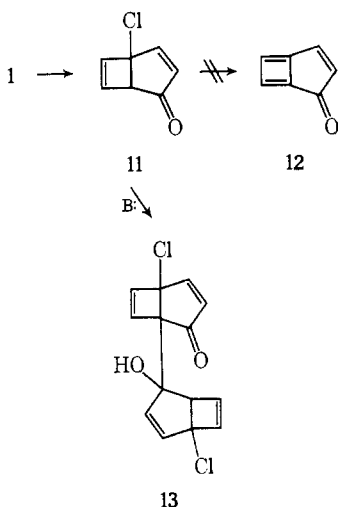Solutions of **9** were not stable over time. Thus the uv spectrum disappeared over several hours at room temperature, while the more concentrated nmr solutions were generated at −48° and the signals assigned to **9** disappeared on warming the solution to −10°. This concentration dependence suggests a dimerization or polymerization of **9**, although well-defined adducts could not be obtained from the decomposition.

An approach to an isomeric trienone was undertaken by treating chlorodiene **1** with *N*-bromosuccinimide in CCl_4 under free radical conditions. A mixture[6,7] of allylic bromides **10** was obtained which was converted with silver tosylate and DMSO, followed by sodium bicarbonate, to chlorodienone[6] **11**, bp 40–42° (0.7 Torr). By contrast with **7** this resisted all attempts at HX elimination, as did the bromodienone[6] corresponding to **11** (derived from the bromodiene[6] related to **1**). Thus treatment of **11** with strong bases such as DBN or NaH at reflux for many hours led to recovered starting material, and even with an excess of lithium diethylamide some starting material was recovered. The principal product from this latter reaction is, however, the dimer[6] **13** obtained from an aldol re-

action; this dimer could be converted to the corresponding acetate,[6] mp 134–135°. Thus when the enolate derived from **11** is in fact formed with base, it does not lose chloride ion but instead undergoes a bimolecular aldol addition reaction.

These data indicate clearly that the bicyclotropones **9** and **12** do not share the stability of tropone itself. While **9** seems to have some stability on solution and is thus perhaps a more stable molecule than is cyclopentadienone, **12** seems to be extremely unstable, as evidenced by the failure of the enolate derived from **11** to lose chloride ion. Thus the properties of **9** and **12** seem to reflect the stabilities of their component rings, rather than that of the peripheral trienone system.

Acknowledgment. Support of this work by the National Institutes of Health is gratefully acknowledged.

(7) W. Washburn, Ph.D. Thesis, Columbia University, 1971.

R. Breslow,* M. Oda, T. Sugimoto

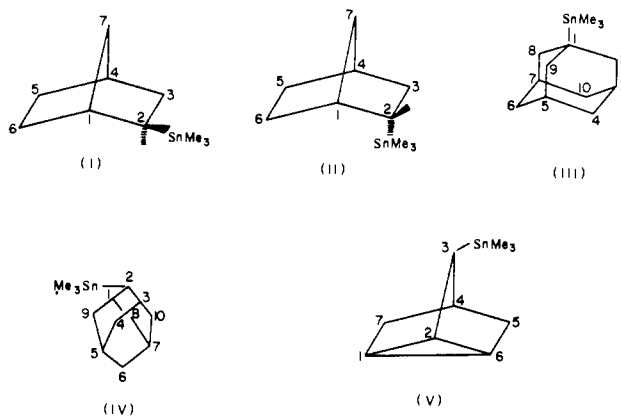*Department of Chemistry, Columbia University
New York, New York 10027*
Received November 28, 1973

Karplus-Type Dependence of Vicinal $^{119}Sn-^{13}C$ Coupling[1]

Sir:

It has been reported recently that the magnitude of ^3J ($^{119}SnCC^{13}C$) is dependent upon the dihedral angle between the coupling nuclei.[1] In the present communication, we report the ^{13}C nmr parameters for a series of compounds which incorporate a range of SnCCC dihedral angles and define more precisely the relationship between ^3J(SnCCC) and the dihedral angle.

The new compounds studied are *exo*- and *endo*-2-norbornyl, 1- and 2-adamantyl, and 3-nortricyclyltrimethylstannane (I–V), respectively. All yielded satis-

factory elemental analysis and ^1H nmr spectra. The ^{13}C chemical shift and coupling constant data are given in Table I. Assignments were made by (i) off-resonance decoupled spectra, (ii) the magnitude of $^1J(^{119}Sn-^{13}C)$ for ^{13}C nuclei directly attached to ^{119}Sn, (iii) comparisons of the chemical shift with the parent hydrocarbons and of the shifts of ^{13}C resonances on substitution in other hydrocarbons, (iv) the relative magnitudes of vicinal $J(^{119}SnCC^{13}C)$ coupling constants, and (v) general considerations of compression effects on ^{13}C nuclei in γ positions.

