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ALKYL REDISTRIBUTION REACTIONS OF $(CH_3)_nSnX_{4-n}$ COMPOUNDS (X = Cl, Br, I)

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INTRODUCTION

Redistribution reactions between SnR_4 and SnX_4 (X = Cl, Br) are of great interest for the synthesis of alkyltin halides by the Kozeschkow method[1]. These syntheses proceed according to the overall reaction equations (a), (b) and (c):

$$\text{(a)}\ 3\ R_4Sn + SnX_4 \rightarrow 4\ R_3SnX,$$

$$\text{(b)}\ R_4Sn + SnX_4 \rightarrow 2\ R_2SnX_2,$$

$$\text{(c)}\ R_4Sn + 3\ SnX_4 \rightarrow 4\ RSnX_3;$$

reaction (c) does not occur for $R = CH_3$.
The following reaction mechanisms are proposed for reactions (a) and (b):

$$\text{(a)}\ R_4Sn + SnX_4 \rightarrow R_3SnX + RSnX_3 \qquad (1)$$

$$R_3SnX + RSnX_3 \rightarrow 2\ R_2SnX_2 \qquad (2)$$

$$2\ R_4Sn + 2\ R_2SnX_2 \rightarrow 4\ R_3SnX \qquad (3)$$

$$\text{(b)}\ R_4Sn + SnX_4 \rightarrow R_3SnX + RSnX_3 \qquad (1)$$

$$R_3SnX + RSnX_3 \rightarrow 2\ R_2SnX_2 \qquad (2)$$

The first and the second step for reactions (a1) and (a2), and (b1) and (b2) are seen to be the same in both sequences. It has been shown by Neumann and Burkhardt[2] that the reaction between one mole of $(C_2H_5)_4Sn$ and one mole of $SnCl_4$ results first in the formation of $(C_2H_5)_3SnCl$ and $C_2H_5SnCl_3$, which at a temperature of 200°, form $(C_2H_5)_2SnCl_2$. For $R = -C_4H_9$, the first step of reaction mechanism (b) serves for the preparation of $(C_4H_9)_3SnCl$ and $C_4H_9SnCl_3$ in a temperature range 0–20°C. The reaction rate of reaction (2) is sufficiently low to allow separation of the tri- and the monochloride by distillation. Only at high temperatures (about 200°) do both products react further with the formation of $(C_4H_9)_2SnCl_2$.

For $R = -CH_3$, however, the reaction rate is obviously very high since on mixing equimolecular amounts of $Sn(CH_3)_4$ and $SnCl_4$ the direct formation of $(CH_3)_2SnCl_2$ can be observed.

In the experiments reported in this paper, we have tried to identify all compounds formed in the intermediate stages of reactions (a) and (b) for mixtures of SnX_4 and $Sn(CH_3)_4$, X = Cl, Br or I. The redistribution was followed by means of NMR in the temperature range 0–120°C.

EXPERIMENTAL

All compounds were prepared in our laboratory by standard methods.

The samples were prepared in NMR glass tubes, which were sealed to prevent evaporation and hydrolysis of the products. The NMR spectra were recorded with a Varian dual-purpose NMR spectrometer V. 4.300-B operating at 56.4 Mc, equipped with an integrator and a variable temperature probe assembly.

Chemical shifts were measured against the TMS signal from a capillary, containing a 10% v/v solution of TMS in $CHCl_3$ as external reference standard. Identification of the compounds was based on the value of J(Sn–C–H) and proton chemical shift. Mixtures of the following compositions were studied: $Sn(CH_3)_4$ and SnX_4 (X = Cl, Br) in molar ratios 1:1 and 3:1; $(CH_3)_3SnX$ and CH_3SnX_3 (X = Cl, Br, I) in molar ratio 1:1; $(CH_3)_2SnX_2$ (X = Cl, Br, I) with an excess of $Sn(CH_3)_4$.

