

an exchange of multiplicity, resulting in the possibility of isomerization, can be accomplished if the photosensitizing species has energy in excess of approximately 60 kcal. mole⁻¹ above its ground state. If this latter condition is satisfied reaction (1) occurs at every collision. Deactivation of the butene-2 triplet produces *cis* and *trans* isomers with equal probability. By using one of the pure isomers and only working with low percentage conversions, it is possible to say that the number of molecules of butene-2 which have been isomerized is one half the number of triplet molecules which undergo the interchange. Accurate estimation of triplet state production is, therefore, possible.

Butene-2 has the advantage that it does not itself absorb light of wave length greater than 2000 Å., the normal photochemical range.

Two examples of systems which we have examined by this method are the direct photochemical decomposition of formic acid and the photochemical isomerization of *cis*-dichloroethylene.

The decomposition of formic acid (20 mm.) into hydrogen, carbon monoxide, carbon dioxide and water was quenched by pressures of *cis*-butene-2 up to 134 mm. In the process, isomerization of *cis*-butene-2 occurred. This shows that a triplet state is involved in the photolysis of formic acid.

The *cis-trans* rearrangement of *cis*-dichloroethylene (15 mm.) is also quenched by butene-2, but without any isomerization of butene-2 at pressures of 120 mm. At lower butene-2 pressures some isomerization did occur. This may be explained by the scheme



At high butene-2 pressures the excited singlet state is deactivated before transition to the triplet can occur. This aspect of the reaction would not have been apparent using the method of Hammond, Leermakers and Turro.

Triplet butene-2 molecules do not isomerize other molecules of butene-2. This combined with the fact that no evidence of reactivity of such species has been found suggests that they are deactivated readily to vibrationally excited ground states by crossing of the potential energy surfaces.⁴ The technique may be extended to studies in solution.

(4) W. J. Potts, Jr., *J. Chem. Phys.*, **23**, 65 (1955).

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RECEIVED JULY 21, 1961

TIN-PROTON SPIN-SPIN COUPLING IN METHYLTIN HALIDES AND RELATED COMPOUNDS

Sir:

Because of recent interest¹ in the configuration and nature of bonding in alkyltin cations and related compounds, we wish to communicate some n.m.r. measurements of indirect tin-proton spin-spin coupling constants in a series of methyltin chlorides. We interpret our results as having a direct

(1) (a) E. G. Rochow, *XVII Internat. Congress Pure and Appl. Chem.*, **1**, 136 (1959); (b) R. Okawara, D. E. Webster and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 3287 (1960); (c) R. Okawara and H. Sato, *J. Inorg. Nuclear Chem.*, **16**, 204 (1961).

bearing on the nature of hybridization of the tin atom in the compounds studied here.

The first reports² of the proton magnetic resonance spectra of methyl derivatives of Group IVb elements have dealt solely with the single sharp, strong absorption that arises from methyl protons, and of its variation in chemical shift with respect to substitution and electronegativity of the central atom. More recently, brief mention has been made³ of tin-proton coupling observed for dimethyltin dichloride in water and acetone solutions, and for tetramethyltin, from the measured line separations in ¹¹⁹Sn n.m.r. spectra.

We have measured⁴ the doublet-satellite resonances appearing at relative intensity of 3-4% of the main peak, in a number of methyl derivatives of tin. These doublets arise from the coupling of methyl protons with naturally occurring isotopes ¹¹⁷Sn and ¹¹⁹Sn (both with *I* = 1/2; relative abundances 7.67 and 8.68%, respectively). Results are presented in Table I.

TABLE I

Compound ^a	T, °C.	Coupling Constants (c.p.s.) ^b	
		¹¹⁷ Sn-CH ₃	¹¹⁹ Sn-CH ₃
(CH ₃) ₄ Sn	31	51.5	54.0
51% CCl ₄	31	51.4	53.8
5% CCl ₄	31	51.6	53.7
(b)			54
(CH ₃) ₃ SnCl	40	57.4	59.7
38% CCl ₄	31	56.0	58.5
62% C ₆ H ₆	31	56.5	59.2
56% H ₂ O	31	65.2	68.4
(CH ₃) ₂ SnCl ₂	110	68.0	71.0
satd. < 14% CCl ₄	31	66.6	69.7
47% H ₂ O	31	97.4	101.9
(b)			98
CH ₃ SnCl ₃	55	95.7	100.0
46% CCl ₄	31	95.3	99.5
51% C ₆ H ₆	31	95.4	99.9
49% H ₂ O	31	125.4	131.1

^a Compounds first listed as neat liquids, then as per cent. by weight in solution of various solvents. ^b Data from ref. 3. ^c Values are given to a precision of ±0.5%.

