. This slope ratio of ca. 3 is responsible for $\sum J$ being relatively constant for all compounds. The trends in the 1J values are consistent with redistribution of 5s character in the (binding) hybrid tin orbitals directed toward CH₂ or CH₃, in response to electron-density changes (primarily at CH₂) as the substituent is changed. Thus, for *p*-OCH₃ with presumed (and supported by the $^{13}\text{CH}_2$ chemical shift) increased electron density at C₁, 5s character in the tin bonding orbital to C₁ will be increased, with an increased 1J , and a consequential reduction in $^1J_{\text{Sn}-\text{CH}_2}$, if 5s character (Fermi contact) is the dominant determinant of the one-bond coupling. Analogous arguments apply to electron-withdrawing substituents such as *p*-Cl or *m*-CF₃, for example.

A positive SCS (+0.23 ppm, Table VIII) is observed for (*o*-methylbenzyl)trimethylstannane which is significant when compared with the negative SCS (-1.80 ppm) for the *p*-methylbenzyl compound. Had the explanation advanced for the mercury case been completely applicable here, a negative SCS would have been observed, as ^{119}Sn responds oppositely to ^{199}Hg to increases in electron density in the benzylic carbon-metal bond. Although steric shielding (γ -gauche effect) between the *o*-CH₃ and CH₂ is in evidence (^{13}C shifts, Table VII) a complication not present in the mercuric chloride is interaction between the *o*-CH₃ and Sn(CH₃)₃ groups. $\sum ^1J$ about tin is 1265 Hz, significantly lower than for the meta- and para-substituted derivatives ($\sum ^1J = 1276.1 \pm 2.8$) and $\delta_{\text{CH}_3-\text{Sn}}$ is -9.65 ppm, also the lowest of all. These variations indicate the operation of effects at Sn(CH₃)₃ associated with the proximity of the *o*-CH₃ group, and formally the tin atom is δ to the methyl group.³⁰

(30) S. H. Grover, J. P. Guthrie, J. B. Stothers, and C. T. Tan, *J. Magn. Reson.*, **10**, 227 (1973).

(31) A. W. Nesmeyanov and K. A. Kocheshkov, Eds., "Methods of Elemento-organic Chemistry", North-Holland Publishing, Amsterdam, 1967, Vol. 4, p 27.

The above data, showing a "normal" response of δ_{Sn} to substituent changes in benzyltrimethylstannanes, suggested that examination of a benzylic tin system in which the C-Sn bond was constrained to the aromatic π nodal plane, (no σ - π interaction) would be useful. Synthetic procedures recently developed^{21a} permitted the synthesis of a few 6- and 7-substituted 1-(trimethylstannyl)-4-methyl-1,4-ethano-1,2,3,4-tetrahydronaphthalenes. The available methodology, based on electrophilic aromatic substitution of the appropriate bridgehead-substituted precursors, provides the 6- and 7-fluoro and -dimethylamino derivatives which on reaction with $(\text{CH}_3)_3\text{SnLi}$ yield the stannanes. Careful nitration of the parent stannane yielded a mixture of the 6- and 7- NO_2 isomers, and isomer identification is established by ^{13}C NMR. The 7 isomer dominates and is ca. 2:1 for the fluoro and nitro mixtures and ca. 3:1 for the $\text{N}(\text{CH}_3)_2$ system. The ^{13}C and ^{119}Sn NMR data are located in Table IX.



