

with ether/pentane (10–50% ether). They are transformed to the corresponding ketones by stirring with a small amount of *p*-toluenesulfonic acid. The hydrocarbons were separated by GLC (SE 30, 15%, 3 m), the cyclopropane compounds **3** and **13** being eluted after the olefins **4** and **14**, respectively, while the brendane **5** was eluted before the mixture of **4** and **6** (not separated).

Tricyclo[4.2.1.0^{2,8}]nonane (3): IR (CHCl₃) 3020 cm⁻¹; ¹H NMR (CDCl₃) δ 1.1–2.4 (m, 13 H), 0.64–0.94 (m, 1 H); ¹³C NMR (CDCl₃) δ 33.9 (t, 20), 33.3 (d, 18), 32.6 (t, 50), 24.4 (t, 22), 22.5 (t, 24), 21.5 (d, 32), 17.0 (d, 10); mass spectrum 122 (P, 17), 80 (100).

Tricyclo[4.2.1.0^{3,7}]nonane (brendane) (5):¹⁰ IR (CDCl₃) 1453, 1311, 1288, and 1149 cm⁻¹; ¹H NMR (CDCl₃) δ 1.15–1.9 (m, 12 H), 0.87 (s, 1 H), 0.70 (s, 1 H); ¹³C NMR (CDCl₃) δ 48.2 (d, 38, C-7), 41.0 (t, 99, C-2, C-9), 40.0 (t, 51, C-8), 39.1 (d, 66, C-3, C-6), 35.8 (d, 43, C-1), 32.3 (t, 100, C-4, C-5); mass spectrum 122 (P, 17), 80 (100).

Tricyclo[3.2.1.0^{2,7}]octane (13):²⁴ IR (CHCl₃) 3020 cm⁻¹; ¹H NMR (CDCl₃) δ 1.15–1.95 (m, 11 H), 0.5–0.75 (m, 1 H); ¹³C NMR (CDCl₃) δ 31.3 (t, 73), 30.4 (d, 25), 28.1 (t, 39), 16.8 (t + d, 100), 12.9 (d, 27); mass spectrum 108 (P, 25), 79 (100).

Decompositions of Tosylhydrazones 1, 2, 11, and 12 by Sodium Methoxide in Ethylene Glycol. The tosylhydrazones were treated as above in ethylene glycol (distilled over sodium). The compounds were separated by chromatography on silica gel and eluted on the following order: hydrocarbons (pentane), ketones (4–5% yield, ether/pentane 10:90), ether alcohols (ether/pentane 50:50).

(2'-Hydroxy)-2-ethoxybicyclo[4.2.1]nonane (9): IR (CHCl₃) 3620, 3460, 1100, and 1050 cm⁻¹; ¹H NMR (CDCl₃) δ 3.2–3.8 (m, 5 H), 2.2–2.8 (m, 2 H), 1.2–2.2 (m, 13 H); mass spectrum 184 (P, 7), 123 (P – OCH₂CH₂OH, 29), 122 (P – HOCH₂CH₂OH, 100).

(2'-Hydroxy)-3-ethoxybicyclo[4.2.1]nonane (10): IR (CHCl₃) 3580, 3430, 1100, and 1050 cm⁻¹; ¹H NMR (CDCl₃) δ 3.2–3.8 (m, 5 H), 1.1–2.6 (m, 15 H); mass spectrum 184 (P, 10), 122 (P – HOCH₂CH₂OH, 100).

(2'-Hydroxy)-2-ethoxybicyclo[3.2.1]octane (17): IR (CHCl₃) 3670, 3590, 3450, 1105, and 1050 cm⁻¹; ¹H NMR (CDCl₃) δ 3.2–3.8 (m, 5 H), 2.5 (s, 1 H), 2.3 (br s, 1 H), 2.1 (br s, 1 H), 1.1–1.9 (m, 10 H); mass spectrum 170 (P, 17), 109 (P – OCH₂CH₂OH, 100), 108 (P – HOCH₂CH₂OH, 96).

