gics calculated by the extended Hückel method are not particularly reliable, the qualitative argument which emerges could possibly be invoked to explain why alkyl substitution appears to impart special thermodynamic stability to many small ring systems (e.g., thiiranes,[14] ethylenehalonium ions,[15] diaziridinones,[16] and α-lactones[17]), all of which possess potential acceptor orbitals positioned for hyperconjugation with the alkyl substituents. Further investigation of the generality of this effect is planned, using more appropriate semiempirical molecular orbital methods.

References and Notes

(1) Presented in part at the 8th Annual Organosilicon Award Symposium, St. Louis, Mo., March 31, 1974.
(2) W. Ando, A. Sekeiguchi, T. Hagiwara, and T. Migita, *J. Chem. Soc., Chem. Commun.*, 372 (1974).
(3) See, for example, J. D. Roberts and S. Dev, *J. Am. Chem. Soc.*, **73**, 1879 (1951); P. S. Skell and E. J. Goldstein, *ibid.*, **86**, 1442 (1964); J. C. Thompson, J. L. Margrave, and P. L. Timms, *Chem. Commun.*, 566 (1966); O. M. Nefedov and M. M. Manakov, *Angew. Chem.*, **78**, 1039 (1966); J. W. Connolly, *J. Organomet. Chem.* **11**, 429 (1968).
(4) R. L. Lambert, Jr., and D. Seyferth, *J. Am. Chem. Soc.*, **94**, 9246 (1972).
(5) The Seyferth group has also prepared hexamethylsilacyclopropane and found it to be much less stable than the dispiro compounds: D. Seyferth and D. C. Annarelli, *J. Am. Chem. Soc.*, **97**, 2273 (1975).
(6) At least one other group has obtained spectroscopic evidence of a stable silacyclopropane in solution, but attempts at isolation have not been fruitful: P. R. Jones, private communication, North Texas State University.
(7) See, for example, C. J. Attridge, *Organomet. Chem. Rev., Sect. A*, **5**, 323 (1970); C. G. Pitt, *J. Organomet. Chem.*, **61**, 49 (1973); E. Ebsworth in "Organometallic Compounds of the Group IV Metals: The Bond to Carbon", Vol. I, Part 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N.Y., 1968, p 1; B. G. Ramsey, "Electronic Transitions in Organometalloids", Academic Press, New York, N.Y., 1969, p 65.
(8) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962). The following Si parameters were used (orbital, Coulomb integral in eV, Slater exponent): 3s, −17.30, 1.383; 3p, −9.20, 1.383; 3d, −6.00, 1.383.
(9) See chapters by H. G. Richey and by K. B. Wilberg, B. A. Hess, Jr., and A. J. Ashe, III, in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, pp 1201,1295.
(10) A. D. Walsh, *Nature (London)*, **159**, 167, 712 (1947); A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); R. Hoffmann, "Special Lectures at the XXIIIrd International Congress of Pure and Applied Chemistry", Vol. II, Butterworths, London, 1971, p 233.
(11) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, New York, N.Y., 1970, pp 166, 203.
(12) Linear combinations of the other components of the degenerate Walsh orbital sets give rise to semidelocalized orbitals transforming as a_1 and b_2. These can in turn interact with Si 3d orbitals lying in the plane of the silacyclopropane ring; however, because of the small coefficients at the sites of interaction, the effect will be minor. See W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, N.Y., 1973, pp 153, 206, 208.
(13) D. B. Boyd and R. Hoffmann, *J. Am. Chem. Soc.*, **93**, 1074 (1971).
(14) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. Oneal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).
(15) J. W. Larsen and A. V. Metzner, *J. Am. Chem. Soc.*, **94**, 1614 (1972).
(16) F. D. Greene, J. C. Stowell, and W. R. Bergmark, *J. Org. Chem.*, **34**, 2254 (1969); F. D. Greene and J. F. Pazos, *ibid.*, **34**, 2269 (1969).
(17) W. Adam and R. Rucktäschel, *J. Am. Chem. Soc.*, **93**, 557 (1971); O. L. Chapman, P. W. Wojtkowski, W. Adam, O. Rodriguez, and R. Rucktäschel, *ibid.*, **94**, 1365 (1972).

Studies of Interactions of Adjacent Carbon–Metal σ Bonds by Photoelectron Spectroscopy[1]

Akira Hosomi and T. G. Traylor*

Contribution from the Department of Chemistry, University of California, San Diego, La Jolla, California 92037. Received August 23, 1974

Abstract: The uv photoelectron spectra of 1,2- and 1,3-bis(trimethylstannyl)- and bis(trimethylsilyl)alkanes were determined along with several reference tetraalkyltin compounds. The ionization energies reveal a 2.6-eV interaction between adjacent carbon–tin bonds in $Me_3SnCH_2CH_2SnMe_3$ and an approximately 1.2-eV interaction in *trans*-2,3-bis(trimethylstannyl)norbornane. In the latter compound, the torsional angle between C–Sn σ bonds is 120° as compared with a possible 180° in the former. This σ–σ interaction is compared with σ–π, n–π, and π–π interactions.

