# THE PROPERTIES OF TETRAALLYLSILANE, -GERMANE AND -TIN

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## SUMMARY

The preparations and some properties of tetraallylsilane, -germane and -tin are reported. The variation in stability of the M–C bonds is reflected by the fact that while tetraallyltin readily undergoes redistribution reactions (involving both $\sigma$–$\sigma$ and $\sigma$–$\pi$ transitions) the corresponding silicon and germanium compounds do not enter into such reactions even at elevated temperatures.

## INTRODUCTION

Although several allyl derivatives of the main group elements have been characterised[1], the available information on their properties and reactions is often limited. This is particularly true of the Group IVB elements (Si, Ge, Sn and Pb), and we have therefore undertaken a study of the allyl derivatives of these elements (with the exception of lead). In particular we wished to ascertain whether they may be conveniently used instead of allyllithium, or allylmagnesium halides in exchange reactions since the latter reagents are only conveniently prepared as solvated species in ethereal solution[2,3]. Tetraallylsilane[4,5], -germane[6] and -tin[7] have been briefly reported previously, although with lead only two allyl groups may be bonded to the metal to form an isolable compound[8].

Two classes of allyl compounds have been recognised for the main group elements: (*i*) those possessing an ionic structure, *e.g.* $Na^+C_3H_5^-$, $K^+C_3H_5^-$, where the carbanion has been suggested to be a symmetrical delocalised $\pi$-allyl system[9] (I), and (*ii*) those containing a more covalent metal–carbon $\sigma$-bond. The latter type may be subdivided into those in which the M–C bond is fluxional (II), and those in which the M–C bond is static (III). The dynamic, or fluxional, class is typified by $LiC_3H_5$[10], $Mg(C_3H_5)_2$[11] and $C_3H_5MgX$[12], and give rise to $AX_4$-type NMR spectra, while compounds containing elements from Groups IIIB and IVB form the static type (giving $ABCX_2$-type NMR spectra)[1], where any inter- (or intra-) molecular exchange of allyl groups is too slow to be observed spectroscopically even at elevated temperatures. The only exception to this generalisation is triallylborane where exchange has been observed[13] at 135°. All the main group metal allyls are air-reactive although the silicon, germanium and tin compounds decompose only very slowly.

RESULTS AND DISCUSSION

*Preparation and physical properties*

The tetraallyl compounds of silicon, germanium and tin may be prepared in reasonable yields (60–70%) from the tetrachlorides by the action of allylmagnesium halide in ethereal solution.

$$MCl_4 + 4 \, C_3H_5MgCl \rightarrow (C_3H_5)_4M + 4 \, MgCl_2$$
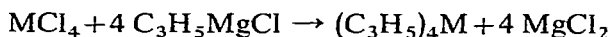
Even after extended reaction times in the presence of excess Grignard reagent some triallylchloro compound contaminates the product, this being particularly true for the tin compound. While the triallylchloro compounds are not apparently easily hydrolysed, and are difficult to remove from the tetraallyl by distillation they may be conveniently removed by treatment with a dilute potassium fluoride solution which precipitates the triallyl fluoride compound.

All the tetraallyl derivatives are colourless liquids with pleasant odours, they are soluble in all common organic solvents, and react only slowly in air depositing a white solid. They are immiscible with water, and appear to react only slowly becoming cloudy over several hours. No definite melting points could be observed, and some polymerisation of the materials is apparent at temperatures above 100°. Some physical properties are summarised in Table 1.

TABLE 1

SOME PHYSICAL PROPERTIES OF TETRAALLYLSILANE, -GERMANE AND -TIN

| Compound | B.p. (°C/mm) | $n_D^{25}$ | $d^{20}$ |
|---|---|---|---|
| $(C_3H_5)_4Si$ | 87/10 | 1.482 | 0.837 |
| $(C_3H_5)_4Ge$ | 105/10 | 1.501 | 1.015 |
| $(C_3H_5)_4Sn$ | 52/0.2 | 1.536 | 1.179 |