(2'-Hydroxy)-3-ethoxybicyclo[3.2.1]octane (18): IR (CHCl₃) 3670, 3600, 3450, 1110, and 1050 cm⁻¹; ¹H NMR (CDCl₃) δ 3.3–3.8 (m, 5 H), 2.62 (s, 1 H), 2.26 (br s, 2 H), 1.7–2.1 (m, 2 H), 1.1–1.7 (m, 8 H); mass spectrum 170 (P, 19), 109 (P – OCH₂CH₂OH, 93), 108 (P – HOCH₂CH₂OH, 100).

Registry No. 1, 70941-65-0; 2, 70941-66-1; 3, 27197-55-3; 4, 5307-64-2; 5, 1521-75-1; 6, 16456-33-0; 9, 70941-67-2; 10, 70941-68-3; 11, 70941-69-4; 12, 64850-60-3; 13, 285-43-8; 14, 823-02-9; 17, 70941-70-7; 18, 70941-71-8; bicyclo[4.2.1]nonan-2-one, 3850-55-3; bicyclo[4.2.1]nonan-3-one, 3850-54-2; bicyclo[3.2.1]octan-2-one, 5019-82-9; bicyclo[3.2.1]octan-3-one, 14252-05-2; tosylhydrazine, 1576-35-8.

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Organometals as Electron Donors. Effects of Alkyl Groups on the Ionization Potentials of Tetraalkyltin Compounds in the Correlation with Taft σ* Values

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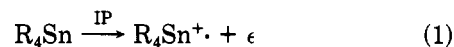
Organometals, particularly those with alkyl groups as ligands, are excellent electron donors. As electron-rich

Table I. Photoelectron Spectra of Tetraalkyltin Compounds

SnR ₄		-Σσ*	IP ₁ , eV	IP, eV		IP̄, eV
1	Me	0	9.7			9.7
2	Et	0.40	8.93			8.93
3	<i>n</i> -Pr	0.46	8.82			8.82
4	<i>i</i> -Pr	0.76	8.46			8.46
5	<i>n</i> -Bu	0.52	8.76			8.76
6	<i>i</i> -Bu	0.50	8.68			8.68
7	<i>s</i> -Bu	0.84	8.45			8.45
8	neopentyl	0.66	8.67			8.67
Me ₂ SnR ₂		-Σσ*	IP ₁ , eV	IP ₂ , eV	IP ₃ , eV	IP̄, eV
9	Et	0.20	9.01	9.28	9.64	9.31
10	<i>n</i> -Pr	0.23	8.8	9.2	9.5	9.17
11	<i>i</i> -Pr	0.38	8.56	8.99	9.55	9.03
12	<i>n</i> -Bu	0.26	8.8	9.2	9.5	9.17
13	<i>t</i> -Bu	0.6	8.22	8.74	9.47	8.81
Me ₃ SnR		-Σσ*	IP ₁ , eV	IP ₂ , eV	IP̄, eV	
14	Et	0.10	9.1	9.5 ^b	9.37	
15	<i>n</i> -Pr ^a	0.115	9.1			9.76
16	<i>i</i> -Pr	0.19	8.9	9.45	9.37	
17	<i>n</i> -Bu	0.13	9.0	9.49 ^b	9.33	
18	<i>i</i> -Bu	0.125	9.05	9.50 ^b	9.35	
19	<i>t</i> -Bu	0.30	8.50	9.62 ^b	9.24	
20	Et ₃ MeSn	0.30	8.95	9.3	9.07	

^a Taken from ref 8. ^b Not completely resolved.

species, they are subject to cleavage by various organic electrophiles including acids, alkyl halides, carbonyl and nitro compounds, as well as metal complexes.² Since alkylmetals have rather low ionization potentials, electron-transfer mechanisms are also possible in which the rate is limited by the ability of the organometal to transfer an electron to an electrophile acting as an electron acceptor. In order to delineate the energetics of such processes, it would be desirable to evaluate quantitatively the effects of alkyl ligands on the ionization potentials IP of organometals such as tetraalkyltin compounds, i.e.,



where R represents the same or different saturated alkyl groups.