X = 6-F, 6- $\text{N}(\text{CH}_3)_2$, 6- NO_2 , 7-F, 7- $\text{N}(\text{CH}_3)_2$, 7- NO_2 , H

That carbon-tin hyperconjugative electron donation is essentially completely suppressed in the ethanotetrahydronaphthyl compound is confirmed by the C_6 and C_7 chemical shifts in the parent hydrocarbon compared with those in the 1-trimethylstannyl compound (Table IX). The shifts are identical. In contrast, the change neopentylbenzene \rightarrow benzyltrimethylstannane leads to increased shielding of C_{para} by ca. 2.5–3.0 ppm.²⁴ The above results agree with the diminution of $J_{^{119}\text{Sn}-^{13}\text{C}}$ in the bridgehead series (Table IX) compared with *m*- and (*p*-fluorobenzyl)trimethylstannanes. ^{13}C data in Table IX and the ^1H data are unexceptional and the normal values of substituent α , β , and γ effects of $\text{Sn}(\text{CH}_3)_3$ and ^{119}Sn - ^{13}C coupling are found, which greatly facilitate certain assignments.

The ^{119}Sn chemical shift (–3.89 ppm relative to $(\text{CH}_3)_4\text{Sn}$) of the parent benzobicyclooctenylstannane (Table IX) is consistent with other data,⁵ and the substituent chemical shifts for the 6- and 7-fluoro, -nitro, -dimethylamino, and -dimethylammonium (Table IX) derivatives confirm that polar influences are important in determining the ^{119}Sn shifts. Moreover, the negative SCS values for the dimethylamino isomers indicate that the polar field causing differential polarization of the bonds about tin has two components—a primary field (due to the dipole (or pole) associated with the substituent) and a secondary field (due to polar and resonance-induced charges in the benzene ring). Electric field calculations suggest that the former is slightly greater in the 7 than the 6 position, and the same order seems to apply for the latter component as well. The observed trends can be rationalized qualitatively along these lines. While it may not be surprising that the C-Sn bond does respond relatively sensitively to remote polar influences, we are currently examining simpler series of bicyclic bridgehead stannanes

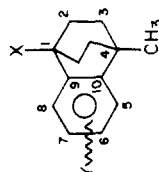
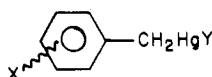


Table IX. ^{13}C and ^{119}Sn NMR Data^c for Some Ethanotetrahydronaphthyl Compounds

X =	Y =	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-CH ₃	Sn-CH ₃	δ_{Sn} ^b	SCS
H	H	34.65	27.11	33.65	34.43	120.68	125.68	125.51	123.28	144.15	146.23	23.03			
$\text{Sn}(\text{CH}_3)_3$	H	33.04	31.02	35.14	34.19	121.09	125.69	125.50	125.08	146.63	148.64	23.42	-10.82	-3.89	0.00
				[50.8]		[6.8]	[~5]	[~5]	[38.6]	[4.6]	[36.6]		[312.5]		
H	6-F	34.95	27.04	33.31	34.17	108.42	161.76	111.61	124.23	139.52	148.26	22.93			
				(22.0)		(241.2)	(21.0)	(21.0)	(7.8)	(2.9)	(6.8)				
$\text{Sn}(\text{CH}_3)_3$	6-F	nl	30.97	34.70	34.63?	108.88	161.55	111.50	125.90	142.00	150.81	23.35	-10.79	-2.84	+1.05
				(22.00)		(242.3)	(21.4)	(21.4)	(7.9)	(2.4)	(6.7)				
H	7-F	34.89	26.91	33.65	33.96	121.94	111.74	161.31	110.54	145.98	141.68	23.08			
				(7.8)		(21.0)	(21.0)	(21.5)	(21.5)	(7.3)	(2.9)				
$\text{Sn}(\text{CH}_3)_3$	7-F	33.95	30.90	35.12	34.77	122.17	112.34	161.14	111.66	148.76	144.12	23.52	-10.84	-2.74 ^e	+1.15
				(7.9)		(242.3)	(20.8)	(242.3)	(20.8)	(6.7)	(2.4)		[315.9]		
$\text{Sn}(\text{CH}_3)_3$	6- $\text{N}(\text{CH}_3)_2$ ^d	nl	31.26	35.29	34.55	107.12	149.33*	109.49	125.45	135.15	149.23*	23.44	-10.87	-4.09	-0.20 ^f
				[~51]					(~39)						
$\text{Sn}(\text{CH}_3)_3$	7- $\text{N}(\text{CH}_3)_2$ ^d	33.34	31.26	35.70	34.02	121.55	109.81	148.94	111.17	147.26	137.12	23.44	-10.70	-5.22	-1.33 ^g
				[51.3]				[42]					[309.44]		
$\text{Sn}(\text{CH}_3)_3$	6- NO_2	nl	30.58	34.62	nl	116.39	146.41	121.27	125.60	nl	150.36	23.19	-10.75	-1.64	+2.25
$\text{Sn}(\text{CH}_3)_3$	7- NO_2	nl	30.58	34.51	nl	121.89	121.41	146.14	119.86	148.30	157.00	23.30	-10.86	-0.77	+3.12