TABLE 2

$^1$H NMR DATA FOR TETRAALLYLSILANE, -GERMANE AND -TIN

| Element | Chemical shifts $\tau^{a,b}$ | | | | Coupling constants $J$ (Hz)$^c$ | | |
|---|---|---|---|---|---|---|---|
| | $\tau_1$ (H$_{1,2}$) | $\tau_2$ (H$_3$) | $\tau_3$ | | $J_{1,3}$ | $J_{3,4}$ | $J_{3,5}$ |
| | | | (H$_4$) | (H$_5$) | | | |
| Si | 8.44 | 4.25 | 5.16 | 5.15 | 8 | 10 | 17 |
| Ge | 8.28 | 4.15 | 5.17 | 5.13 | 8 | 9 | 17 |
| Sn | 8.04 | 4.11 | 5.30 | 5.17 | 8 | 9 | 16 |

$^a$ Relative intensities of the absorptions at $\tau_1$, $\tau_2$ and $\tau_3$ are 2/1/2, respectively, $\tau$-values are relative to TMS = 10 as internal standard. $^b$ Errors in $\tau$ values given are ±0.02 Hz. $^c$ Errors in $J$ are ±0.5 Hz.

*Spectroscopic properties*

All the tetraallyl compounds are conveniently characterised from their $^1$H NMR spectra which consist of a high field doublet ($\tau_1$), and two multiplets ($\tau_3$ and

$\tau_2$) to lower field. The chemical shifts and coupling constants are given in Table 2. The numbering is as follows:

$$\begin{array}{ccc} H_1 & H_3 & H_4 \\ | & | & | \\ M—C—C{=}C \\ | & & | \\ H_2 & & H_5 \end{array}$$
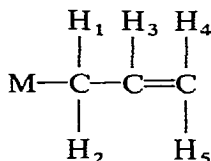
The $^1$H NMR spectrum of tetraallyltin has been briefly discussed previously[14,15], and the various coupling constants measured accurately[14]. The present results show good agreement with this data. In all three compounds the $H_1$ and $H_2$ protons are equivalent and give rise to the simple doublet with a small splitting superimposed on each peak from long-range coupling with the $H_4$ and $H_5$ protons.

For the tin compound the $J$ values have been given as $J(H_1–H_4)$ $-1.24$ Hz and $J(H_1–H_5)$ $-0.67$ Hz, and while we have not measured the corresponding values for the silicon and germanium compounds to this degree of accuracy they are both similar being of the order of 1 Hz. The multiplet from the $H_3$ proton contains six major signals for each compound, again with small splittings on each signal (except for the two outer signals as expected) arising from the small differences in the values of $J(H_3–H_4)$ and $J(H_1–H_3)$ (Table 2). In contrast to an earlier report[15] we have been unable to detect unambiguously any coupling between the $H_3$ proton and the tin atom, and although such coupling is clearly resolved with the $H_1$ and $H_2$ protons, $J[H_{1(2)}–$ $^{119}$Sn], the two satellite signals from the $^{117}$Sn and $^{119}$Sn isotopes are not clearly resolved at 100 MHz. The signal from the $H_4$ and $H_5$ protons is a set of four signals
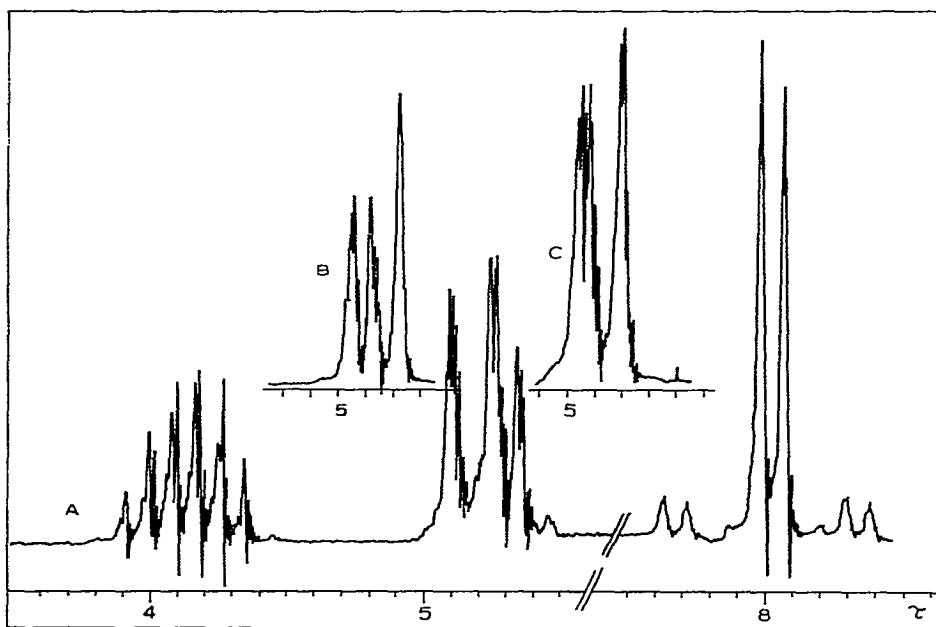