The similarity of strained or polarized bond orbitals to n or π orbitals in delocalization phenomena has recently become more clearly demonstrated.[2-6] For example, σ–π conjugation of C–metal bonds can be as large as n–π conjugation of the –$\ddot{N}H_2$ lone pair in its effect upon aromatic electrophilic substitution[7] rates (eq 1) or ionization potentials


(1)
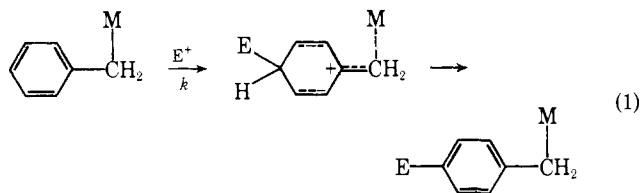
(eq 2). Thus, expressing the electron donation by the group Y in PhY as the usual $\sigma^+(Y)$ values, the values $\sigma^+(p\text{-OMe})$ = −0.78 and $\sigma^+(p\text{-benzylmercuryl-}CH_2\text{-})$ = −1.1 were determined by either the rate of reaction 1[7] or ionization


(2)
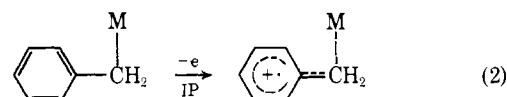
potentials 2.[2] The magnitudes and stereoelectronic requirements for π–π, n–π, and σ–π conjugations are now rather well understood.[2-6]

The decrease in hydrocarbon ionization potentials with chain length[8,9] and the low ionization potentials of polysilanes[10] indicate that σ delocalizations are to be expected. It remains to choose well-defined pairs of single σ bonds with which to delineate the behavior of σ–σ conjugation of either bent C–C bonds or C–metal bonds or their combinations. Spectroscopic studies have revealed large σ–σ interactions in the compounds shown:
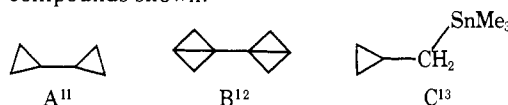
These large interactions, previous results on other kinds of conjugation, and stereochemistry of chemical reactions converting two σ bonds to a π bond imply certain preferred geometries for σ–σ conjugation shown below (provided that the delocalization is dominated by interactions of p orbit-

best geometry   no effect   some effect
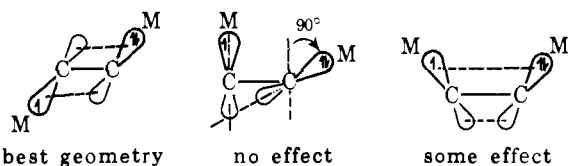
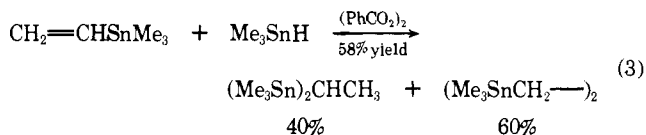als). Experimental tests of these suggestions are very much in order.

Therefore, we have prepared 1,2-dimetalloalkanes having either free rotation or rigid geometry and compared their ionization energies with those of 1,3-dimetalloalkyl compounds and with reference monometalloalkyl compounds.

free rotating
anti conformer

reduced π overlap

1   2
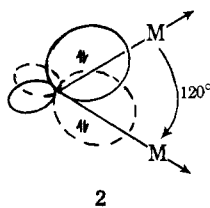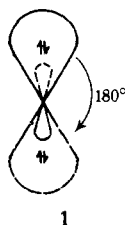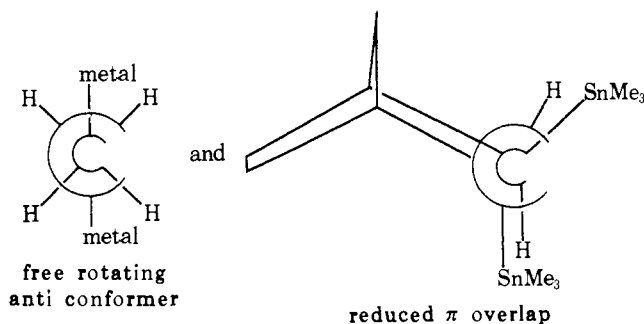
The results should reveal both the size of the interaction at maximum overlap and its dependence upon interorbital angle.

Results

The simple alkyltrimethyltin compounds were prepared by well-known Grignard methods. Because this method is not applicable to the preparation of 1,2-dimetalloalkanes, they were prepared from the requisite vinylmetal compounds by addition of the metal hydride.[14a,b] Interestingly, the addition of trimethylstannane to vinyltrimethyltin by the usual benzoyl peroxide catalyzed radical chain process produced a mixture of 40% 1,1-ditin and 60% 1,2-ditin compounds.

$$CH_2\text{=}CHSnMe_3 + Me_3SnH \xrightarrow[58\% \text{ yield}]{(PhCO_2)_2}$$
$$(Me_3Sn)_2CHCH_3 + (Me_3SnCH_2\text{—})_2 \quad (3)$$
$$40\% \qquad\qquad 60\%$$

The uv photoelectron spectra, determined as described by Turner,[15] are shown in Figures 1–5, and the ionization energies of these and other reference compounds are listed in Table I.

Discussion

Although the choice of reference compounds from which to calculate the σ–σ interactions in 1,2-dimetalloalkanes is somewhat arbitrary, we can reasonably assume, from previous results,[16] that the inductive effect of Me_3SnCH_2- is