Pure I (from *exo*-2-bromonorbornane and $(CH_3)_3$-SnLi)[2] was examined in conjunction with a mixture of I and II (from[3] the Grignard reagent of *exo*-2-bromonorbornane and $(CH_3)_3SnCl$). Note that C_7 in I (γ effect −0.1 ppm) is upfield from C_7 in II (γ effect +2.2 ppm) by 2.3 ppm, while C_6 in II (γ effect −0.4 ppm) is upfield from C_6 in I (γ effect +3.3 ppm) by 3.9 ppm.[4] (The corresponding γ effects for C_7 are 3.7 ppm in *exo*-2-methylnorbornane and +0.2 in *endo*-2-methylnorbornane. For C_6, γ effects of −1.1 and −7.7 ppm are observed for *exo*- and *endo*-2-methylnorbornanes, respectively.)[5] Because of difficulties in differentiating C_5 and

(1) (a) This is paper II of the series "^{13}C Fourier Transform Nmr Study of the Organotin Compounds," by the group from Albany; Paper I of this series: H. G. Kuivila, J. L. Considine, R. J. Mynott, and R. H. Sarma, *J. Organometal. Chem.*, **55**, C11 (1973). (b) See also D. Doddrel, M. L. Bullpitt, C. J. Moore, C. W. Ford, W. Kitching, W. Adcock, and B. D. Gupta, *Tetrahedron Lett.*, 665 (1973).

(2) For method used, see (a) G. S. Koermer, M. L. Hall, and T. G. Traylor, *J. Amer. Chem. Soc.*, **94**, 7206 (1972); (b) H. G. Kuivila, J. L. Considine, and J. D. Kennedy, *ibid.*, **94**, 7202 (1972).

(3) F. R. Jensen and K. L. Nakamaye, *J. Amer. Chem. Soc.*, **88**, 3437 (1966).

(4) Notice that the γ-shifts are slightly negative for situations with strong compressional interaction with $(CH_3)_3Sn$, but positive (*i.e.*, to lower field) otherwise. These γ-shifts are small considering the data for the *exo*,*endo*-2-methylnorbornanes.

(5) Data from G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance," Wiley-Interscience, New York, N. Y., 1972, p 46, and references therein.

Table I. ^{13}C Nmr Parameters^{a,b}

	C$_1$	C$_2$	C$_3$	C$_4$	C$_5$	C$_6$	C$_7$	C$_8$	C$_9$	C$_{10}$	C$_{Me}$
					Chemical Shifts^c						
I	40.3	27.6	37.6	34.9	29.5	34.0	38.6				−10.8
II	40.9	28.7	33.8	36.9	30.3	30.1	40.9				−10.2
III	28.3	42.2	29.5	38.0	29.5	38.0	29.5	42.2	42.2	38.0	−13.0
IV	32.4	40.0	32.4	36.6	29.1	38.3	28.7	41.0	36.6	41.0	−9.5
V	10.0	13.9	31.8	33.2	32.9	9.9	35.0				−10.4
					Coupling Constants^d						
I	9.0	416	12.0	23.0	N.o.^{e}	69.0	~0.0				N.d.^{f}
II	10.0	432	N.d.^{f}	22.0	N.o.^{e}	34–38	59				N.d.^{f}
III	451.7^g	12.2	51.1^g	7.3	51.1^g	7.3	51.1^g	12.2	12.2	7.3	290.4^g
IV	12.3	406.6^g	12.3	8.5	N.o.^{e}	N.o.^{e}	6.5^h	60.0^i	8.5^i	60.0^i	295.8^g
V	53.6^g	6.0	411.8^g	12.4	9.7	8.0	57.8^g				313.9^g

^{a} Compounds I, II, and III were examined at 15.18 and 22.63 MHz, and III, IV, and V at 25.16 MHz, in the Fourier transform mode. Samples were usually neat or concentrated solutions in CS$_2$ or cyclohexane. ^{b} The carbon-numbering system as shown on the structural formulas. ^{c} Chemical shifts quoted relative to TMS (±0.1 ppm). Positive values indicate nuclei downfield (less shielded than TMS). ^{d} Coupling constants in Hertz quoted relative to the center of unresolved^{119,117}Sn satellites. ^{e} N.o., not observed. ^{f} N.d., not determined. ^{g} Quoted for ^{119}Sn coupling. ^{h} ±2.0 Hz. ^{i} ±1.5 Hz. Other couplings ±1.0 Hz or better.