Fig. 1. The $^1$H NMR spectrum of tetraallyltin (A), and the variations in the multiplet at $\tau$ ~5.2 for tetraallylgermane (B) and -silane (C).

each of which contains two overlapping triplets. The relative chemical shifts of the four pairs of triplets determines the overall shape of the signal which varies as shown in Fig. 1.

Although no structural details are available for the tetraallyl compounds the relatively high value of the coupling constant for the protons $H_1$–$H_3$ ($J_{1,3}$ 8 Hz) is consistent with the gauche isomer being the preferred configuration in all three allyl derivatives[16]. Related to this is the interesting variation observed in the chemical shifts over the series associated with the $\tau_1$, $\tau_2$ and $\tau_3$ protons. The $\tau_1$ and $\tau_2$ sets occur at highest field for the silicon compound and show a progressive shift to lower field in the order Si > Ge > Sn, while for the $\tau_3$ protons only a small variation occurs for $H_5$, but $H_4$ shows a definite shift to high field in the tin compound with the order Sn > Ge ⪆ Si.

In comparison for the allyl halides, X–$CH_2$–CH=$CH_2$, where X = Cl, Br or I, it is the $\tau_1$ and $\tau_3$ sets which move to lower field, and it is the $\tau_2$ set which moves to higher field, with increasing electronegativity of X[16]. While the chemical shifts in these halide compounds have not been discussed in detail, Bothner-By and Naar-Colin have suggested that in the alkyl derivatives, R–$CH_2$–CH=$CH_2$, with R = H, Me or Et, where the shifts are more random, neither electronegativity nor anisotropy effects can account satisfactorily for the observed shifts[17]. Instead they suggest that the major influence arises from permanent electric fields (dipoles) within the molecules which distort the orbitals near the hydrogen atom. Such an effect must also operate in the present systems, and the results also show that, as in the alkyl systems, no simple relationship exists between the electronegativities for the central atom (Allred–Rochow values are: Si, 1.74; Ge, 2.02; Sn 1.72) and the shifts of the $\tau_1$, $\tau_2$ and $\tau_3$ protons. The most reasonable effect to account for the observed shifts here is the diamagnetic anisotropies of the M–C and C=C bonds which would be enhanced compared with the alkylated propenes discussed above, and which might be expected to increase down the series Si–C < Ge–C < Sn–C. The difficulties associated with estimating such anisotropies have been pointed out previously[14], but the magnitude of the effect is likely to be greater for the methylene $CH_2$ group and the vinyl CH group than for the vinyl $CH_2$ group. An additional shielding effect arising from the C=C bond would also affect the *cis* proton ($H_4$), and would be less noticeable for the *trans* proton ($H_5$), which could therefore account for the high field shift observed for the former[14].

The spectra of all the compounds emphasise the stability of the M–C bond, since if any exchange occurred (either by an intra- or intermolecular process) the $H_1$, $H_2$ and $H_4$, $H_5$ protons would become equivalent as is observed for $C_3H_5MgX$[9], and an $AX_4$ type spectrum would be obtained. All the spectra reported here are invariant over a wide temperature range ($-60°$ to $+150°$), and the slight broadening of the signals which occurs at lower temperatures may be ascribed to viscosity effects. Similar $ABCX_2$ spectra have been reported for other allyl derivatives such as $C_3H_5$-Mn(CO)$_5$[18], [($C_3H_5$)$_2$RhCl]$_2$[19] and allylpalladium complexes containing phosphines or dimethylsulphoxide as ligands[20,21].

