used, the observed high yields of crude reaction products reported in this paper are attributed to an increased reactivity of the mixture of germanium and copper powder due to a smaller average particle size. Also, the flow rate of methyl chloride is significant. In these studies the average flow rate was of the order of 400 to 600 cc/min as compared to *ca.* 2–3 bubbles per sec (approximately 50 cc/min) reported by others[3]. At such high flow rates, a considerable amount of methyl chloride passes through the reaction zone without having reacted and condenses in the cold trap. However, the condensed methyl chloride can be recycled directly by connecting the trap to the reaction tube and letting the contents warm up to room temperature. The flow rate is then just about of the same order of magnitude as required.

For methyl bromide, the yield per hour in terms of crude reaction product in this case could be increased to about 60 g per hour and only about 20 % of the methyl bromide had passed through the reaction tube unreacted and had collected in the cold trap. In total, three moles of methyl bromide had been used per gram-atom of germanium. Similar results were obtained for the methyl iodide reaction. From these data, it appears that the reaction with methyl bromide is the method of choice when larger amounts of methylgermanium halides are to be prepared conveniently within a short period of time.

Acknowledgement

The author thanks RAY MILLER for some of the experimental work and NMR measurements.

Central Research Department, KURT MOEDRITZER
Monsanto Company, St. Louis, Missouri (U.S.A.)

1 E. G. ROCHOW, *J. Am. Chem. Soc.*, 69 (1947) 1729.
2 J. J. ZUCKERMAN, *Advan. Inorg. Chem. Radiochem.*, 6 (1964) 383.
3 M. SCHMIDT AND I. RUIDISCH, *Z. Anorg. Allgem. Chem.*, 311 (1961) 331.
4 V. A. PONOMARENKO AND G. YA. VZENKOVA, *Bull. Acad. Sci. USSR (Engl. Transl.)*, (1957) 1020.
5 R. ZABLOTNA, K. AKERMAN AND A. SZUCHNIK, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, 12 (1964) 695; *Chem. Abstr.*, 62 (1965) 13167*b*.
6 E. G. ROCHOW, *J. Am. Chem. Soc.*, 70 (1948) 436.

Received January 10th, 1966

J. Organometal. Chem., 6 (1966) 282–284

Proton magnetic resonance spectra of tetravinyltin and tetraallyltin: d_π–p_π bonding

Considerable evidence for d_π–p_π interaction between Si and sp^2 carbon orbitals has been reported by a variety of spectroscopic studies[1–6]. In particular, the anomalous low-field shifts in the proton resonance spectra of a number of vinylsilanes[7–9] have been interpreted in terms of back-donation of electron density from the vinyl group to the vacant *d* orbitals of the Si atom. It is reasonable to expect that the deshielding due to d_π–p_π interaction should be enhanced in vinyl derivatives of higher Group IVB

J. Organometal. Chem., 6 (1966) 284–287

elements because of their lower lying *d* orbitals. In this communication we wish to report evidence on this point.

Experimental

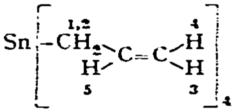
The spectra for tetravinyltin and tetraallyltin were recorded at 35° using a Varian A-60 spectrometer; the sweep ranges were calibrated with a Hewlett Packard 200 ABR audio-oscillator and a Hewlett Packard 5245 L counter. Neat liquids were used, without further purification. The tetraallyltin was obtained from M & T Chemicals, Inc., New York, New York and the tetravinyltin from Peninsular Chem-Research, Inc., Gainesville, Florida. The analysis of the two compounds was made by an iterative method[10] using a Control Data Corporation 3600 computer. Assignment of the signals for the tetraallyl compound was confirmed by double resonance experiments.

Results

The results of the analysis for tetraallyltin and tetravinyltin are shown in Tables 1 and 2 respectively. The chemical shifts, δ, are in parts per million (ppm) relative to internal tetramethylsilane, a negative sign implying a downfield displacement. Coupling constants, J, are quoted in cycles per second (c/s).