^a For CDCl_3 solutions relative to internal Me_4Si . ^b Relative to $(\text{CH}_3)_4\text{Sn}$. ^c Values in parentheses are ^{13}C - ^{119}Sn couplings. ^d NCH_3 at 41.06 ppm. ^e $J_{^{119}\text{Sn}-^{13}\text{C}}$ = 1.8 Hz. ^f SCS becomes +2.31 on protonation. ^g SCS becomes +2.43 on protonation. ^h SCS becomes +2.43 on protonation. * interchangeable.

(32) B. F. Hegarty, Ph.D. Dissertation, University of Queensland, 1969.
 (33) W. Kitching, W. Adcock, and B. F. Hegarty, *Aust. J. Chem.*, 21, 2411 (1968).
 (34) D. H. Hey, D. A. Shingleton, and G. H. Williams, *J. Chem. Soc.*, 1958 (1963).
 (35) R. J. Ouellette, Ph.D. Dissertation, University of California, 1962 (University Microfilms Inc., No. 63-5442).

Table X. Melting Points and Analyses of Benzylmercurials^b

X =	Y =	anal. (C, H)		mp, ^a °C	
		found	calcd	found	lit.
H	C ₆ H ₅ CH ₂	44.4, 3.9	43.9, 3.7	109	111 ³¹
H	Cl	25.8, 2.2	25.7, 2.1	104.5	104 ³¹
<i>o</i> -CH ₃	Cl	27.9, 2.8	28.1, 2.6	92	
<i>p</i> -CH ₃	<i>p</i> -CH ₃ C ₆ H ₄ CH ₂	46.6, 4.6	46.8, 4.4	109	
<i>p</i> -CH ₃	Cl	28.2, 2.8	28.1, 2.6	143	
<i>m</i> -F	<i>m</i> -FC ₆ H ₄ CH ₂	40.7, 3.4	40.1, 2.9	98	96-97 ³²
<i>m</i> -F	Cl	24.6, 1.9	24.3, 1.7	122	119 ³³
<i>p</i> -F	<i>p</i> -FC ₆ H ₄ CH ₂			75	74-75 ³²
<i>p</i> -F	Cl	24.4, 1.9	24.3, 1.7	142	137 ³³
<i>m</i> -Cl	Cl ^b	22.3, 1.7	23.2, 1.7	135	141
<i>p</i> -Cl	<i>p</i> -ClC ₆ H ₄ CH ₂	37.3, 2.6	37.2, 2.7	147.5	149.5 ³⁴
<i>p</i> -Cl	Cl	24.1, 2.0	23.2, 1.7	144	144.4-145.2 ³⁴
<i>m</i> -CF ₃	<i>m</i> -CF ₃ C ₆ H ₄ CH ₂	38.1, 2.6	37.0, 2.3	98	
<i>m</i> -CF ₃	Cl	24.9, 1.6	24.3, 1.5	184	