The most characteristic absorption in the IR spectra of the tetraallyl compounds arises from the stretching vibration associated with the olefinic –C(H)=$CH_2$ bond, which occurs at 1629, 1631 and 1625 cm$^{-1}$ for the silicon, germanium and tin compounds respectively. These values are of the correct order for an unperturbed

olefinic bond, and may be compared with the corresponding absorption in the allyl halides (1645–1640 cm$^{-1}$)[22], and the silicon, germanium, and tin tetravinyl derivatives (1600–1595 cm$^{-1}$)[23]. The stretching vibration associated with the metal–carbon bond lies in the region 600–400 cm$^{-1}$, and decreases as expected through the silicon, germanium and tin compounds as 600, 535 and 488 cm$^{-1}$ respectively. The remaining absorptions show only little variation over the three compounds and are given in detail in the experimental section. The mass spectra of the compounds are discussed in detail elsewhere[24].

The comparative reactivity of the tetraallyl compounds was studied by a series of redistribution reactions. For example, tetraallyltin and tin tetrachloride react rapidly and exothermically at 25° producing the allyltin chlorides. All the chlorides may be obtained by the use of the appropriate molar ratios, and can be distilled without disproportionation.

$$x \, Sn(C_3H_5)_4 + (4-x) \, SnCl_4 \rightarrow 4 \, (C_3H_5)_x SnCl_{4-x} \qquad (x = 1, 2 \text{ or } 3)$$
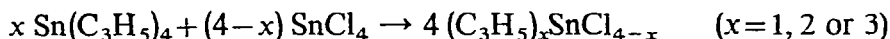
Similar rapid reactions occur with tin tetrabromide, and the PMR spectra of
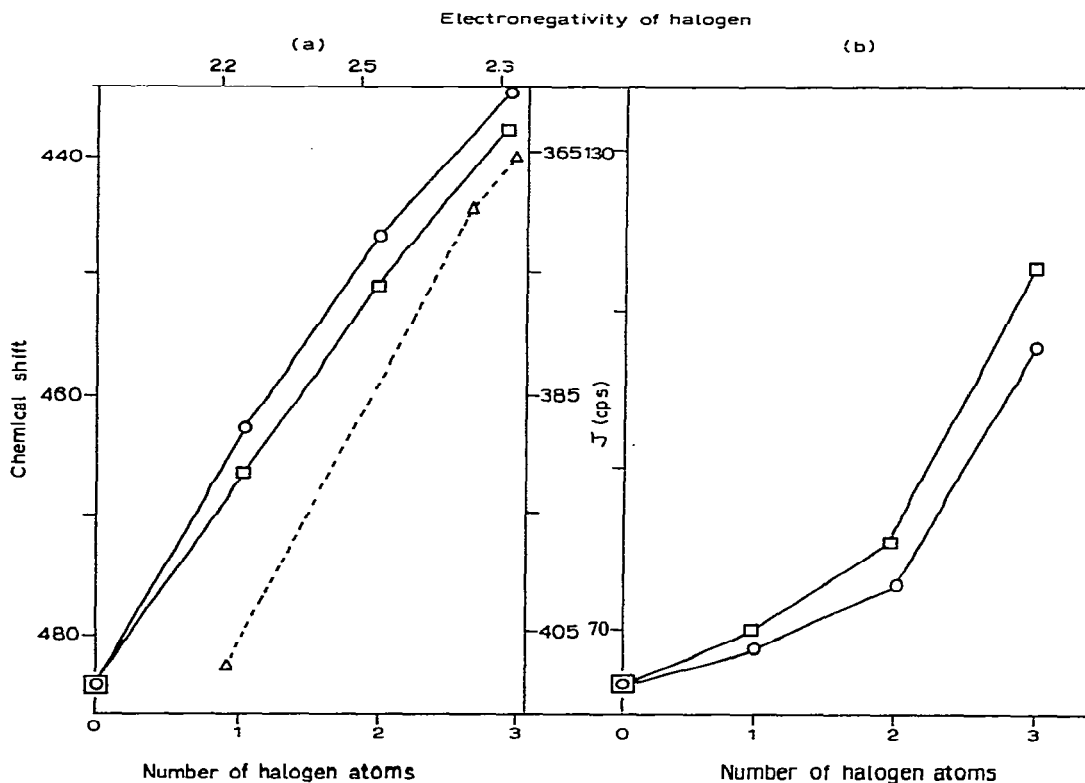