The UV photoelectron spectrum (PES) of the parent member of the series, tetramethyltin, shows two well-defined, but broad, bands, A and B, centered at 9.65 and 13.4 eV, respectively, with a shoulder at 14.8 eV.³ The lowest-energy band A, which is of principal concern to us, is associated with ionization from the Sn–C σ-bonding orbital.^{3–5} Semiempirical calculations for tetramethyltin with tetrahedral (*T_d*) symmetry are in agreement with a highest occupied molecular orbital (HOMO) which is triply degenerate (3t₂).^{3,6,7}

The lowest vertical ionization potentials of three series of homologous tetraalkyltin compounds, viz., R₄Sn,

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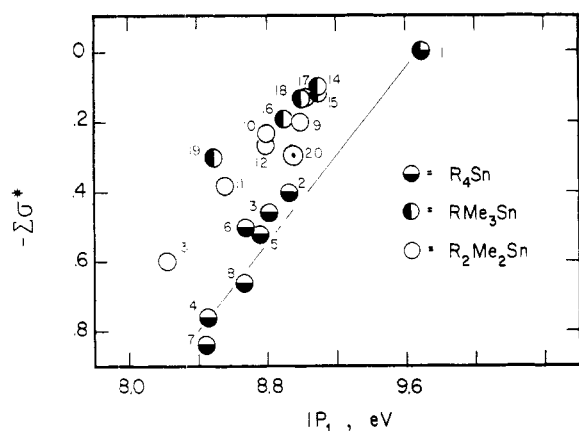


Figure 1. Relationship between the first vertical ionization potentials of a homologous series of symmetrical R_4Sn (●) and unsymmetrical R_3SnMe (◐) and R_2SnMe_2 (○) tetraalkyltin compounds and the sum of the Taft polar substituent parameters $\Sigma\sigma^*$. Numbers refer to the listing of compounds in Table I. The straight line is drawn through R_4Sn compounds only (see text).

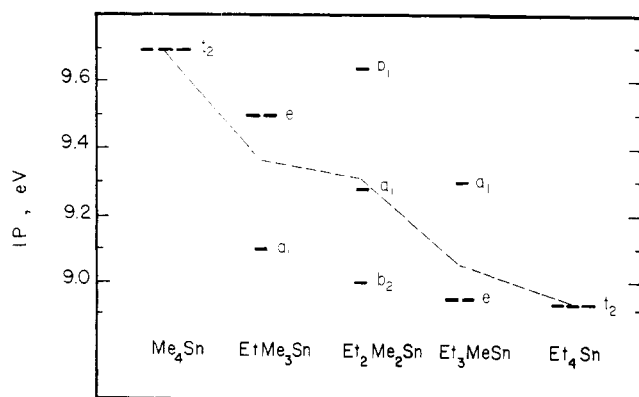


Figure 2. Correlation diagrams for the triply degenerate t_2 molecular orbital of tetramethyltin as a result of successive substitution of ethyl for methyl ligands.

R_3SnMe_3 , and R_2SnMe_2 , are listed in Table I.⁸ For the symmetrical tetraalkyltins, R_4Sn , the values of the first vertical ionization potentials are more or less linearly related to the sums of the Taft polar substituent parameters (σ^*) of the alkyl groups,⁹ as shown by the straight line drawn through these points in Figure 1. However, if the two series of methyl-substituted analogues R_3SnMe_3 and R_2SnMe_2 are included, considerable scatter is encountered for all the points considered in the same plot. [A close examination of Figure 1 reveals that a linear correlation exists in each set, viz., R_4Sn , R_3SnMe_3 , or R_2SnMe_2 considered separately.]