Ramsey,⁵ Karplus and Anderson⁶ and others have shown that the Fermi contact contribution to the spin-spin coupling constant *A_N'* between two nuclei is directly proportional to the product ρ(O)_Nρ(O)_{N'} of the electron densities of the two bonding orbitals, through which they interact, at their respective nuclei. For covalently bonded hydrogen, ρ(O)_H usually is considered to be the same as that for the hydrogen atom in the 1s state. For other atoms, in particular those with hybridized bonding orbitals, a simple LCAO treatment predicts that ρ(O)_N is proportional to the per cent. s-character in the hybridized atomic orbital used in forming the

(2) (a) A. L. Allred and E. G. Rochow, *ibid.*, **5**, 269 (1958); (b) M. P. Brown and D. E. Webster, *J. Phys. Chem.*, **64**, 698 (1960).

(3) J. J. Burke and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 326 (1961).

(4) Proton resonances were observed at 40 Mc. using a Varian V-4300 B spectrometer. Frequency measurements were made by the side-band method using a calibrated Hewlett-Packard Model 200D audiofrequency oscillator.

(5) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).

(6) M. Karplus and D. H. Anderson, *J. Chem. Phys.*, **30**, 6 (1959).

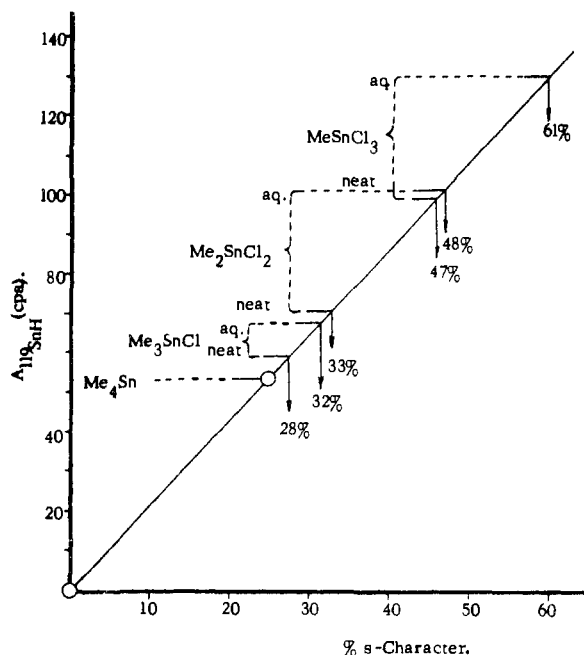


Fig. 1.—Apparent s-character of Sn atomic orbital in Sn-C bond in tetramethyltin and the methyltin halides.

bond. This relationship was first pointed out by Karplus and Grant⁷ and appears to hold remarkably well in the case of $^{13}\text{C}-\text{H}$ coupling in the series methane-ethylene-acetylene reported recently by Shoolery,⁸ in spite of certain assumptions implicit in this treatment. The coupling constant $A_{13\text{C}-\text{H}}$ varies linearly with the per cent. s-character in the bonding orbitals on carbon, and extrapolates to zero coupling for a pure p_σ orbital on carbon. Muller and Pritchard⁹ also have related $A_{13\text{C}-\text{H}}$ values observed in hydrocarbons and substituted methanes to differences in the hybridization of the atomic orbitals on carbon.

We believe a similar relationship, that shown in Fig. 1, exists between the tin-proton couplings reported here and the hybridization of the atomic orbitals on tin. The line in Fig. 1 is drawn with the assumption that the contact mechanism makes the dominant contribution to Sn-C-H coupling and that, except for rehybridization of the tin atom, other components of the bonding system Sn-C-H do not change appreciably. This latter assumption receives some support from our separate observation that the $^{13}\text{C}-\text{H}$ spin-spin interactions within the methyl groups remain nearly constant in the series of compounds considered here.