Fig. 2. (a) A plot of the chemical shift of the aliphatic CH$_2$ protons in (C$_3$H$_5$)$_{4-n}$SnX$_n$ compounds (where X = Cl or Br) vs. the number of halogen atoms in the molecule (n = 0, 1, 2 or 3). The dotted line represents a plot for similar protons in the allyl halides vs electronegativity of the halogen atom (based on the Allred–Rochow scale). (b) A plot of the coupling constant, $J$($^{119}$Sn–C–H), for the aliphatic CH$_2$ protons vs. the number of halogen atoms in (C$_3$H$_5$)$_{4-n}$SnX$_n$ compounds (where X = Cl or Br). □ represents the Cl compounds, ○ the Br compounds. The chemical shift is given in Hz with respect to TMS 600 Hz.

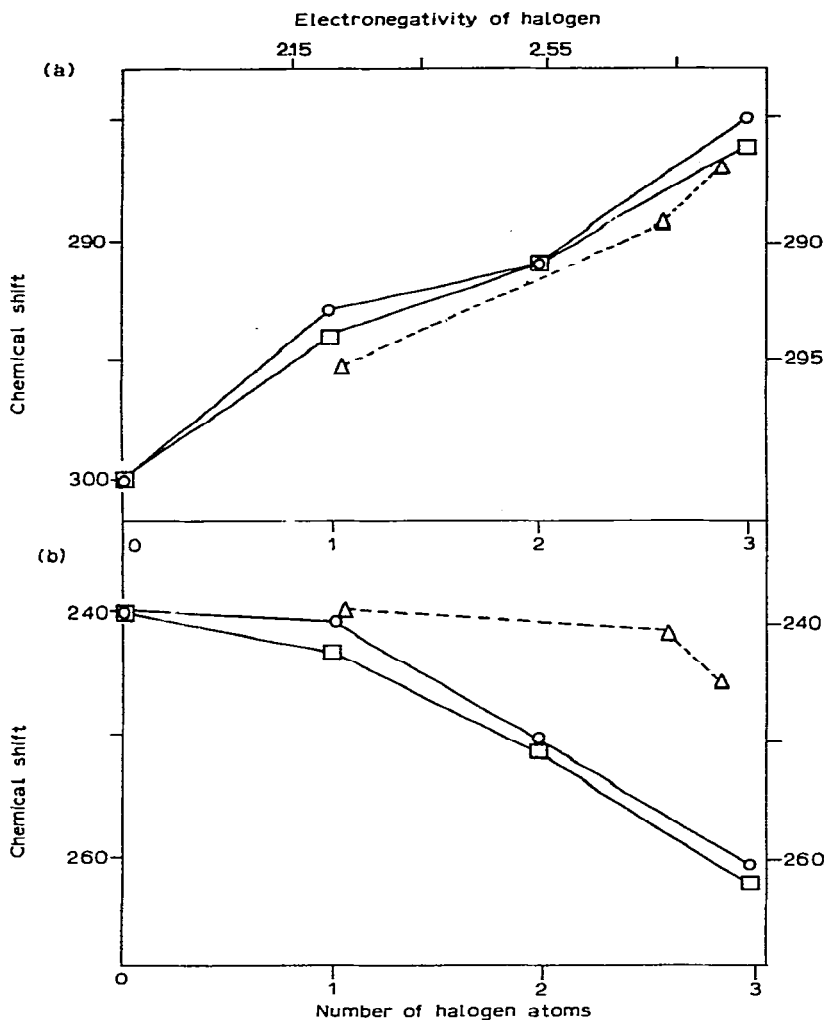Fig. 3. (a) A plot of the chemical shift of the vinyl $CH_2$ protons in $(C_3H_5)_{4-n}SnX_n$ compounds (where $X = Cl$ or Br) *vs.* the number of halogen atoms in the molecule ($n = 0, 1, 2$ or 3). (b) A similar plot for the vinyl CH proton. The dotted lines in the plots represents a plot for the corresponding protons in the allyl halides *vs.* electronegativity of the halogen atom. □ represents the Cl compounds, ○ the Br compounds. The chemical shift in both plots is given in Hz with respect to TMS 600 Hz.