Table I. Ionization Potentials of Organotin and Organosilicon Compounds

No.	Compd	Vertical ionization energies			
		I	II	III	IV
1	$Me_3Sn(CH_2)_3SnMe_3$	9.4$_6$	11.4	13.2$_3$	
2	$Me_3Sn(CH_2)_2SnMe_3$	8.0$_6$	9.5$_2$	10.6$_6$	11.6$_5$
3	$(Me_3Sn)_2CHCH_3$	8.2$_5$	9.4$_7$	10.1$_8$	
4	[structure]	8.0	9.3$_8$	10.5$_3$	11.5$_4$
5	Et_4Sn	8.8$_7$	11.9$_2$		
6	Me_4Sn	9.7$_5$ (9.7)^a	~13		
7	$EtSnMe_3$	9.1	9.5$_4$	11.9	13.3
8	n-$PrSnMe_3$	8.9	9.6	11.6	13.8
9	i-$PrSnMe_3$	8.7$_7$	9.5$_1$	11.6	11.5$_6$
10	cyclopentyl-$SnMe_3$	8.7$_2$	9.5	10.9	11.4
11	cyclohexyl-$SnMe_3$	8.5$_7$	9.5$_5$	10.3$_2$	11.4
12	t-$BuSnMe_3$	8.6$_5$	9.6$_8$	11.5	13.4
13	[structure]	8.4$_5$	9.5$_8$	10.7$_2$	
14	$CH_2\text{=}CHSnMe_3$	9.7	10.5		
15	$(Me_3Si)_2CH_2$	9.5	10.4	11.4	
16	$Me_3SiCH_2CH_2SiMe_3$	8.7$_8$	10.4$_7$	11.3	13.8
17	$Me_3Si(CH_2)_3SiMe_3$	9.4$_1$	10.4$_7$	11.5	
18	Me_4Si^a	10.57	13.06	14.08	15.58

[a] S. Evans, J. C. Green, P. J. Joachim, and A. F. Orchard, J. Chem. Soc., Faraday Trans. 2, 68, 905 (1972).

very similar to that of CH_3-. If this is true, then the ionization potential of $EtSnMe_3$ should reveal the energy of the appropriate orbital for mixing with itself to give the splitting interaction.

The association of the first ionization potential with C–M bonds is indicated by the large change in this ionization energy with change in alkyl groups in, e.g., Me_4Sn to $EtSnMe_3$ to i-$PrSnMe_3$. The Me_4Sn tetrahedral symmetry is removed in $EtSnMe_3$ and i-$PrSnMe_3$, and the lower ionization potentials 9.15 and 8.77 eV in the latter two compounds are attributed to the orbitals associated with the Et–Sn and i-Pr–Sn bonds, respectively. The second orbital at ~9.5 eV is relatively insensitive to substitution and is attributed to orbitals associated with the $SnMe_3$ group. These assignments are consistent with the lower first ionization energy of tetraethyltin in which the fourfold symmetry is restored but the electron donation by the alkyl groups increased. Therefore, we take as the basis orbital for estimating the interactions of $Me_3SnCH_2CH_2SnMe_3$ and in $(Me_3Sn)_2CHCH_3$ that having the lower of the two ionization potentials in $EtSnMe_3$, i.e., 9.15 eV. These interactions are estimated, based upon Koopman's theorem, from the appearance of new ionization potentials in 2 and 3 which are not present in $EtSnMe_3$. These energy levels are interpreted as interactions between C–Sn σ bonds by the usual simplification of interaction of isolated orbitals.[17] The interactions for these two compounds are diagrammed in Figure 6.

A similarly strong interaction between two C–Si bonds is clearly demonstrated in the ionization energy of 1,2-bis(trimethylsilyl)ethane (16) compared with the 1,3-bis(trimethylsilyl)propane (17) or tetramethylsilane. Although this observation demonstrates the generality of such σ–σ interactions of C–metal bonds, we will confine our discussion to the tin compounds where the magnitudes of the interactions are more clearly and accurately demonstrated.

The interaction between adjacent C–Sn σ bonds is in qualitative agreement with the CNDO/2 calculations of Pitt.[4] However, the observation that this interaction is larger than the σ–π interaction in allyltrimethyltin (Table II) is
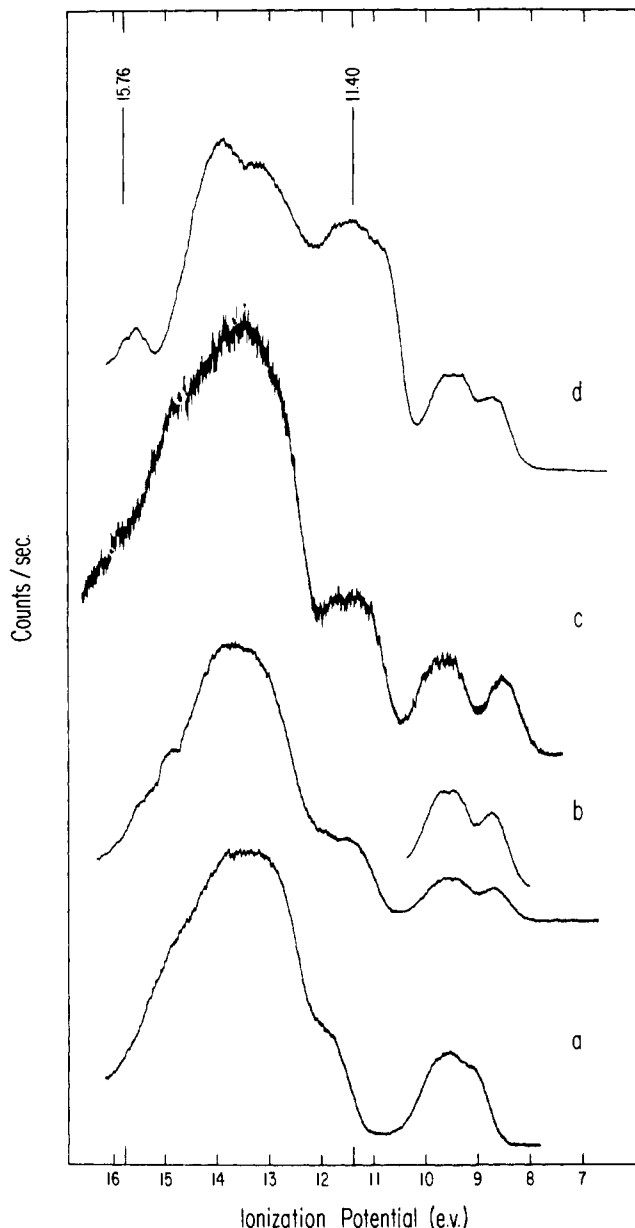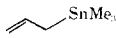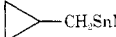
Figure 1. Photoelectron spectra of alkyltrimethylstannanes. The 14-eV region amounts to about 700 counts/sec in each spectrum. In this and other figures, there are less than 10 counts/sec at 7 eV: (a) EtSnMe₃ (7); (b) i-PrSnMe₃ (9); (c) t-BuSnMe₃ (12); (d) cyclopentyl-SnMe₃ (10).