In these unsymmetrical tetraalkyltins, symmetry considerations predict the band A of R_4Sn to be split into additional bands.^{10,11} In particular, for the monosubstituted derivatives R_3SnMe_3 with C_{3v} symmetry, band A would be split into an a_1 and a doubly degenerate e set, whereas for the disubstituted analogues R_2SnMe_2 with C_{2v} symmetry, it would be split into an a_1 , b_1 , and b_2 set, as the correlation diagram in Figure 2 illustrates for the complete series of five methylethyltin compounds. Indeed, the experimental spectrum for $Me_3Sn-t-Bu$ shown in

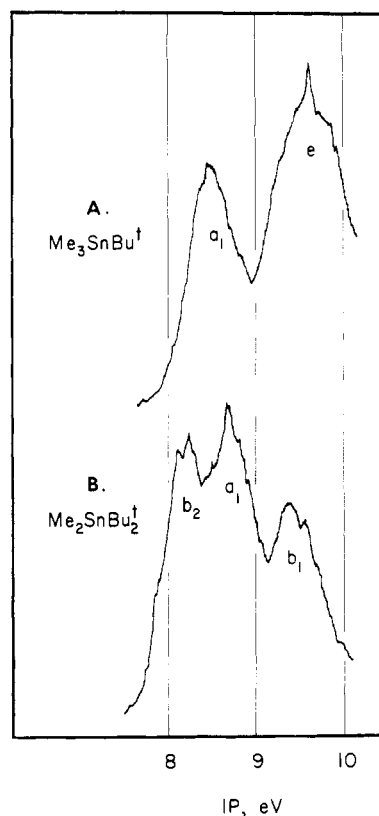


Figure 3. Typical splitting patterns of the lowest-energy bands in the photoelectron spectra of unsymmetrical tetraalkyltins: Me_3SnR (upper) and Me_2SnR_2 (lower).

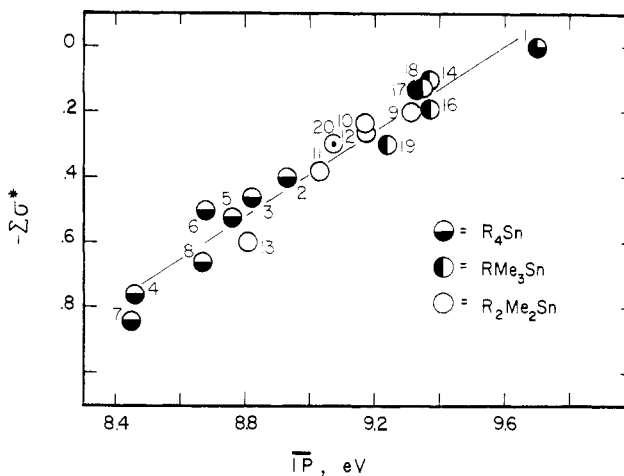


Figure 4. Linear correlation of the weighted average ionization potentials \bar{IP} and Taft $\Sigma\sigma^*$ parameters for the same tetraalkyltin compounds listed in Figure 1.

Figure 3A shows a doublet splitting with the expected 1:2 intensity ratio for this low-energy band. It is noteworthy that a similar splitting pattern is observed with Et_3SnMe but in a reversed 2:1 intensity ratio. Furthermore, the PES spectrum of $Me_2Sn-t-Bu_2$ in Figure 3B shows two distinct splittings associated with the three energy levels predicted by this simple formulation.¹²

If we take cognizance of these splittings of the HOMO of tetramethyltin, as they are induced by methyl substitutions, it would appear that the Taft σ^* parameter should correlate better with the weighted (center of gravity) average of all the vertical ionization potentials

(8) For the early work on the PES of various organotin compounds, see A. Hosomi and T. G. Traylor, *J. Am. Chem. Soc.*, **97**, 3682 (1975).

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(11) Ignoring Jahn-Teller distortion of the 2T_2 state of the parent molecule ion.

(12) (a) A similar splitting has been observed in the PES of a series of alkylgermanes, i.e., R_4Ge , R_3GeH , R_2GeH_2 , $RGeH_3$, and GeH_4 . (b) G. Beltram, T. P. Fehlner, K. Mochida, and J. K. Kochi, *J. Electron Spectrosc.*, in press.