the various mixtures show that in this case well defined progressive shifts occur for the protons of the allyl group as the halogen content varies. Thus both the aliphatic $CH_2$ protons, and to a lesser extent the vinyl $CH_2$ protons both move progressively to lower field as the halide content in $(C_3H_5)_xSnX_{4-x}$ increases. In contrast to these shifts, and those in the tetraallyl compounds, it is the vinyl CH proton which shows different behaviour in that a shift to high field is observed as the halogen content increases. The various chemical shifts are shown in Figs. 2(a) and 3. Again a direct comparison may be made with the respective protons in the allyl halides, $CH_2=CH-CH_2-X$ where $X = Cl$, Br or I, and the chemical shifts over this series are also plotted in

Figs. 2(a) and (3). It is seen that similar shifts are obtained for the allyl group protons in both series so that the electronegativity increases for the Y group in $CH_2=CH-CH_2-Y$ where Y varies as $Cl > Br > I$ and $SnX_3 > SnX_2 > SnX$ (where $X = Cl$ or $Br$), while the steric requirements of the halogen groups follow the reverse order. As mentioned above the shifts in the allyl halides have not been discussed, but it has been noted that in the series of ethylgermanium halides, $(C_2H_5)_xGeX_{4-x}$, for $X = I$ the methylene protons shift to lower field on increasing iodine substitution while the methyl protons in fact shift to higher field over the same series[25]. Since both the methylene and methyl protons shift to low field in the chloro and bromo compounds it was suggested that the anomalous high-field shift of the methyl protons in the iodo compound arose from an induced electronic circulation due to direct contact between the methyl hydrogen and iodine atom. A similar situation obtains in the allyltin halides where, for the preferred gauche isomer, direct contact between the chlorine (or bromine) atoms and the vinyl CH proton occurs (Fig. 4), and could
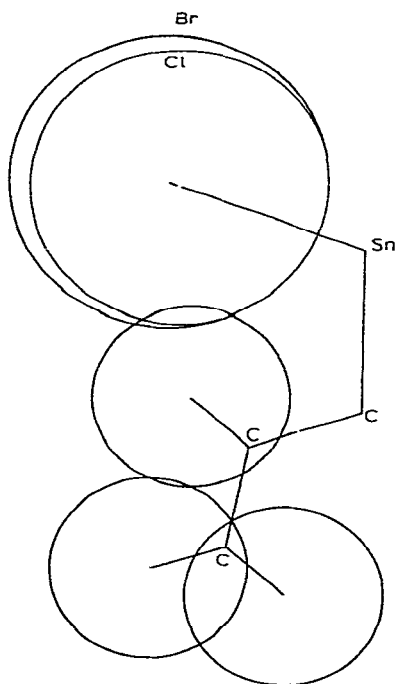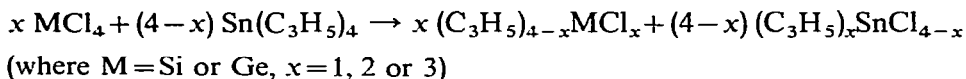


Fig. 4. A diagramatic representation of the interaction of the vinyl CH proton with the halogen atom in the compounds $(C_3H_5)_{4-n}SnX_n$, where $X = Cl$ or Br and $n = 1, 2$ or 3.

similarly produce a high field shift. It appears probable that other factors such as the bond anisotropy of the Sn–X bond (which would be expected to produce a low-field shift for the CH proton), or any intermolecular solution effects (the chemical shifts remain invariant over a range of concentrations) are not therefore of major significance in this case.