^a Uncorrected. *m*-Methylbenzylmercuric chloride (mp 112) was obtained in very low yield and characterized by its ¹H, ¹³C, and ¹⁹⁹Hg spectra, as was the bis compound. Bis(*o*-methylbenzyl)mercury showed the following: ¹H NMR δ 2.36 (6 H, s, CH₃), 2.40 (4 H, s, CH₂), 6.98-7.28 (8 H, m, aromatics), $J_{\text{CH}_2\text{-Hg}} = 130$ Hz, $J_{\text{CH}_3\text{-Hg}} = 13$ Hz. ^b Some contamination with the mercuric bromide.

to establish more precisely the nature of this response. In a series of the corresponding (benzobicyclooctenyl) fluorides, encompassing a wide variety of 6 and 7 substituents, the ¹⁹F SCS were confined^{21a} to a very narrow range (in contrast to the situation in meta- and para-substituted benzyl fluorides), consistent with almost complete suppression of benzylic C-F aryl conjugation.

Summary

The present investigations confirm that the chemical shifts of the metal nuclides ¹⁹⁹Hg and ¹¹⁹Sn respond in a regular fashion to substituent changes in benzyl compounds, albeit in different directions. A priori, it is difficult to predict what response will be elicited in various benzyl metal compounds with substituent changes, and examination of the ²⁰⁷Pb resonances of benzyllead compounds would be of interest in this regard. The range of shifts associated with remote substituent changes (where proximity-induced shifts are not a problem) in the benzyltin and -mercury systems is not large, and a number of influences, with some acting in opposition, may compete. The data herein suggest that understanding of heavy-metal NMR chemical shifts is limited and provision of data from further model series is required to formulate patterns of chemical shift behavior and empirical relationships.

Experimental Section

Benzylmercurials were obtained in a standard way from the appropriate Grignard reagent and mercuric chloride. Generally a large excess of Grignard reagent was employed to produce the dibenzylmercurial which was purified. Treatment of the dibenzylmercurial with 1 molar equiv of mercuric chloride in tetrahydrofuran at room temperature for several hours provided the corresponding benzylmercuric chloride. As in situ procedures are not useful for mercuric halide reactions, the Grignard reagent was fully formed prior to addition of the mercuric chloride. This procedure, however, frequently results in production of substantial amounts of dibenzyls (coupled product) which can be separated from mercurial product in the crystallization step from ethanol. Details of the ¹H, ¹³C, and ¹⁹⁹Hg NMR are located in the text, and the melting point and analyses are summarized below in Table X.

Benzyltrimethylstannanes were available from the collection of Dr. C. J. Moore and Dr. M. Bullpitt and have been fully described and characterized previously. If required, these are

distilled prior to measurements, and the ¹H, ¹³C and ¹¹⁹Sn NMR spectra confirmed a high purity.

1-(Trimethylstannyl)-4-methyl-6/7-substituted-1,4-ethano-1,2,3,4-tetrahydronaphthalenes (except for the nitro derivatives) were obtained (50% yield) by treatment of the corresponding 1-iodo compounds with (trimethyltin)lithium in tetrahydrofuran in the standard way. A full description of the synthesis of the 1-iodo precursors will be presented elsewhere.³⁶ The parent 1-(trimethylstannyl)-4-methyl-1,4-ethano-1,2,3,4-tetrahydronaphthalene was a colorless oil: bp 105-110 °C (0.05 mm); n_D^{25} 1.5580; mass spectrum m/e 336, 334, 332 (M^+); ¹H NMR (CDCl₃) δ 0.20 (9 H, s, SnCH₃), 1.28-2.01 (8 H, m, CH₂CH₂), 1.37 (3 H, s, CCH₃), 6.96-7.30 (4 H, m, aromatic). Anal. Calcd for C₁₆H₂₄Sn: C, 57.36; H, 7.22. Found: C, 58.05; H, 7.11.