RESULTS AND DISCUSSION

A. *Methyltin chlorides*

1. $Sn(CH_3)_4$ and $SnCl_4$ in molar ratio 1:1 (Fig. 1). After the reactants have been mixed at −10°C, the NMR spectrum shows three absorptions signals which must be ascribed to $(CH_3)_3SnCl$, $(CH_3)_2SnCl_2$, and CH_3SnCl_3, respectively. On increasing the temperature, the intensities of the $(CH_3)_3SnCl$ and CH_3SnCl_3 signals slowly decrease while that of $(CH_3)_2SnCl_2$ increases. In the temperature range 90°–120°C these relative intensity changes are very fast, so that at 120°C the CH_3SnCl_3 signal has disappeared, the intensity of the $(CH_3)_2SnCl_2$ signal reaching a maximum and that of $(CH_3)_3SnCl$, a minimum. These observations are in accordance with steps (1) and (2) of the reaction mechanism proposed above. The reaction rate of the second step increases with increasing temperature. The presence of some $(CH_3)_3SnCl$ after completion of the redistribution at higher temperatures could be explained by two reaction mechanisms.

1. Some of the CH_3SnCl_3 formed by reaction (1) reacts with $Sn(CH_3)_4$:

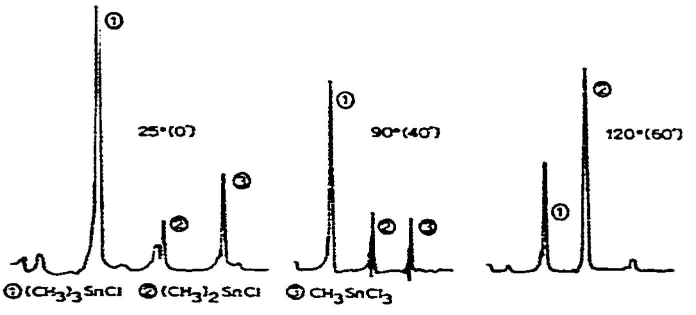
$$2\ Sn(CH_3)_4 + CH_3SnCl_3 \longrightarrow 3\ (CH_3)_3SnCl \qquad (4)$$

2. $(CH_3)_2SnCl_2$ formed by reaction (2) reacts further with $Sn(CH_3)_4$ according to reaction (a3).

It was found by Kozeschkow that the reactions with molar ratios of reactants as in (4) result essentially in the formation of R_2SnCl_2 with only a small amount of R_3SnX.

This indicates that the excess of $(CH_3)_3SnCl$ remaining after completion of the scrambling reaction must be due to the fact that reactions (a2) and (a3) are so fast that they proceed to a considerable extent before all the reactants of reaction (a1) are consumed.

2. $(CH_3)_3SnCl$ and CH_3SnCl_3 in molar ratio 1:1. In order to verify reaction (a2),



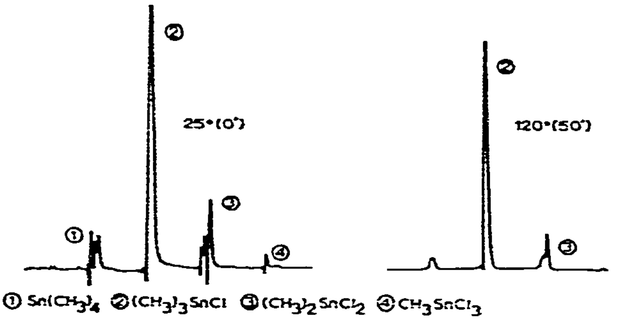


Fig. 1. Redistribution of $Sn(CH_3)_4$ and $SnCl_4$ in molar ratio 1:1.

Fig. 2. Redistribution of $Sn(CH_3)_4$ and $SnCl_4$ in molar ratio 3:1.

we investigated the redistributions in an equimolecular mixture of $(CH_3)_3SnCl$ and CH_3SnCl_3. The formation of some $(CH_3)_2SnCl_2$ can already be observed at 25° by the appearance of a weak signal between the main signals of $(CH_3)_3SnCl$ and CH_3SnCl_3. At temperatures above 90°C, the redistribution is very fast, and after the sample has been heated for one hour at 120°, the NMR spectrum shows only a $(CH_3)_2SnCl_2$ signal.

3. $Sn(CH_3)_4$ and $SnCl_4$ in molar ratio 3:1 (Fig. 2). Immediately after the preparation of the mixture at —10°C, the NMR spectrum shows 4 absorption signals due to $Sn(CH_3)_4$, $(CH_3)_3SnCl$, $(CH_3)_2SnCl_2$ and CH_3SnCl_3.