Table II. Comparisons of $\sigma-\sigma$ and $\sigma-\pi$ Interactions

Compd	$\pi_1-\pi_2$ splitting, eV
~~	2.3,[a] 2.4[b]
▷◁	2.2[c]
~~SnMe₃	2.2[d]
▷—CH₂SnMe₃	1.6[d]
Me₃SnCH₂CH₂SnMe₃	2.6

[a] Reference 9b, p 182. [b] Reference 6d. [c] Reference 6b. [d] Reference 13.

unexpected. This large interaction is consistent with there being better overlap between adjacent σ bonds than between adjacent π bonds or cyclopropane orbitals. Two π symmetry orbitals shown below are envisioned for the electrons having the lowest ionization potential and that having an IP = 10.66 eV. An alternate description involving inter-
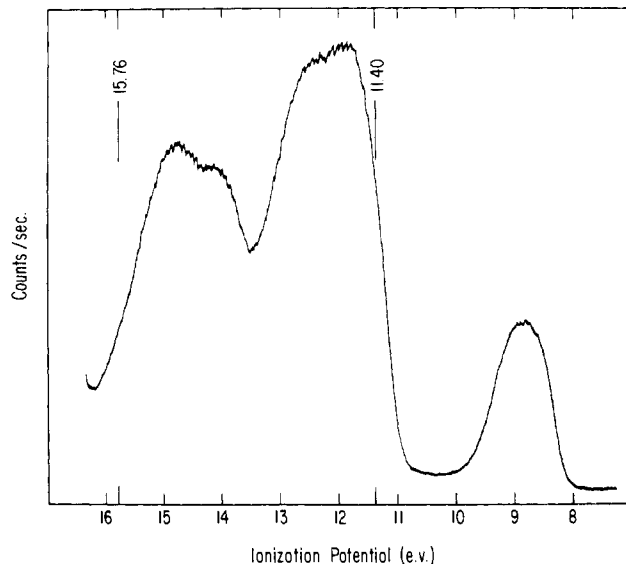

Figure 2. Photoelectron spectrum of Et₄Sn (5). Maximum counts/sec are 1000.
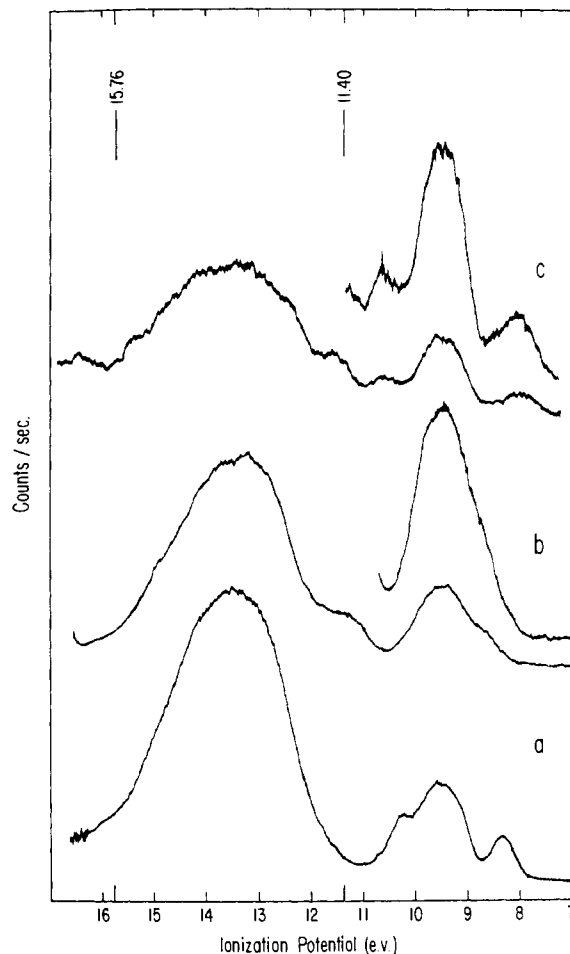

Figure 3. Photoelectron spectra of ditin compounds. The counts/sec in the 14-eV region are 700, 400, and 200 for a, b, and c, respectively. The 8–11-eV regions of b and c were recorded at higher sensitivities (insets): (a) (Me₃Sn)₂CHCH₃ (3); (b) Me₃Sn(CH₂)₃SnMe₃ (1); (c) (Me₃SnCH₂)₂ (2).