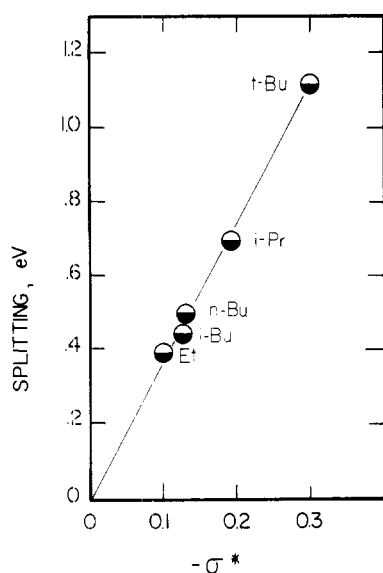


Figure 5. Electronic effects of alkyl ligands (R) measured by Taft σ^* values on the splitting of the e and a_1 levels in a series of alkyltrimethyltin $R\text{SnMe}_3$ compounds. Note the extrapolation through the origin.

Table II. Experimental and Calculated Values of the First Vertical Ionization Potentials of Alkyltrimethyltin Compounds

$R\text{SnMe}_3$, R	IP_1 (exptl), eV	IP_1 (calcd), eV
Me	9.70	9.70
Et	9.1	9.27
<i>n</i> -Bu	9.0	9.14
<i>i</i> -Bu	9.05	9.16
<i>i</i> -Pr	8.9	8.88
<i>t</i> -Bu	8.5	8.41

included in the first band A. Such an averaging procedure is tantamount to choosing a single (imaginary) ionization potential, \overline{IP} , to represent each tetraalkyltin, irrespective of its substitution pattern. [The dashed line in Figure 2 is drawn through \overline{IP} for each $\text{Me}_4\text{-Et}_n\text{Sn}$.] Indeed, Figure 4 shows that the averaged ionization potentials for all the various tetraalkyltins included in Figure 1 are now well correlated with the Taft σ^* values by a single line.

In the series of monosubstituted tetraalkyltins, $R\text{SnMe}_3$, the energy difference Δ between the e and a_1 molecular orbitals (see Figure 2) reflects the perturbation of the triply degenerate t_2 levels in tetramethyltin as a result of successive methyl substitutions at a single methyl ligand [i.e., $R = \text{CH}_3, \text{CH}_3\text{CH}_2, \text{CH}_3\text{CH}_2\text{CH}_2, (\text{CH}_3)_2\text{CH}, (\text{CH}_3)_3\text{C}$, etc.].¹³ As such, it is reasonable to expect the magnitude of this splitting to be reflected in the Taft σ^* value for R, as shown in Figure 5. It is noteworthy that the linear correlation passes through the origin, i.e.,

$$\Delta = -3.7\sigma^* \text{ eV} \quad (2)$$

in accord with this simple formulation. It follows that for a series of unsymmetrical alkyltrimethyltins $R\text{SnMe}_3$, the first vertical ionization potential from HOMO_1 ¹⁴ should be simply related to the ionization potential ($IP_1 = 9.70$ eV) of tetramethyltin from its Taft σ^* value. The relationship in eq 3 is obtained from a least-squares fit of the

$$IP_1(R\text{SnMe}_3) = 9.70 + 4.3\sigma^* \quad (3)$$

data, and the experimental and calculated ionization

potentials for a series of $R\text{SnMe}_3$ are compared in Table II.

Recently, the inductive parameter σ_I has been redefined from gas-phase acidities and basicities.¹⁵ These values of σ_I eliminate solvation effects and should be more directly applicable to the IP data from PES measurements. The type of correlation shown in Figure 4 is also applicable to these σ_I values since there is a linear correlation of σ^* and σ_I for alkyl groups.