Table II. Magnitudes of Vicinal ^{119}SnCC^{13}C Coupling Constants and Associated Dihedral Angles

Compd	C	J, Hz	θ,^{b} deg	Compd	C	J, Hz	θ,^{b} deg
I	4	23	120	V	1	53.6	154
	6	69	170		5	9.7	67
	7	≃0	85		6	8.0	83
II	4	22	120		7	57.8	174
	6	36 ± 2	35	VI^a	3,5	51.9	165
	7	59	160		4	65.8	180
III	3,5,7	51.1	180	VII^a	2,3	67.5	175
IV	4,9	8.5	70		5,6	11.9	56
	8,10	60.0	180				

^{a} Data previously reported in ref 1. ^{b} θ = SnC$_\alpha$C$_\beta$C dihedral angle about C$_\alpha$–C$_\beta$ bond.

C$_6$ in II, a range of 34–38 Hz is given for C$_6$; even though not determined exactly, this value demonstrates the large increase in $|^3J(^{119}$SnC^{13}C$)|$ as θ decreases. In IV, C$_4$ and C$_9$ on the one hand and C$_8$ and C$_{10}$ on the other are distinguished by (i) the resonance of the former being 4.4 ppm to higher field and (ii) the vicinal coupling to C$_4$ and C$_9$ falling in the range previously found for gauche nuclei, while that for C$_8$ and C$_{10}$ is in the range for trans nuclei.[1] In V, except for the three methyl carbons there are no symmetrically equivalent carbon nuclei; all seven resonances were resolved. The resonances of C$_1$, C$_2$, and C$_6$ are found to higher field than the others, as expected for cyclopropylcarbons (compare the parent–nortricyclene[6]); C$_2$ experiences a deshielding β effect (+4.0 ppm) while C$_1$ and C$_6$ show much smaller γ shifts of +0.1 and 0.0. This is consistent with results from other compounds.[6] Since C$_1$ and C$_7$ are nearly trans to tin and C$_6$ and C$_5$ are approaching gauche, the four carbons are hence distinguished, since the smaller coupling identifies C$_5$ and C$_6$.

The magnitudes of the vicinal ^{119}Sn–^{13}C coupling constants and the associated dihedral angles are collected in Table II. This also contains data for 1- and 7-norbornyltrimethylstannanes (VI and VII, respectively) previously reported.[1] These data were processed through a computer program to fit a curve of the form $J = A + B \cos \theta + C \cos 2\theta$. The best equation with the minimum mean and mean-square deviations was found to be $J = 30.4 − 7.6 \cos \theta + 25.2 \cos 2\theta$; the mean deviation was 3.75 Hz. The computer drawn curve is shown in Figure I. If it is assumed that the
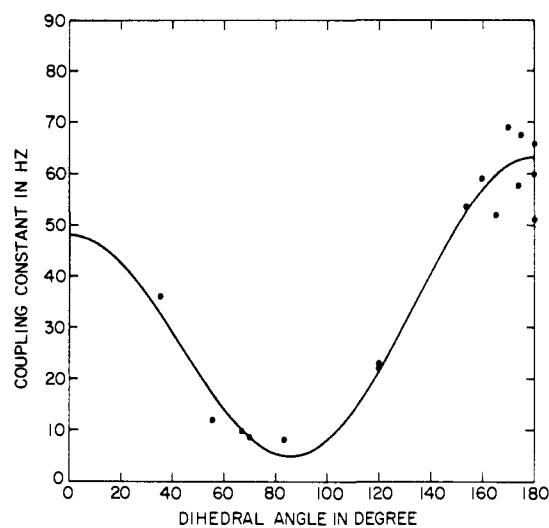

Figure 1. Magnitudes of $^3J(^{119}$SnCC^{13}C) plotted against the dihedral angle θ, plotted from data given in Table II. Dihedral angles are estimated from Dreidig models or, in the case of V, from the structural data for 4-chloronortricyclene (J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *Tetrahedron*, **25**, 369 (1969)).

vicinal coupling has the same relative sign for all, then the curve is similar to that given by the Karplus equation.[7] This finding should be of great benefit to the study of the structure and conformation of organotin compounds. In this connection it may be noted that angular dependence has been established for *three-bond*

(6) Unpublished results of the authors.

(7) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

coupling across, *PCCC*,[8] *POCC*,[9] *POCH*,[10] *CCCH*,[11] and HCCN[12] and for four-bond coupling across *HC-COP*.[13–16] Preliminary measurements[17] indicate that such relationships may exist for coupling across CCCC and MCCC where M is either lead or mercury.