action of the Sn–CH₃ bonds by C–C through bond coupling would require interaction of orbitals of very disparate energies. Figure 6 also reveals a large interaction between the C–Sn bonds in 1,1-bis(trimethylstannyl)ethane. This split-
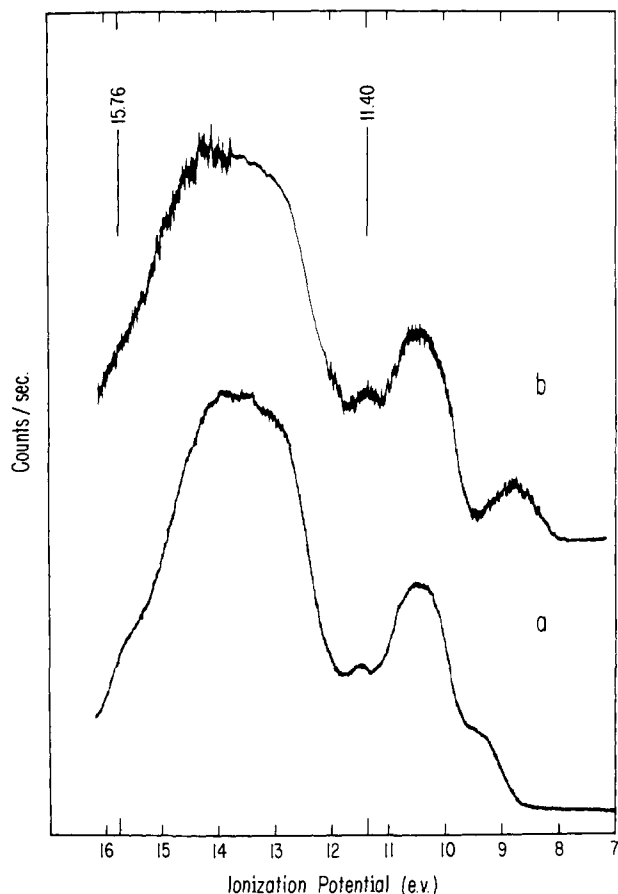
Figure 4. Photoelectron spectra of disilanes: (a) $Me_3Si(CH_2)_3SiMe_3$ (17); (b) $Me_3SiCH_2CH_2SiMe_3$ (16). Part (12–14 eV) of the b spectrum was recorded with a longer time constant.

π_1 (10.66 eV) π_2 (8.06 eV)
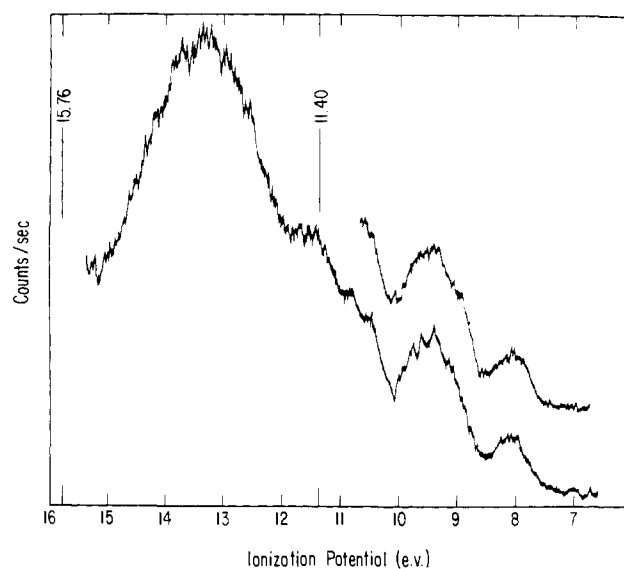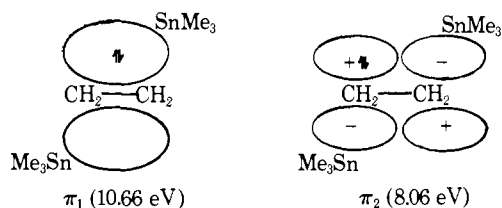
ting is depicted below as a linear combination of σ bonds.

π_1 (10.18 eV) π_2 (8.25 eV)

The 1.93-eV splitting of geminal σ bonds is comparable to the 1.87-eV geminal n orbital splitting in dimethyl ether[17,18] and provides a further illustration of the similarity between polarized σ bonds and lone-pair orbitals. Although π_2 in this molecule has a very low ionization energy and should therefore interact strongly with adjacent electron deficiency, this has not been observed. For example there is a rather small effect of a second C–Si bond compared with the first upon the ionization potentials of substituted toluenes.[5] This small effect could result from a larger difference between the π_2 and benzene orbitals in eq 4[17] or from decrease in overlap between the more diffuse π_2 orbital and the C^+ orbital as illustrated in D vs. E.

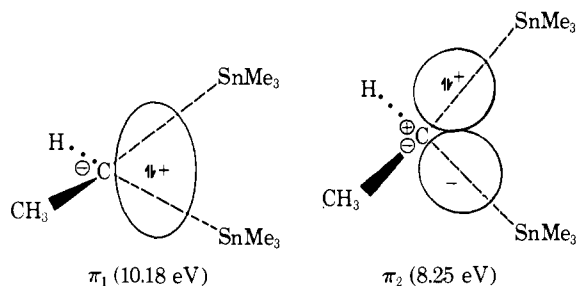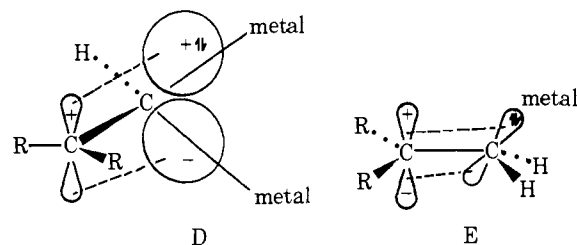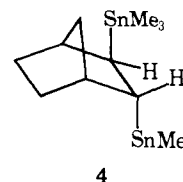Figure 5. Photoelectron spectrum of 4. At 13 eV, there were 100 counts/sec.