The $(CH_3)_3SnCl$ signal has the highest intensity. On increasing the temperature to 120°, the signals of $Sn(CH_3)_4$ and CH_3SnCl_3 disappear while the signal of $(CH_3)_2SnCl_2$ slowly decreases and that of $(CH_3)_3SnCl$ increases. Complete redistribution thus yields principally $(CH_3)_3SnCl$ with some $(CH_3)_2SnCl_2$. These reactions, together with the results of sections A1 and A2 of this report, indicate that redistribution occurs according to the proposed mechanism, *i.e.*, the consecutive reactions (a1), (a2) and (a3).

It was not possible, however, to observe the equimolecular formation of $(CH_3)_3SnCl$ and CH_3SnCl_3 postulated by reaction (a1). This must be ascribed to the fact that reactions (a2) and (a3) are very fast and proceed simultaneously with (a1). From the presence of some $(CH_3)_2SnCl_2$ after complete redistribution, it follows that the reaction rate for (a3) must be greater than that for (a2).

4. *$(CH_3)_2SnCl_2$ in excess $Sn(CH_3)_4$.* At room temperature, $(CH_3)_2SnCl_2$ remains insoluble in $Sn(CH_3)_4$. Only above 70°C does $(CH_3)_2SnCl_2$ dissolve and the NMR spectrum then shows three absorption signals due to $Sn(CH_3)_4$, $(CH_3)_3SnCl$ and $(CH_3)_2SnCl_2$.

When the temperature is increased to 100°C, the $(CH_3)_2SnCl_2$ peak gradually disappears, the $Sn(CH_3)_4$ signal decreases and the $(CH_3)_3SnCl$ peak steadily increases, showing that further redistribution is taking place. When complete redistribution is achieved only, the monochloride signal is observed.

These data clearly establish the concomitant reaction (a3) and so provide evidence for our suggestion relating to the mechanism of the formation of excess $(CH_3)_3SnCl$ observed for 1:1 molar mixtures of $(CH_3)_4Sn$ and $SnCl_4$ at equilibrium.

B. Methyltin bromides

1. *$Sn(CH_3)_4$ and $SnBr_4$ in molar ratio 1:1.* $SnBr_4$ dissolves easily in an equimolecular amount of $Sn(CH_3)_4$ at −10°C. The NMR spectrum taken at 25° shows two absorption signals due to the formation of $(CH_3)_3SnBr$ and CH_3SnBr_3 in equimolecular amounts. When, after 45 min the temperature has reached 100°C, only a little $(CH_3)_2SnBr_2$ has been formed, indicated by a very weak signal ③ appearing between the $(CH_3)_3SnBr$ ① and the CH_3SnBr_3 ② signals (Fig. 3). It was necessary to keep the sample at 100° for 24 h to obtain complete redistribution into $(CH_3)_2SnBr_2$. It is evident that, compared with the analogous reaction of the methyltin chlorides, the redistribution between $(CH_3)_3SnBr$ and CH_3SnBr_3 proceeds much more slowly. This is also confirmed by the fact that after complete reaction, no $(CH_3)_3SnBr$ can be found.