1-(Trimethylstannyl)-4-methyl-6/7-(dimethylamino)-1,4-ethano-1,2,3,4-tetrahydronaphthalene was a pale yellow liquid: bp 120-125 °C (0.05 mm); mass spectrum, m/e 379, 377, 375 (M^+); ¹H NMR (CDCl₃) for major 7 isomer δ 0.31 (9 H, s, SnCH₃, $J_{\text{H-Sn-}^1\text{H}} = 48$ Hz), 1.20-2.1 (8 H, CH₂CH₂), 1.41 (3 H, s, CCH₃), 3.00 (6 H, s, N(CH₃)₂), 6.5-7.2 (3 H, m, aromatics). Signals at δ 0.25 (SnCH₃), 1.43 (CCH₃), and 3.02 (N(CH₃)₂) are associated with the minor 6-N(CH₃)₂ isomer in admixture. The aromatic ¹H pattern is as expected for the ca. 3:1 mixture and strongly perturbed by the N(CH₃)₂.

1-(Trimethylstannyl)-4-methyl-6/7-fluoro-1,4-ethano-1,2,3,4-tetrahydronaphthalene was a colorless liquid: bp 105-110 °C (0.05 mm); mass spectrum, m/e 354, 352, 350 (M^+); ¹H NMR (CDCl₃) δ 0.38 (9 H, s, SnCH₃, $J_{\text{H-Sn-}^1\text{H}} = 50$ Hz), 1.25-2.15 (8 H, CH₂CH₂), 1.50 (3 H, s, CCH₃), 6.6-7.2 (3 H, m, aromatics). Signals at δ 0.37 (SnCH₃) and 1.48 (CCH₃) are characteristic of the minor 6-fluoro isomer.

1-(Trimethylstannyl)-4-methyl-6/7-nitro-1,4-ethano-1,2,3,4-tetrahydronaphthalene. Following the procedure of Tanida and Muneyuki,³⁷ a solution of 1-(trimethylstannyl)-4-methyl-1,4-ethano-1,2,3,4-tetrahydronaphthalene (0.336 g, 0.001 mol) in nitromethane (15 mL) was treated at 0 °C with a nitrating agent (1.77 g, 0.001 mol) prepared from nitric acid (d^{22} 1.375), sulfuric acid (d^{22} 1.835), and water in the weight ratio 1.05:18:16. After being stirred (0 °C) for 2 h, the reaction mixture was poured onto ice and extracted with dichloromethane. The extract was dried and solvent removed (reduced pressure). VPC and ¹³C NMR analyses of the crude product indicated that the required nitro derivatives were present in 20-25% yield. Separation from higher boiling impurities was achieved by Kugelrohr distillation, and a sample (0.80 g; 21%) was obtained as a pale yellow liquid: bp

(36) W. Adcock and A. N. Abeywickrema, to be published.

(37) H. Tanida and R. Muneyuki, *J. Am. Chem. Soc.*, **87**, 4794 (1965).

130–140 °C (0.01 mm); mass spectrum, m/e 381, 379, 377 (M^+); ^1H NMR (CDCl_3) δ 0.27 (9 H, s, SnCH_3 , $J_{119\text{Sn}-^1\text{H}} = 52$ Hz) and δ 1.42 (CCH_3) are associated with the major (7) isomer, while corresponding signals at δ 0.24 and δ 1.45 characterize the 6- NO_2 isomer. Consistent alkyl proton absorption (CH_2CH_2) (δ 1.20–2.1) and two regions of aromatic resonance (ca. δ 7.0–7.42 and 7.9–8.2) are observed. (Some impurities are revealed by the ^1H and ^{13}C NMR spectra.)