The variation of the Sn–H coupling constant for the protons of the methylene

CH$_2$ group in the chloro derivatives, $J(^{119}$Sn–C–H$)$, shows an increasing deviation with the number of chlorine atoms present [Fig. 2(b)], and is similar to previous results obtained for the methyltin halides[26]. These deviations from direct additivity for the latter compounds were correlated with the pair-wise interaction equation derived by Vladimiroff and Malinowski[27] for indirect couplings, and only become apparent in the di- and trisubstituted products, similar to the present results. The deviations for the methyltin derivatives have been suggested[26] to arise from variations in the effective nuclear charge parameter which is related to the electronegativity of the substituents, and the present results would similarly be consistent with such an explanation.

Significant differences are observed in the reactivity of the silicon and germanium compounds compared with that of the tin. No halogen–allyl exchange occurs in the mixtures Si(C$_3$H$_5$)$_4$+SiCl$_4$ or Ge(C$_3$H$_5$)$_4$+GeCl$_4$ even after heating to 70°. The small shift observed in the $^1$H NMR spectra may be attributed to the variation in the bulk magnetic susceptibility of the mixture. The important factor would appear to be the stability of the M–C bond because halogen–allyl exchange does occur slowly (and not 'ways to completion) when tetraallyltin is mixed with either silicon or german: _n tetrachloride.

$$x \text{ MCl}_4 + (4-x)\,\text{Sn(C}_3\text{H}_5)_4 \;\rightarrow\; x\,(\text{C}_3\text{H}_5)_{4-x}\text{MCl}_x + (4-x)\,(\text{C}_3\text{H}_5)_x\text{SnCl}_{4-x}$$

(where M = Si or Ge, $x = 1$, 2 or 3)

These reactions indicated that tetraallyltin is the most suitable reagent for effecting exchange reactions involving the allyl group, and some reactions of this type were therefore investigated.

In addition to the reactions described above where the allyl group is involved in exchange from one $\sigma$-bonding situation to another ($\sigma$–$\sigma$ exchange) it may also be involved in a $\sigma$–$\pi$ exchange reaction. Thus when tetraallyltin is added to sodium chloropalladite Na$_2$PdCl$_4$ in methanol, an immediate yellow crystalline deposit of $\pi$-allylpalladium chloride dimer was formed. However, similar reactions involving palladium chloride and potassium chloroplatinite yielded only black metallic deposits. No reaction was observed between either tris(triphenylphosphine)rhodium(I) chloride or bis(triphenylphosphine)rhodium(I) carbonyl chloride and tetraallyltin even at elevated temperatures.

Phenyllithium also reacts readily with tetraallyltin in ether at 25° precipitating tetraphenyltin with allyllithium remaining in solution as reported previously[28]. The reaction did not usually proceed to completion, and only about 80% yields of allyllithium could be obtained. The $^1$H NMR spectrum of the ethereal solution showed the expected $AX_4$ type spectrum for allyllithium with only traces of signals from other species (phenyllithium, etc.).

In summary therefore the tetraallyl derivatives of silicon, germanium and tin are easily prepared and characterised, the tin compound in particular readily undergoes redistribution reactions involving both $\sigma$–$\sigma$ and $\sigma$–$\pi$ allyl group exchange.

EXPERIMENTAL

The PMR spectra were measured at 100 MHz using a Varian HA 100 with a

variable temperature probe. Tetramethylsilane was normally included as an internal reference. The IR spectra were obtained using a Perkin–Elmer SP 100 spectrometer.

*Preparation of tetraallyltin*

Allyl chloride (131.7 g, 1.72 mole) in 900 ml of ether was added dropwise to magnesium turnings (45.5 g, 1.90 mole) and 2.5 l of ether contained in a 5 l flask fitted with a condenser, stirrer, dropping funnel and inlet and outlet tubes for dry nitrogen. The addition was carried out at −15° (after the reaction had initiated by small quantities of dibromoethane) and was completed in about 2 h. The Grignard reagent was then estimated by acid titration, and the yield was usually 65–70% theoretical.

Stannic chloride (65.6 g, 0.252 mole) was added dropwise to the allyl Grignard reagent (127 g, 1.26 mole) in 3.5 l of ether. When the addition was complete the mixture was refluxed for 18 h. The excess Grignard reagent was then hydrolysed with 500 ml of 0.1 *M* hydrochloric acid, the ether layer separated and dried over magnesium sulphate. After reducing the solution to a volume of 100 ml by distilling off the ether, 50 ml of a 5% solution of potassium fluoride was added to remove any triallyltin chloride by precipitation as triallyltin fluoride. The ether layer was again separated, dried as before, and after distilling off the ether the product was distilled at reduced pressure (0.2 mm). The yield of pure product was 38.4 g (53% theoretical, based on the stannic chloride addition).

