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Preliminary communication

EXCHANGE AND ADDITION REACTIONS INVOLVING TIN—ALLYL COMPOUNDS

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Summary

Allyltin chlorides (or bromides) may be prepared by simple exchange reactions between tetraallyltin and the corresponding tetrahalide. Hydroboration of allyltrimethyltin yields the air-reactive borane, $[Me_3Sn(CH_2)_3]_3B$, which is readily oxidised to the corresponding alcohol $Me_3Sn(CH_2)_3OH$.

It is known that exchange reactions involving the tetraalkyl compounds MR_4 (M = Si, Ge, Sn) occur with the relative rates of such reactions increasing in the order $SiR_4 < GeR_4 < SnR_4$ [1]. Thus with the corresponding tetrachlorides the following temperatures are required to effect exchange in MMe_4/MCl_4 mixtures, M = Si (250°C) [2], Ge (120°C) [3], Sn (25°C) [4]. However, no information is available on corresponding exchange reactions involving allyltin derivatives although reactions with various transition metal compounds yielding π-allyls are well documented [5]. Also, while numerous reactions involving addition to the olefinic bond have been reported for allyl derivatives of silicon (e.g. [6, 7]) very few are known for tin derivatives. In hydroboration of $Me_3SiCH_2CH{=}CH_2$ the addition product, although not identified, has been assumed to be $[Me_3SiCH_2CH_2CH_2]_3B$ since oxidation yields the organosilicon alcohol $Me_3Si(CH_2)_3OH$ [8, 9]. We have investigated these types of reactions in more detail to clarify the behaviour of some allyltin compounds.

When tin tetrachloride (or bromide) is added to tetraallyltin in the absence of solvent, a white solid is immediately obtained, but the reaction is exothermic and difficult to control. However, a rapid and clean reaction occurs in benzene solution at 25°C and the various allyltin chlorides (and bromides) may be obtained by mixing the appropriate molar ratios of reactants.

$$x\,Sn(C_3H_5)_4 + (4-x)\,SnX_4 \rightarrow 4\,(C_3H_5)_xSnX_{4-x}$$

(X = Cl or Br; x = 1, 2 or 3)

In each case the ^1H NMR spectrum of the mixture immediately after mixing shows only one signal from the allyl groups, indicating that reaction is complete, since addition of $Sn(C_3H_5)_4$ to a solution containing, say, $(C_3H_5)_3SnCl$ gives an NMR spectrum containing two sets of signals for the allyl groups, corresponding to the values expected for the two compounds. As the halide content is increased through the series, well defined shifts occur for the protons of the allyl groups. Thus theresonance from the aliphatic CH_2 group, and, to a lesser extent, that from the vinyl CH_2 group move to lower field as the halide content in $(C_3H_5)_xSnX_{4-ne}$increases, whereas the vinyl CH group shows a high field shift which is intermediate in magnitude between that of the aliphatic and vinyl CH_2 groups (Table 1). Similar variations in shift values are observed for the respective protons in the allyl halides $CH_2{=}CHCH_2X$ (X = Cl or Br) [10].

TABLE 1

THE CHEMICAL SHIFTS IN THE ^1H NMR SPECTRA OF A SERIES OF ALLYLTIN HALIDES, $(C_3H_5)_xSnX_{4-x}$

Allyl group protons[a]	ne	X			
		3	2	1	0
Aliphatic CH_2	Cl	7.28	7.48	7.77	8.03
Aliphatic CH_2	Br	7.23	7.42	7.70	8.03
Vinyl CH	Cl	4.43	4.31	4.18	4.13
Vinyl CH	Br	4.42	4.29	4.14	4.13
Vinyl CH_2	Cl	5.22	5.25	5.30	5.40
Vinyl CH_2	Br	5.18	5.25	5.28	5.40

[a] Recorded from benzene solutions, shifts (in ppm) relative to TMS = 10.00.

As in the case of the alkyltin derivatives, significant differences are observed in the reactivity of the silicon and germanium compounds in that the mixtures $M(C_3H_5)_4/MCl_4$ (M = Si or Ge) show no allyl exchange even at 70°C, and the small shifts (2—3 Hz) of the allyl protons in the various ^1H NMR spectra may be attributed to the variation in the bulk magnetic susceptibility of the liquid. When $Sn(C_3H_5)_4$ is mixed with either $SiCl_4$ or $GeCl_4$ then allyl–halogen exchange does occur, albeit slowly at 50°C, but a mixture of products is obtained as indicated by the complexity of the ^1H NMR spectrum in the allyl region. The trimethyl derivatives of boron and aluminium do not react with tetraallyltin at room temperature, but we have verified an earlier report [11] that phenyllithium reacts rapidly in ethereal solution precipitating tetraphenyltin with the allyllithium (~80% yield) remaining in solution.

The addition of the B—H bond across the olefinic bond in $Me_3SiCH_2CH{=}CH_2$ has been effected using either sodium borohydride [8] or diborane [9]. We have confirmed that using diborane in tetrahydrofuran affords only 3-trimethylsilyl-1-propanol after oxidation of the assumed silylborane $[Me_3Si(CH_2)_3]_3B$ intermediate, and have extended the reaction to the corresponding tin compound, $Me_3SnCH_2CH{=}CH_2$ (I) to identify the borane. Thus, when diborane, 9.6 mmol is distilled on to I, 57.6 mmol dissolved in 10 ml of ether or tetrahydrofuran in a Hoke bomb (100 ml), and the mixture warmed to 50°C for 2 h, no diborane or any adduct containing B—H bonds remains in the bomb, and no olefinic bonds can be detected in the IR spectrum of the reaction mixture. After removal of the solvent, the air-sensitive colourless liquid (15.5 mmol based on formulation below, 82% yield) shows only one sharp peak in a GLC analysis, and analytical data confirm the formulation $[Me_3Sn(CH_2)_3]_3B$. The liquid, which decomposes above 100°C and cannot therefore be distilled, shows an IR spectrum similar to that of I except for the absence of bands near 1630 cm^{-1} from the olefinic bond, and the addition of bands near 1300 cm^{-1} which are reasonably assigned to B—C stretching modes. The ^1H NMR spectrum shows two triplets and a multiplet at τ 8.57 (rel. intensity 2), 8.19(2) and 7.78(2) respectively from the methylene protons, and a sharp singlet at τ 9.50(9) from the methyl groups. Oxidation of the borane with alkaline hydrogen peroxide yields only the alcohol $Me_3Sn(CH_2)_3OH$ as indicated by GLC, IR and NMR data; as with the trimethylsilyl analogue the product did not contain either 1-propanol or 1-trimethylstannyl-2-propanol which would be obtained from the internal boron adduct [12].

These reactions therefore offer convenient routes to mixed allylhalostannanes and stannylorganoboranes, and we are investigating further the synthetic potential of the latter reagent.

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