^{13}C spectra were obtained on the JEOL FX-100 spectrometer at 25.04 MHz. The solvent employed was a mixture (60:40) of deuteriochloroform and dichloromethane, and spectra were referenced to $^{13}\text{CDCl}_3$ as 77.00 ppm. ^{199}Hg spectra were obtained on the same spectrometer modified for multinuclear observation. The operating frequency was 17.82 MHz (benzylmercuric chlorides) and 17.83 MHz (dibenzylmercury series). The solvent was again 60:40 CDCl_3 – CH_2Cl_2 and 10-mm tubes were used. The chemical shifts are referenced to the (unsubstituted) parent compounds, so that the differences represent the substituent chemical shifts. The variation in shift between the mono- and dibenzyl mercurials is in excess of 400 ppm, and relative to $(\text{CH}_3)_2\text{Hg}$, the shifts can be calculated to be ca. –1120 and –700 ppm, respectively (i.e., upfield). Concentrations of mercurials were very close to 0.4 M, and in most cases, known mixtures of two compounds were examined, and the ^{199}Hg shifts obtained were little different from those when single compounds were examined. Usually a fluoro-substituted benzyl mercurial was a member of the mixture, as this ^{199}Hg resonance (with ^{199}Hg – ^{19}F coupling) could be easily recognized. The dibenzyl mercurials provide sharp spectra, whereas some broadening characterized the spectra of the mercuric chlorides. ^{119}Sn spectra were obtained on the JEOL FX-100 spectrometer at a frequency of 37.70 MHz for solutions 0.5 M in 65:35 CDCl_3 – CH_2Cl_2 solvent. Internal tetramethyltin (CH_3) $_4\text{Sn}$ was used as reference, and dilution studies showed very minor concentration effects.

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Registry No. $\text{C}_6\text{H}_5\text{CH}_2\text{HgCl}$, 2117-39-7; $o\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{HgCl}$, 4109-87-9; $m\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{HgCl}$, 19224-35-2; $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{HgCl}$, 4158-22-9; $m\text{-FC}_6\text{H}_4\text{CH}_2\text{HgCl}$, 2357-53-1; $p\text{-FC}_6\text{H}_4\text{CH}_2\text{HgCl}$, 2357-55-3; $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{HgCl}$, 4109-90-4; $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{HgCl}$, 4109-88-0; $m\text{-CF}_3\text{C}_6\text{H}_4\text{CH}_2\text{HgCl}$, 76807-70-0; $\text{C}_6\text{H}_5\text{CH}_2\text{HgCH}_2\text{C}_6\text{H}_5$, 780-24-5; $o\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{HgCH}_2\text{C}_6\text{H}_4\text{-}o\text{-CH}_3$, 76807-71-1; $m\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{HgCH}_2\text{C}_6\text{H}_4\text{-}m\text{-CH}_3$, 35597-66-1; $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{HgCH}_2\text{C}_6\text{H}_4\text{-}p\text{-CH}_3$, 10507-46-7; $m\text{-FC}_6\text{H}_4\text{CH}_2\text{HgCH}_2\text{C}_6\text{H}_4\text{-}m\text{-F}$, 10507-43-4; $p\text{-FC}_6\text{H}_4\text{CH}_2\text{HgCH}_2\text{C}_6\text{H}_4\text{-}p\text{-F}$, 10507-45-6; $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{HgCH}_2\text{C}_6\text{H}_4\text{-}p\text{-Cl}$, 10507-42-3; $m\text{-CF}_3\text{C}_6\text{H}_4\text{CH}_2\text{HgCH}_2\text{C}_6\text{H}_4\text{-}m\text{-CF}_3$, 76807-72-2; $\text{C}_6\text{H}_5\text{CH}_2\text{Sn}(\text{CH}_3)_3$, 4314-94-7; $p\text{-FC}_6\text{H}_4\text{CH}_2\text{Sn}(\text{CH}_3)_3$, 706-26-3; $o\text{-OCH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Sn}(\text{CH}_3)_3$, 51755-57-8; $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Sn}(\text{CH}_3)_3$, 19962-42-6; $p\text{-C}_6\text{H}_5\text{C}_6\text{H}_4\text{CH}_2\text{Sn}(\text{CH}_3)_3$, 61760-10-9; $m\text{-OCH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Sn}(\text{CH}_3)_3$, 51517-27-2; $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{Sn}(\text{CH}_3)_3$, 41037-63-2; $m\text{-FC}_6\text{H}_4\text{CH}_2\text{Sn}(\text{CH}_3)_3$, 30590-70-6; $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{Sn}(\text{CH}_3)_3$, 27640-06-8; $m\text{-CF}_3\text{C}_6\text{H}_4\text{CH}_2\text{Sn}(\text{CH}_3)_3$, 27640-07-9; $o\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Sn}(\text{CH}_3)_3$, 19962-44-8; trimethyl(2-naphthalenylmethyl)stannane, 61760-08-5; trimethyl(6-methyl-2-naphthalenylmethyl)stannane, 61760-09-6; trimethyl(1-naphthalenylmethyl)stannane, 51220-36-1; 4-methyl-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 33673-05-1; 1-(trimethylstannyl)-4-methyl-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-73-3; 4-methyl-6-fluoro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-74-4; 1-(trimethylstannyl)-4-methyl-6-fluoro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-75-5; 4-methyl-7-fluoro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-76-6; 1-(trimethylstannyl)-4-methyl-7-fluoro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-77-7; 1-(trimethylstannyl)-4-methyl-6-(dimethylamino)-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-78-8; 1-(trimethylstannyl)-4-methyl-7-(dimethylamino)-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-79-9; 1-(trimethylstannyl)-4-methyl-6-nitro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-80-2; 1-(trimethylstannyl)-4-methyl-7-nitro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-81-3; 1-iodo-4-methyl-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-82-4; 1-iodo-4-methyl-6-fluoro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-83-5; 1-iodo-4-methyl-7-fluoro-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-84-6; 1-iodo-4-methyl-6-(dimethylamino)-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-85-7; 1-iodo-4-methyl-7-(dimethylamino)-1,4-ethano-1,2,3,4-tetrahydronaphthalene, 76807-86-8.