Acknowledgment. This research was supported by the Australian Research Grants Committee and by the

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(9) I. C. P. Smith, H. H. Mantsch, R. D. Lapper, R. Deslauriers and T. Schleich, Conformation of Biological Molecules and Polymers. The Jerusalem Symposia on Quantum Chemistry and Biochemistry, Vol. V, 381 (1973).
(10) L. D. Hall and R. B. Malcolm, *Chem. Ind. (London)*, 92 (1968).
(11) R. Wasylishan and T. Schaefer, *Can. J. Chem.*, 50, 2710 (1972).
(12) R. Wasylishan and T. Schaefer *Can. J. Chem.*, 50, 2989 (1972).
(13) L. D. Hall and R. B. Malcolm, *Can. J. Chem.*, 50, 2092 (1972).
(14) L. D. Hall and R. B. Malcolm, *Can. J. Chem.*, 50, 2102 (1972).
(15) B. Donaldson and L. D. Hall, *Can. J. Chem.* 50, 2111 (1972).
(16) R. H. Sarma, R. J. Mynott, F. E. Hruska, and D. J. Wood, *J. Amer. Chem. Soc.*, 95, 6457 (1973).
(17) Unpublished results with I. Burfitt and D. Praeger.

(18) Queen Elizabeth Research Fellow, 1973–1974.

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Additions and Corrections

Stable Carbocations. CXXX. Carbon-13 Nuclear Magnetic Resonance Study of Halocarbenium Ions. Degree of Halogen "Back-Donation" and Relative Stability of Halocarbenium Ions [*J. Amer. Chem. Soc.*, **94**, 3551 (1972)]. By GEORGE A. OLAH,* Y. K. MO, and Y. HALPERN, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

The ^{13}C nmr shift of the carbocation center in the dimethylfluorocarbenium ion [$(CH_3)_2C^+F$] was reported, due to a computational error made using the indor method, as -142.7 (from CS_2). The correct value is -89.1 (as also shown by recent FT measurements).

Conformational Analysis. XXVI. Conformational Equilibria in 5,5-Disubstituted 1,3-Dioxanes [*J. Amer. Chem. Soc.*, **94**, 8072 (1972). By ERNEST L. ELIEL* and RUDYARD M. ENANOZA, Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556].

Professor Anteunis has informed us that Table I in ref 26, part 2 does not correspond to our Table II inasmuch as it refers to the equilibrium B $\rightleftarrows$ A, not A $\rightleftarrows$ B in Scheme II. Therefore the $\Delta G°$ values for the last five entries in our Table II taken from ref 26 should read -0.19, -0.03, -0.32, -0.38, -0.17 kcal/mol, and the signs of $\Delta G°$ in Table II do agree with those in Table III, entries 2, 5, 6, and 7. Moreover, in the case of 5-methyl-5-phenyl-1,3-dioxane the nmr method of ref 26 does lead to a clear choice as to which isomer predominates, based on the chemical shift of the 5-methyl group below the coalescence temperature.

We have also found that the infared data reported on page 8076, Scheme III were subject to a calibration error; the correct frequencies are **27**, 3435 cm⁻¹; **28**, 3450, 3434 cm⁻¹. We are not sure whether the NH absorption in **27** indicates intramolecular H bonding;

rather the double absorption in **28** may be due to cis–trans isomerism of the amide. Configurational assignments are not affected by this uncertainty since they rest on the dipole determination of **19**. We thank Dr. W. F. Bailey for experimental assistance and Dr. Jan Stanek (Prague, Czechoslovakia) for helpful correspondence.

Excited State Carbonyl Species from the Thermal Decomposition of 3,3-Dibenzyl-1,2-dioxetane [*J. Amer. Chem. Soc.*, **94**, 9277 (1972)]. By WILLIAM H. RICHARDSON,* FREDERICK C. MONTGOMERY, and MARY B. YELVINGTON, Department of Chemistry, California State University, San Diego, San Diego, California 92115.

Figure 1, line 4 should read "bibenzyl" rather than "dibenzyl ketone."

Hydrolysis of Imidate Esters Derived from Weakly Basic Amines. Influences of Structure and pH on the Partitioning of Tetrahedral Intermediates [*J. Amer. Chem. Soc.*, **95**, 1253 (1973)]. By TADASHI OKUYAMA, TERRY C. PLETCHER, DAVID J. SAHN, and GASTON L. SCHMIR,* Department of Molecular Biophysics and Biochemistry, Yale University School of Medicine, New Haven, Connecticut 06510.

In Table I, the heading of column 5 should read $10^{-7}k_7$; the heading of column 7 should read $10^{-4} \cdot (k_5/K_a)$. The uppermost line in Figure 6 should be labeled $10^{-5}k_7$.

Stable Carbocations. CXLII. 1-Acenaphthenium Ions [*J. Amer. Chem. Soc.*, **95**, 3698 (1973)]. By GEORGE A. OLAH,* GAO LIANG, and PHILIP WESTERMAN, Department of Chemistry, Case Western Reserve University, Cleveland Ohio 44106.