TABLE 1

NMR ANALYSIS OF TETRAALLYLTIN

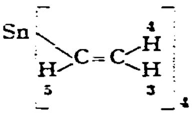


$\delta_{2,1}$	δ_3	δ_4	δ_5						
−1.880	−4.719	−4.831	−5.877						
J_{12}	J_{13}	J_{14}	J_{15}	J_{23}	J_{24}	J_{25}	J_{34}	J_{35}	J_{45}
0.00	−0.67	−1.24	8.00	−0.67	−1.24	8.00	1.98	9.39	16.90

Errors $\delta \pm 0.001$ ppm, in $J \pm 0.1$ c/s.

TABLE 2

NMR ANALYSIS OF TETRAVINYLTIN



δ_5	δ_4	δ_3	J_{34}	J_{35}	J_{45}
−6.390	−5.751	−6.211	3.14	13.78	20.69

Errors $\delta \pm 0.001$ ppm, $J \pm 0.03$ c/s.

The tin–proton coupling constants $J(^{117}\text{Sn–CH}_2)$ and $J(^{119}\text{Sn–CH}_2)$ in tetraallyltin could not be determined separately because of extensive overlap at the satellites. However, a magnitude of $J(^{117}\text{Sn–CH}_2) \simeq J(^{119}\text{Sn–CH}_2) = 63 \pm 1$ c/s was obtained from the mid-points of the satellites. In tetravinyltin the couplings are $J(^{117}\text{Sn–H}_{gem}) = \pm 91.2$ c/s and $J(^{119}\text{Sn–H}_{gem}) = \pm 96.0$ c/s.

Discussion

The magnitudes of the coupling constants for tetravinyltin and tetraallyltin are in general agreement with values reported previously for other vinyl[7,8,9,12] and allyl[13,14] derivatives. The sum of the three vinyl proton coupling constants is appreciably greater in tetravinyltin (37.61 c/s) than in tetraallyltin (28.27 c/s) as would be expected on the basis of the greater electronegativity of the CH_2 group compared with the Sn atom.

The long-range proton–proton *gauche* and *trans* couplings in tetraallyltin, $J_{14,24} = -1.24$ c/s and $J_{13,23} = -0.67$ c/s, are in the ranges observed for other allyl derivatives[13,14]. For couplings of the type H–C–C=C–H the π-contribution to J_{trans} and J_{cis} is predicted theoretically[15] to be negative and hence the larger value for the *cis* coupling is consistent with a greater π-contribution to this coupling. Also, by analogy with other allylic molecules, the magnitude of the long-range couplings are consistent with a preferred population of the gauche conformer[13,14] for the tetraallyltin.

The chemical shifts for the vinyl protons differ very markedly in the tetravinyl and tetraallyl compounds. Upfield shifts of 0.513 ppm, 0.920 ppm, and 1.432 ppm are noted for the *gem*, *cis*, and *trans* protons respectively when a CH_2 group is introduced between the Sn and sp^2 C atoms. The three factors which are most likely to affect the shifts in the present compounds are: (*a*) electronegativity differences between Sn and C; (*b*) the diamagnetic anisotropies of the Sn–C and C=C bonds; and (*c*) d_π–p_π interaction between Sn and the sp^2 C atom of the vinyl group. Considering the effect of (*a*), the replacement of an Sn atom by a more electronegative methylene C would lead to a downfield shift of the vinyl protons in the allyl compound in disagreement with the observed change.

The effect of bond anisotropies upon the chemical shifts in tetravinyl and tetraallyltin is difficult to calculate with accuracy because of the lack of data for bond angles, distances and anisotropies. In earlier work[16] it has been shown that the Sn–C bond anisotropy acts to deshield the vinyl protons in tetravinyltin in the order *gem* > *trans* > *cis* with the *gem* deshielding approximately three-fold greater than the *trans*, in agreement with the observed relative shifts. However, the magnitude of this deshielding is not sufficient by approximately 0.5 ppm to account for the shifts relative to propene derivatives and an additional deshielding contribution due to d_π–p_π interaction between Sn and the sp^2 carbon was postulated[16]. In tetralalyltin the presence of a CH_2 group alters the angles subtended and distances between the Sn–C dipole and the vinyl protons in the gauche conformer in such a manner as to lead to a shielding of the latter protons relative to tetravinyltin.