Experimental Section

Materials. Tin tetrachloride, obtained as a generous sample from M and T Chemical Co. Inc., was used in all of the syntheses of tetraalkyltin compounds. The symmetrical $R_4\text{Sn}$ were prepared by the exhaustive alkylation of SnCl_4 with the appropriate Grignard reagent.¹⁶ A typical example is: 70 g (0.27 mol) of stannic chloride was added dropwise to 1.5 mol of EtMgBr in ether under a nitrogen atmosphere. The reaction was refluxed for 4 h after the addition was completed and hydrolyzed with dilute (0.1 N) aqueous HCl. After repeated extractions with ether, the combined ethereal layer was finally washed with saturated NaHCO_3 and dried over CaCl_2 . Distillation following the removal of solvent afforded Et_4Sn , bp 84 °C (11 mm).¹⁶ Others were, $R_4\text{Sn}$ (bp): Me_4Sn (78 °C (758 mm)),¹⁶ $n\text{-Pr}_4\text{Sn}$ (79 °C (2 mm)),¹⁶ $i\text{-Pr}_4\text{Sn}$ (102 °C (30 mm)),¹⁶ $n\text{-Bu}_4\text{Sn}$ (92 °C (1 mm)),¹⁶ $i\text{-Bu}_4\text{Sn}$ (101 °C (1.5 mm)),¹⁶ $s\text{-Bu}_4\text{Sn}$ (108 °C (0.8 mm)),¹⁷ and (neopent)₄Sn (mp 124 °C, after three recrystallizations from *n*-hexane).¹⁸

The unsymmetrical tetraalkyltin compounds, $R\text{SnMe}_3$ and $R_2\text{SnMe}_2$, were prepared by a similar procedure starting with Me_3SnCl and Me_2SnCl_2 , respectively. Trimethyltin chloride was prepared either from Me_4Sn by HCl cleavage or by syn proportionation with a stoichiometric amount of SnCl_4 . Dimethyltin dichloride was prepared from Me_4Sn and SnCl_4 at 130 °C for 4 h. Triethyltin chloride was prepared from Et_4Sn and acetyl chloride in the presence of aluminum chloride. $R\text{SnMe}_3$, (bp): EtSnMe_3 (105 °C (760 mm)),¹⁶ $n\text{-PrSnMe}_3$ (131 °C (760 mm)),¹⁹ $i\text{-PrSnMe}_3$ (123 °C (120 mm)),²⁰ $n\text{-BuSnMe}_3$ (150 °C (750 mm)),¹⁶ $t\text{-BuSnMe}_3$ (56 °C (36 mm)).²¹ $R_2\text{SnMe}_2$ (bp): Et_2SnMe_2 (65 °C (50 mm)),¹⁹ $n\text{-Pr}_2\text{SnMe}_2$ (74 °C (30 mm)),¹⁹ $i\text{-Pr}_2\text{SnMe}_2$ (66 °C (30 mm)),¹⁶ $n\text{-Bu}_2\text{SnMe}_2$ (70 °C (4 mm)),¹⁶ $t\text{-Bu}_2\text{SnMe}_2$ (75 °C (30 mm)).^{16,22} $i\text{-Bu}_2\text{SnEt}_2$ ¹⁶ was prepared from $i\text{-BuMgCl}$ and Et_2SnCl_2 (from Et_4Sn and SnCl_4) (bp 124 °C (13 mm)).

All the spectra were obtained with a Perkin-Elmer PS-18 photoelectron spectrometer, using the He(I) resonance line at 21.22 eV. The spectra were calibrated with Ar lines at 15.759 and 15.937 eV. In most cases, the vapor pressures of the tetraalkyltin were sufficient to carry out the spectral studies at ambient temperatures.

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Registry No. 1, 594-27-4; 2, 597-64-8; 3, 2176-98-9; 4, 2949-42-0; 5, 1461-25-2; 6, 3531-43-9; 7, 6031-41-0; 8, 13356-21-3; 9, 4282-05-7; 10, 56535-52-5; 11, 66363-02-8; 12, 1528-00-3; 13, 35569-11-0; 14, 3531-44-0; 16, 3531-46-2; 17, 1527-99-7; 18, 1118-10-1; 19, 3531-47-3; 20, 2097-60-1; SnCl_4 , 7646-78-8; Me_3SnCl , 1066-45-1; Me_2SnCl_2 , 753-73-1; Et_2SnCl_2 , 866-55-7.

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(13) The splitting is actually $2/3\Delta$.

(14) Assuming Koopmans' theorem.