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A FAST HIGH-YIELD SYNTHESIS OF AN ORGANOTIN COMPOUND WITH FOUR DIFFERENT ALKYL GROUPS LINKED TO TIN.

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The bromination of tetraalkyltins usually leads to a mixture of mono- and dibromides (1)(2), the amount of R_2SnBr_2 depending on the nature of R. Moreover, it appears that the reaction between halogens and a compound such as R_3SnR' is poorly selective and apparently unpredictable (3). These two facts explain why it has been rather difficult so far to synthesize a pure asymmetrical organotin compound in good yields*. It is important to point out that most of the previous halogenodemetallations have been carried out in non-polar solvents (as defined by GIELEN and NASIELSKI (5)).

We have previously shown (6) by kinetic experiments that, in the $RSnMe_3$ and $RSnEt_3$ series, a high degree of selectivity is achieved in the nucleophilic solvent methanol and that dihalogenation is negligible in these conditions. We have therefore carried out the synthesis of racemic organotin compounds *by using methanol as the solvent for the bromodemetallation and thus achieving monohalogenation and a very high degree of selectivity*.

Pure bromine was added dropwise to a cooled (0ºC) solution of *cyclo*hexyltrimethyltin** in methanol (in dim light (7)); the reaction is instantaneous and the first drop in excess yields a persistent colour. A V.P.C. analysis of the mixture shows MeBr as the *only* alkyl bromide; removal of the solvent yields 99% of a crude bromide which was then reacted with a large excess of *iso*propylmagnesium bromide to give the expected *cyclo*hexyl*iso*propyldimethyltin (76º5/1.7 Torr). This was brominated in methanol as above and the end-point was equally sharp; V.P.C. showed no trace of *cyclo*hexyl or *iso*propyl bromide. After removal of the solvent, there remains a crude bromide (98%), *cyclo*hexyl*iso*propylmethyltin bromide, the first racemic tin derivative of this series, which should prove a ve-

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* Compounds with an asymmetrical tin atom have already been described (4); their isolation from rather complex reaction mixtures however proved to be tedious.

** Prepared from Me_3SnCl by the usual procedure (6) (203-204ºC/760 Torr).

ry usefull intermediate for the preparation of a variety of asymmetrical tetraalkyltin derivatives.

This bromide was then reacted with an excess of ethylmagnesium bromide, yielding 97% of a crude tetraalkyltin (73°5/0.7 Torr) which contains more than 98% of methylethyl*iso*propyl*cyclo*hexyltin (V.P.C.).

The whole synthesis, starting from Me_3SnCl, took less than five days.

The structure of the racemic compound was established by a bromination in chlorobenzene (a non selective reaction), which yielded the four expected alkyl halides, and by its mass spectrum, which shows the expected (8) parent peak and fragment ions.

Iodination of this material in methanol yields over 99% MeI : this observation opens the way to the synthesis of asymmetrical tin derivatives having no methyl group linked to tin. Some of our findings have been confirmed by experiments carried out our laboratory by Mr.J.P.LIEUTENANT (9).

These results are an interesting application of the use of kinetic and mechanistic studies to organometallic synthesis.

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