Figure 6. Orbital correlation diagram for 1,1- and 1,2-bis(trimethylstannyl)ethane.

$$\langle \rangle -CH_n(SiMe_3)_{3-n} \xrightarrow{h\nu} \langle \rangle -CH_n(SiMe_3)_{3-n} \quad (4)$$

TCNE   TCNE$^-$

D   E

The effect of rotation about the C–C bond was studied by preparing *trans*-2,3-bis(trimethylstannyl)[2.2.1]bicycloheptane (4). The first ionization potentials of secondary tri-


4

methyltin compounds such as trimethylstannylcyclopentane or bornyltrimethyltin are about 8.6 eV.[19] Although the sec-

ond ionization potential in **4** is obscured, the first ionization potential, 8.00 eV, indicates that the interaction is about $2(8.6 - 8.0) = 1.2$ eV. This interaction is in satisfactory agreement with the reduced interaction expected for a rota-


2.6 eV   ~1.2 eV
(180°)   (120°)
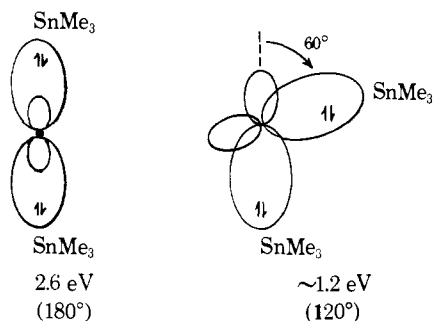
tion of 60° from the anti arrangement $(2.6 \cos 60° = 1.3$ eV).

It is interesting to compare our σ-σ interactions with n–n interactions in tetraalkyl hydrazines studied by Nelson and Bushek.[20] The interactions corresponding to our geometries are shown below.


180°, $\Delta E = 2.4$ eV   ~120°, $\Delta E = 1.8$ eV
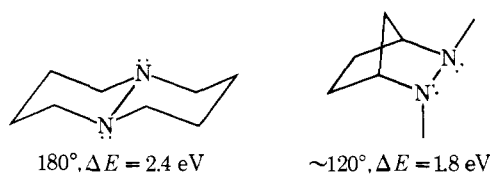
Clearly, the interactions of adjacent C–Sn σ bonds are comparable to those of adjacent nitrogen lone pairs. This confirms our suggestion[13] that C–metal σ bonds behave like lone pairs in delocalization.

The enhanced chemical reactivity consequent upon σ-π conjugation is rather well understood, although its application to synthesis is only beginning.[21,22] For example, the known σ^+ values of –CH$_2$–metal groups makes possible the prediction of occurrence and in some cases the rates of many new reactions of the type shown in eq. 5, where the π bond is olefinic or aromatic.
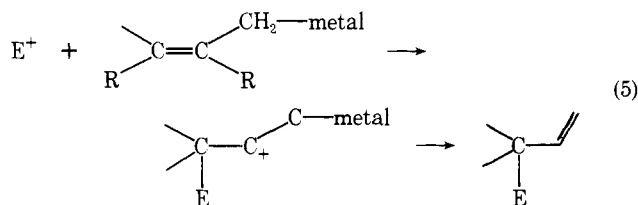
On the contrary, the reactions of 1,2-dimetalloalkanes remain to be explored. Two preliminary observations suggest that enhanced chemical reactivity of 1,2-dimetalloalkanes is to be expected. First, we observed that either **2** or **4** reacts with dilute solutions of trifluoroacetic acid in carbon tetrachloride more rapidly than does tetramethyltin. However, the second-order rate constants vary with the amount of oxygen which is present. In the case of **2** the products are ethylene and methane as volatiles. Although the nature of this reaction is not clear, it is certainly not simple C–metal cleavage by a protonic acid.

A second observation, that tetracyanoethylene reacts with **2** or **4** in an irreversible way, is quite consistent with the low ionization potentials of **2** and **4**. In both of these
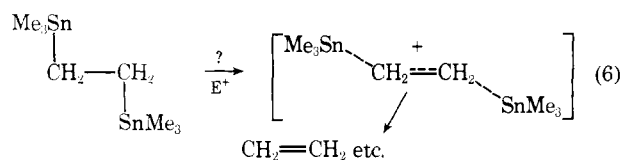
reactions, it is conceivable that a radical cation is formed. The chemical reactivity of these compounds deserves further study.

Experimental Section

Photoelectron spectra were determined on an instrument constructed in our laboratories as previously described.[13] Reference ionization potentials of an acetylene–argon mixture were determined immediately after each ionization potential measurement. Ionization potentials of standard compounds such as norbornadiene when determined on this instrument at various times agreed with literature values and with previous determinations within about ±0.03 eV.[13]

The tetraalkyltin compounds were prepared by standard Grignard procedures unless otherwise specified. The bis(trimethyl)tin compounds required the methods described below. NMR are given in τ values. Tetramethyltin (**6**) and tetraethyltin (**5**) were from Aldrich Chemical Co. and were used without purification. Ethyltrimethyltin (**7**) had: bp 108° [lit.[23] 106° (746 Torr)]; NMR 0.53–1.48 (m, 5 H), 0.09 (s, 9 H). Isopropyltrimethyltin (**9**) [bp 125° (lit.[24] 130.8°); NMR 0.10 (s, 9 H), 1.28 (m, 7 H)], isobutyltrimethyltin [bp 53° (24 Torr)[lit.[23] 140° (746 Torr)]; NMR 0.1 (s, 9 H), 0.87 (d, 2 H), 0.96 (d, 6 H), 1.57–2.29 (m, 1 H)], and *tert*-butyltrimethyltin (**12**) [mp 31° (lit.[25] 31.5°); bp 135°; NMR 0.16 (s, 9 H), 1.25 (s, 9 H)] were prepared by the Grignard method. *n*-Propyltrimethyltin (**8**),[26] cyclopentyltrimethyltin (**10**),[27] cyclohexyltrimethyltin (**11**),[27] 1,3-bis(trimethylstannyl)propane (**1**), and 1,3-bis(trimethylsilyl)propane (**17**)[28] were obtained from other projects and their preparation will be described elsewhere. Vinyltrimethyltin (**14**) [bp 99° (lit.[29] 98–100°); NMR 0.18 (s, 9 H), 5.40–6.78 (m, 3 H)] was prepared by the Grignard method. This compound (330 mg, 2.0 mmol) was heated with an equimolar amount of trimethyltin hydride (from trimethyltin chloride and lithium aluminum hydride) with 20 mg (0.08 mmol) of purified benzoyl peroxide in a sealed tube for 24 hr at 90°. After chromatography on basic alumina, the mixture (yield 410 mg) was separated by gas–liquid chromatography on a Carbowax 20M column at 120°. The tin compounds show a 4:6 peak height ratio with the 1,2-ditin compound (**2**) dominating.