Acylation of Multiple Anions of Poly- β -ketones by Hydroxy- and Alkoxybenzoates. Cyclization of the Resultant Tetraketones to Benzophenones and Xanthenes

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The dianion (2) of 2,4-pentanedione and the trianion (10) of 2,4,6-heptanetrione were acylated by lithium salts of the unprotected hydroxybenzoates methyl 2-hydroxy-4-methoxy-6-methylbenzoate (1b), methyl 2,6-dihydroxy-4-methoxybenzoate (7b), and methyl 2,4-dimethoxy-6-hydroxybenzoate (7c), as well as by the alkoxybenzoates methyl 2,4,6-trimethoxybenzoate (7d) and methyl 2,4,6-tribenzoxybenzoate (7e). The aryl 1,3,5,7-octanetetraones (11b-d and 12) resulting from acylation of 10 were cyclized in biomimetic processes to naturally occurring benzophenones and xanthenes. Hydrogenolysis of 1-(2,4,6-tribenzoxyphenyl)-1,3,5,7-octanetetraone (11e) and cyclization gave norlichexanthone (20).

Acylation by benzoate esters bearing oxy substituents provides a convenient approach to several classes of secondary metabolites including coumarins,¹ coumestans,² xanthenes,³ and alternariol.³ Examples have generally

involved O-alkylated hydroxybenzoates; for example, the synthesis of 9-O-methylalternariol (4) has been accomplished by a route involving acylation of the dianion (2) of 2,4-pentanedione with ester 1a to give triketone 3a³ (Scheme I). After carboxylation of the trianion of 3a, a deprotection step is subsequently required to form 4. It would be advantageous if acylations with hydroxy-sub-

(1) Ellis, G. P., Ed. "Chromenes, Chromanones, and Chromones"; Wiley: New York, 1977; pp 273, 541–542.

(2) Nakanishi, K.; Goto, T.; Ito, S.; Natori, S.; Nozoe, S., Eds. "Natural Products Chemistry"; Kodansha, Ltd.: Tokyo; Academic Press: New York, 1975; pp 248–249.

(3) Harris, T. M.; Hay, J. V. *J. Am. Chem. Soc.* 1977, 99, 1631.