The shielding increases in the order *gem* > *cis* ≃ *trans* and the magnitude estimated for the *gem* proton [assuming reasonable values for $\Delta\chi$(Sn–C)] lies in the range 0.083–0.167 ppm. An additional shielding effect due to adjacent C=C bonds, amounting to approximately 0.333 ppm will predominantly affect the *cis* and *gem* protons. The combined effect of the Sn–C and C=C bond anisotropies is thus not sufficient to account for either the magnitudes or trends in the upfield shifts of the vinyl protons in tetraallyltin relative to tetravinyltin. This is particularly evident for the *trans* proton (upfield shift 1.492 ppm) where the combined effects of bond anisotropies would be least noticeable. It is likely therefore that a significant deshielding contribution due to d_π–p_π interaction is present in tetravinyltin and is effectively blocked by the intervening CH_2 group in tetraallyltin. The magnitude of the deshielding effect in tetravinyltin is similar to that observed in vinylsilanes and suggests that the d_π–p_π interaction is not appreciably altered in the higher tetravinyl.

The magnitudes of the geminal tin–proton couplings in tetraallyltin $J(^{117}\text{Sn–CH}_2) \simeq J(^{119}\text{Sn–CH}_2) = 63 \pm 1$ c/s are appreciably greater than the geminal couplings in tetraethyltin[17] of 50.8 c/s and 52.2 c/s for the ^{117}Sn and ^{119}Sn isotopes respectively, and cannot be rationalized in terms of the different inductive properties of methylene and vinyl groups. Although a variety of factors can contribute to the coupling mechanism it is likely that the larger geminal coupling in tetraallyltin reflects significant contributions from valence-bond structures involving double-bond character in the Sn–CH_2 bond.

Acknowledgement

Part of this work was initiated while S. S. Danyluk and S. Cawley were at the University of Toronto, Toronto, Canada, and financial support by the National Research Council of Canada is gratefully acknowledged. The work was also supported by the U.S. Atomic Energy Commission.

Division of Biological and Medical Research, D. J. Blears
Argonne National Laboratory, Argonne, Ill. (U.S.A.) S. S. Danyluk
State University of New York, Stoney Brook, N.Y. (U.S.A.) S. Cawley

1 H. Soffer and T. DeVries, *J. Am. Chem. Soc.*, 73 (1951) 5817.
2 W. J. Potts and R. A. Nyquist, *Spectrochim. Acta.*, 15 (1959) 679.
3 K. Hedberg, *J. Am. Chem. Soc.*, 77 (1955) 77.
4 H. Buchert and W. Zeil, *Spectrochim. Acta*, 18 (1962) 1043.
5 R. A. Benkeser and H. R. Krysiak, *J. Am. Chem. Soc.*, 75 (1953) 2421.
6 J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, 28 (1963) 487.
7 R. T. Hobgood, J. H. Goldstein and G. S. Reddy, *J. Chem. Phys.*, 35 (1961) 2038.
8 R. T. Hobgood and J. H. Goldstein, *Spectrochim. Acta*, 19 (1963) 321.
9 R. Summitt, J. J. Eisch, J. T. Trainor and M. T. Rogers, *J. Phys. Chem.*, 67 (1963) 2302.
10 J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, 37 (1962) 21.
11 S. Cawley and S. S. Danyluk, *J. Phys. Chem.*, 68 (1964) 1240.
12 D. W. Moore and J. A. Happe, *J. Phys. Chem.*, 65 (1961) 224.
13 A. A. Bothner-By and H. Günther, *Discussions Faraday Soc.*, 34 (1962) 127.
14 A. A. Bothner-By, S. Castellano and H. Günther, *J. Am. Chem. Soc.*, 87 (1965) 2439.
15 M. Karplus, *J. Chem. Phys.*, 33 (1960) 1842.
16 S. Cawley, Ph.D. Thesis, University of Toronto, 1964.
17 G. Klose, *Ann. Physik*, 8 (1961) 220; 9 (1962) 262.

Received October 29th, 1965; received in revised form January 3rd, 1966