1,1-Bis(trimethylstannyl)ethane (**3**) was eluted first and had NMR 0.16 (s, 18 H), 0.60–1.25 (m, 1 H), 1.53 (d, 2 H).

Anal. Calcd: C, 27.02; H, 6.24. Found: C, 27.13; H, 6.25.

1,2-Bis(trimethylstannyl)ethane (**2**) was eluted second: NMR 0.15 (s, 18 H), 1.06 (s, 4 H); mass spectrum *m/e* 356 (parent), 341 (M − 15), 328 (M − 28), 164 (M − 192).

Anal. Calcd: C, 27.02; H, 6.24. Found: C, 27.38; H, 6.26.

2-Norbornenyltrimethyltin (**13**) was prepared in 70% yield by the Grignard method from the corresponding bromide (obtained from previous work):[30] bp 68° (1.0 Torr); NMR 0.19 (s, 9 H), 0.79–1.69 (m, 6 H), 2.96 (m, 2 H), 6.21 (m, 1 H).

Anal. Calcd: C, 46.75; H, 7.06. Found: C, 46.64; H, 6.88.

trans-**2,3-Bis(trimethylstannyl)norbornane** (**4**). 2-Norbornenyltrimethyltin (560 mg, 2.18 mmol) was heated with 1.1 g (6.67 mmol) of trimethyltin hydride and 50 mg of benzoyl peroxide at 90° for 44 hr. After removal of lower boiling products, the mixture consisted of starting material **13** and **4**. Gas–liquid chromatography separation on Carbowax 20M afforded 456 mg (88% yield based on consumed **13**) of **4**: NMR (220 MHz) −0.01 (s, 9 H, H$_1$), 0.03 (s, 9 H, H$_k$), 0.99 (m, 2 H, H$_{i,j}$), 1.19, 1.35, 1.54 (m, 6 H, H$_{a,b,d-g}$), 2.36 (m, 2 H, H$_c$H$_h$).

(l)
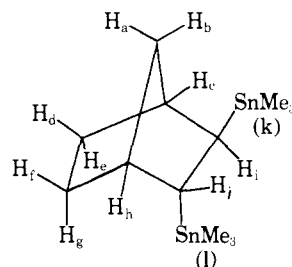
1,1-Bis(trimethylsilyl)methane (**15**) was obtained from Professor H. Sakurai, Tohoku University, Sendai, Japan.

1,2-Bis(trimethylsilyl)ethane (16). Methyldichlorosilane (Alfa) (2.30 g, 20 mmol) and vinyldichlorosilane (Alfa) (2.82 g, 20 mmol) were catalyzed to combine using the usual H_2PtCl_6/i-PrOH catalyst. A vigorous reaction occurred, and the 5.1 g of product was combined without purification with excess methyl magnesium iodide in ether. After 3 hr reflux, the product was washed, dried, and distilled to give 97% yield of 1,2-bis(trimethylsilyl)ethane (16): bp 79° (68 Torr) (lit.[31] 151°); NMR 0.05 (s, 18 H), 0.41 (s, 4 H).

References and Notes

(1) Supported by the National Science Foundation, Grant 38772X.
(2) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Am. Chem. Soc.*, **93**, 5715 (1971).
(3) (a) H. Schmidt, A. Schweig, and G. Manuel, *J. Organomet. Chem.*, **55**, 1 (1973); (b) A. Schweig, U. Weidner, and G. Manuel, *ibid.*, **54**, 145 (1973), and references cited there.
(4) C. G. Pitt, *J. Organomet. Chem.*, **61**, 49 (1973).
(5) A. R. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Organomet. Chem.*, **20**, 49 (1969).
(6) (a) P. Bischof, R. Gleiter, E. Heilbronner, V. Hornung, and G. Schröder, *Helv. Chim. Acta*, **53**, 1645 (1970); (b) R. Gleiter, E. Heilbronner, and A. de Meijere, *ibid.*, **54**, 1029 (1971); (c) E. Heilbronner, R. Gleiter, T. Hoshi, and A. de Meijere, *ibid.*, **56**, 1594 (1973); (d) M. Beez, G. Bieri, H. Bock, and E. Heilbronner, *ibid.*, **56**, 1028 (1973).
(7) W. Hanstein and T. G. Traylor, *Tetrahedron Lett.*, 4451 (1967).
(8) A. Streitwieser, Jr., *Prog. Phys. Org. Chem.*, **1**, 1 (1963).
(9) (a) D. W. Turner, *Adv. Phys. Org. Chem.*, **4**, 31 (1966); (b) D. W. Turner,