Taking as one point the observed coupling constant for tetramethyltin as representing 25% s-character and the origin as the second point, we have generated the line in Fig. 1. When the other coupling constants (Table I) are placed on this line, the distribution of points indicates considerable rehybridization in the tin atom in methyltin halide molecules. For the case of aqueous solutions of methyltin halides, presumed to contain the cor-

(7) M. Karplus and D. M. Grant, *Proc. Nat. Acad. Sci.*, **45**, 1269 (1959).

(8) J. N. Shoolery, *J. Chem. Phys.*, **30**, 1427 (1959).

(9) N. Muller and D. B. Pritchard, *ibid.*, pp. 768, 1471.

responding methyltin cations, almost complete rehybridization is indicated. This result in particular is an agreement with the conclusions of Okawara, Webster and Rochow,^{1b} based on the interpretation of their infrared data, with respect to the configuration of methyltin cations.

We wish to emphasize the fact that the linear relationship assumed in Fig. 1 does not have, at present, as firm a theoretical basis as in the case of directly bonded atoms⁷ and must be presented here as an interesting correlation. Measurements of the $^{13}\text{C}-\text{Sn}$ couplings in these compounds would give a more direct indication of the rehybridization of the tin atom and provide further justification of our assumptions about other changes in the Sn-C-H bonding system.

Preliminary results on the vinyltin halides indicate similar behavior in that series of compounds. Work on the vinyl series and related Group IVb compounds is in progress and will be published in the near future.

We are indebted to Professor Daniel Kivelson of this department for stimulating discussions and to the Research Corporation for financial assistance (J.R.H.) and a Frederick Gardner Cottrell Grant (H.D.K.).

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RECEIVED JUNE 15, 1961

THE TOTAL SYNTHESIS OF TOXOFLAVIN

Sir:

Toxoflavin, a yellow crystalline solid isolated in 1933 from *Pseudomonas cocovenenans*, has been shown to be responsible for certain fatal food poisoning among the natives of Java.^{1,2} This compound has stimulated considerable interest³ because of its high toxicity and potent antibiotic activity.^{3h} The structure of toxoflavin was originally proposed by van Veen and Baars^{3c} as I (desmotropic tautomer⁴ of 1-methylxanthine), but Johnson and Ambelang,^{3e} and Nugteren^{3f} demonstrated the implausibility of this structure. Recently, van Damme, *et al.*,^{3h} reinvestigated the structure of toxoflavin and proposed it as either 1,6-dimethyl-5,7-dioxo-1,5,6,7-tetrahydropyrimido[5,4-e]-*as*-triazine (II) or its structural isomer, IIa. These investigators preferred structure II on the basis of degradation and X-ray diffraction studies.^{3i,3j}

(1) A. G. van Veen and W. K. Mertens, *Proc. Akad. Wetenschappen Amsterdam*, **36**, 666 (1933); *Rec. trav. chim.*, **53**, 257, 398 (1934).

(2) W. K. Mertens and A. G. van Veen, *Geneesk. Tijdschr. Ned. Indië*, **73**, 1223, 1309 (1933); *Meded. Dienst Volksgezondheid Ned. Indië*, **22**, 209 (1933).

(3) (a) D. Amar and A. Grevenstrik, *Geneesk. Tijdschr. Ned. Indië*, **75**, 104 (1935); (b) K. G. Stern, *Biochem. J.*, **29**, 500 (1935); (c) A. G. van Veen and J. K. Baars, *Proc. Akad. Wetenschappen Amsterdam*, **40**, 498 (1937); (d) A. G. van Veen and J. K. Baars, *Rec. trav. chim.*, **57**, 248 (1938); (e) T. B. Johnson and J. C. Ambelang, *J. Am. Chem. Soc.*, **61**, 2483 (1939); (f) D. H. Nugteren, Thesis, Delft, 1956; (g) D. H. Nugteren and W. Berends, *Rec. trav. chim.*, **76**, 13 (1957); (h) P. A. van Damme, A. G. Johannes, H. C. Cox and W. Berends, *Rec. trav. chim.*, **79**, 255 (1960); (i) H. E. Latusan and W. Berends, "The Origin of the Toxicity of Toxoflavin," *Biochem. Biophys. Acta*, in press; (j) A. S. Helleendoorn, R. M. T. Cate-Dhont and A. F. Peerdeman, *Rec. trav. chim.*, **80**, 307 (1961).

(4) H. Blitz, *J. prakt. Chem.*, **145**, 83 (1936).