*Tetraallylsilane and -germane*

These compounds were obtained by the action of the tetrachloride on the allyl Grignard reagent using a procedure similar to that outlined above. The silicon and germanium compounds were isolated in 35% and 45% yields respectively.

The complete IR spectra for the tetraallyls over the range 4000–400 cm⁻¹ are:

$(C_3H_5)_4Si$: 3080 s, 3065 m, 3035 w, 3000 m, 2970 s, 2920 m, 2890 m, 1800 m, 1629 s, 1423 s, 1396 s, 1301 w, 1197 s, 1167 s, 1159 s, 1042 s, 992 s, 927 s, 893 s, 787 s, 701 w and 535 s.

$(C_3H_5)_4Ge$: 3078 s, 3061 m, 3035 w, 3004 m, 2979 s, 2944 m, 2908 m, 1799 w, 1734 w, 1631 s, 1425 s, 1400 m, 1299 w, 1264 w, 1197 s, 1144 s, 1038 s, 988 s, 935 s, 893 s, 804 s, 727 w, 691 w and 600 s.

$(C_3H_5)_4Sn$: 3082 s, 3052 m, 3034 w, 3000 m, 2965 s, 2915 m, 1791 w, 1625 s, 1578 w, 1462 w, 1428 s, 1393 s, 1298 m, 1258 w, 1192 s, 1101 s, 1030 s, 991 s, 932 s, 894 s, 799 w, 754 s, 677 s, 605 m, 553 w and 488 s.

*Reaction of tetraallyltin with tin tetrachloride*

Tetraallyltin (1.45 g, 5.1 mmole) in benzene solution was added to the tetrachloride (1.28 g, 4.9 mmole) at 0° under nitrogen. After warming the mixture to 25° the NMR spectrum of the solution showed only one signal from the allyl groups corresponding to $(C_3H_5)_2SnCl_2$ indicating that reaction was complete. The other compounds were prepared similarly using appropriate molar ratios. In contrast to this rapid exchange the NMR spectra of mixtures of $(C_3H_5)_2SnCl_2 + (C_3H_5)_3SnCl$ and $(C_3H_5)_3SnCl + Sn(C_3H_5)_4$ showed two signals at 25° corresponding to the starting materials indicating that no exchange had occurred, or at least that exchange was extremely slow. The reactions involving the tetrabromide were carried out in a similar manner.

For the reactions involving tetraallylsilane and -germane the mixtures with the tetrachlorides were heated to 50° for 5 h after the NMR spectra had shown that no exchange had occurred at 25°. However, no exchange was observed even at the elevated temperatures. Some heating (50° for 5 h) was also necessary to effect complete reaction between tetraallyltin and silicon and germanium tetrachloride in cyclohexane solution.

*Reaction of tetraallyltin with palladium chloride and sodium chloropalladite*

Tetraallyltin (0.21 g, 0.74 mmole) was added to a suspension of palladium chloride (0.32 g, 1.83 mmole) in 10 ml of methanol, and the mixture was allowed to stand at 25° when a black metallic deposit appeared over a period of a few days. A similar reaction occurred when acetone was used as the solvent. When tetraaallyltin (0.099 g, 0.35 mmole) was added to a solution of sodium chloropalladite (0.2 g, 0.68 mmole) in 6 ml of methanol, the solution immediately changed colour from dark brown to pale yellow, and yellow crystals of allylpalladium chloride dimer (identified by comparison of the NMR spectrum with that of an authentic sample) were deposited in 85% yield (0.1 g).

No reaction was observed between potassium chloroplatinite (0.27 g, 0.65 mmole) and tetraallyltin (0.094 g, 0.33 mmole) after refluxing in chloroform for 4 h and while colour changes did occur (yellow→red) when dimethyl sulphoxide was used as the solvent no allylplatinum complex could be isolated from the reaction mixture.

ACKNOWLEDGEMENTS

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