C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, New York, N.Y., 1970.
(10) (a) V. F. Traven and R. West, *J. Am. Chem. Soc.*, **95**, 6824 (1973); (b) H. Sakurai, M. Kira, and T. Uchida, *ibid.*, **95**, 6826 (1973); (c) H. Bock and W. Ensslin, *Angew. Chem., Int. Ed. Engl.*, **10**, 404 (1971).
(11) N. Bodor, M. J. S. Dewar, and S. D. Worley, *J. Am. Chem. Soc.*, **92**, 19 (1970).
(12) W. R. Moore and C. R. Costin, *J. Am. Chem. Soc.*, **93**, 4910 (1971).
(13) R. S. Brown, D. F. Eaton, A. Hosomi, T. G. Traylor, and J. M. Wright, *J. Organomet. Chem.*, **64**, 249 (1974).
(14) (a) C. Eaborn, "Organosilicon Compounds", Academic Press, London, 1960, p 45; (b) R. C. Poller, "Chemistry of Organotin Compounds", Logos, Plainfield, N.J., 1970, p 107.
(15) S. Evans, A. F. Orchard, and D. W. Turner, *Int. J. Mass. Spectrom. Ion Phys.*, **7**, 261 (1971).
(16) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Am. Chem. Soc.*, **92**, 7476 (1970).
(17) (a) S. Cradock and R. A. Whiteford, *J. Chem. Soc., Faraday Trans. 2*, **68**, 281 (1972); (b) T. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **46**, 1558 (1973).
(18) (a) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971); (b) H. Bock and B. R. Ramsey, *Angew. Chem. Int. Ed. Engl.*, **12**, 743 (1973); (c) W. Kutzelnigy, *ibid.*, **12**, 546 (1973).
(19) D. Eaton (unpublished work) has measured the first ionization energy for bornyltrimethyltin of 8.52 eV.
(20) S. F. Nelson and J. M. Bushek, *J. Am. Chem. Soc.*, **95**, 2011 (1973).
(21) M. Rosenblum, *Acc. Chem. Res.*, **4**, 122 (1974).
(22) G. Hartman and T. G. Traylor, in press.
(23) Z. M. Manulkin, *J. Gen. Chem. USSR*, **13**, 46 (1943).
(24) R. H. Bullard and A. C. Haussman, *J. Phys. Chem.*, **34**, 743 (1930).
(25) C. F. Shaw, III, and A. L. Allred, *J. Organomet. Chem.*, **28**, 53 (1971).
(26) J. Jerkunica and T. G. Traylor, *J. Am. Chem. Soc.*, **93**, 6278 (1971).
(27) T. G. Traylor, H. J. Berwin, J. Jerkunica, and M. L. Hall, *Pure Appl. Chem.*, **30**, 599 (1972).
(28) G. Koermer, unpublished work.
(29) M. M. Koton, T. M. Kiseleva, and N. P. Zapevalova, *Zh. Obshch. Khim.*, **30**, 186 (1960).
(30) T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, **33**, 2614 (1968).
(31) D. N. Andreev and E. V. Kukharskaya, *Dokl. Akad. Nauk SSSR*, **134**, 89 (1960).

An ab Initio Study of Acyloxy Cations

Wilhelm F. Maier* and Manfred T. Reetz*[1]

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720, and Fachbereich Chemie der Philipps-Universität, 3550 Marburg, Lahnberge, West Germany. Received August 26, 1974

Abstract: The geometry, electronic structure, and energy of several acyloxy cations (I) have been determined by ab initio self-consistent field calculations with minimum and double ζ basis sets. The optimized structures show the isomeric cyclic dioxiryl cation (II) to be the lowest energy species. Substituent effects on the decomposition energy of II yielding cations III and carbon dioxide have been examined.

Although many semiempirical and ab initio molecular orbital calculations on carbocations are known, little work on organic cations in which heteroatoms bear the positive charge has been reported to date.[2] In this paper we present the results of an ab initio study of acyloxy cations RCO_2^+. These calculations were performed with the aim of obtaining information of such species in advance of experimental work. Acyloxy cations have been discussed occasionally as possible reactive intermediates in side reactions of the Kolbe electrolysis leading to carbenium ion-derived products, but no consensus regarding their existence has been reached to date.[3] For example, the partial stereospecificity observed in the electrolysis of *cis*- and *trans*-bicyclo[3.1.0]hexane-3-carboxylic acid was cited by Gassman[4] as evidence for the intermediacy of RCO_2^+ ions (Scheme I).

Acyloxy cations have also been invoked in the anodic oxidation of isomeric 3-methyl-2-phenylcyclopropanecarboxylic acids.[5] In analogy to the well-known solvolysis of cyclopropyl halides and tosylates,[6] carbon dioxide evolution with concomitant disrotatory electrocyclic ring opening was as-

sumed (Scheme II). The role of intermediate acyloxy cations in the electrolysis of cyclopropanecarboxylic acids has since been questioned.[7] Similarly, Skell[8] has presented evidence against the formation of RCO_2^+ in the electrolytic oxidation of aliphatic carboxylic acids.

Acyloxy cations have also been postulated to occur in chemical oxidations. Thus, Mosher and Kehr[9] prefer an ionic mechanism for the lead(IV) induced oxidation of carboxylic acids (Scheme III). It should be noted that in *nonpolar* media a radical mechanism has been shown to be operating.[10]

In the references cited above, neither the geometry nor the possible electronic structure of acyloxy cations was considered. Our initial investigation[11] of these species with semiempirical SCF–MO calculations at the MINDO/2[12] level resulted in a potential energy surface which shows a pronounced energy gain in going from the acyloxy cation I (R = H) to the isomeric dioxiryl cation II (Scheme IV). The latter species had not been mentioned previously in the literature.