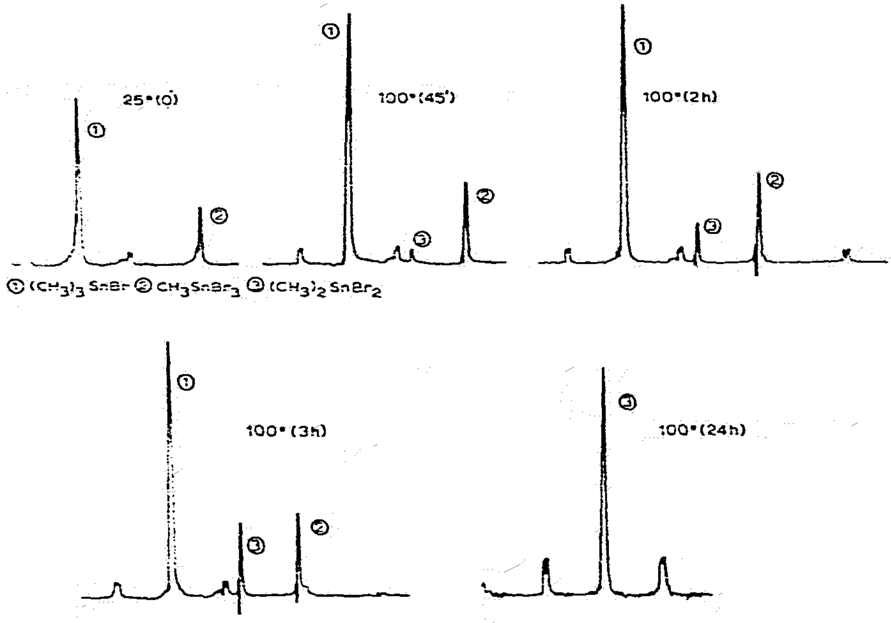


Fig. 3. Redistribution of $Sn(CH_3)_4$ and $SnBr_4$ in molar ratio 1:1.

2. *$(CH_3)_3SnBr$ and CH_3SnBr_3 in molar ratio 1:1.* A pure mixture of equimolecular

amounts of $(CH_3)_3SnBr$ or CH_3SnBr_3 behaves as in the preceding experiment. Complete redistribution with formation of pure $(CH_3)_2SnBr_2$ was observed only on keeping the sample at 100°C for several hours.

3. $Sn(CH_3)_4$ and $SnBr_4$ in molar ratio 3:1 (Fig. 4). In the NMR spectrum of this mixture at 25°C we observed three main signals which must be ascribed to $Sn(CH_3)_4$, $(CH_3)_3SnBr$ and CH_3SnBr_3. The relative intensity of the signal indicate that $(CH_3)_3$-SnBr and CH_3SnBr_3 have been formed in equimolecular amounts leaving some $(CH_3)_4Sn$ in excess. This was not observed for the methyltin chlorides and must be caused by the lower reaction rate for the redistributions between the methyltin bromides.

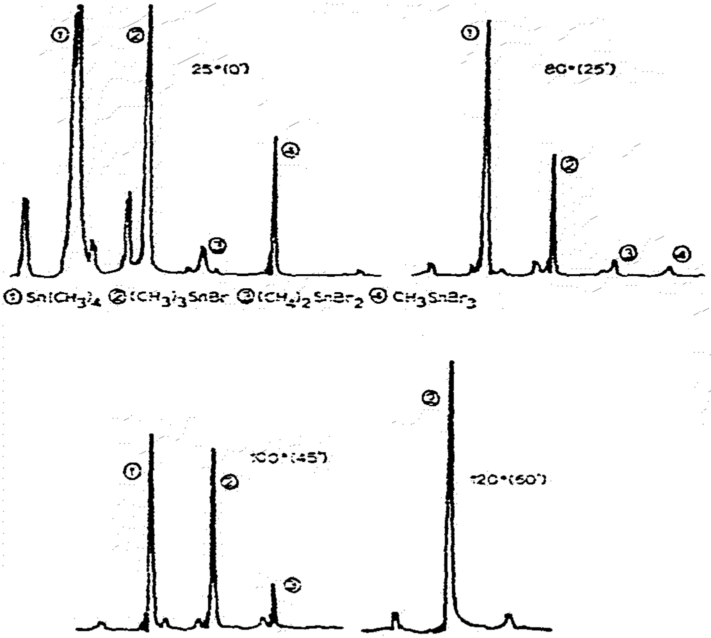


Fig. 4. Redistribution of $Sn(CH_3)_4$ and $SnBr_4$ in molar ratio 3:1.

When the temperature was raised to 120°C, further redistribution is in complete agreement with the successive reactions (a2) and (a3). First, the CH_3SnBr_3 signal gradually disappears, strong signals remaining for $(CH_3)_4Sn$ and $(CH_3)_3SnBr$; the $(CH_3)_2SnBr_2$ signal first slightly increases and then decreases. Finally, only the $(CH_3)_3SnBr$ signal remains.

4. $(CH_3)_2SnBr_2$ in an excess $Sn(CH_3)_4$. During the temperature rise from 25° to 120°C no redistribution to $(CH_3)_3SnBr$ was observed. This could only be completed after heating the sample for 24 h at 120°C.

C. The methyltin iodides

The previous results indicate that redistribution between the methyltin iodides must be very slow or may not even proceed at all. This then is probably the reason why these redistributions are not mentioned by Kozeschkow. We investigated, therefore, the behaviour of an equimolecular mixture of $(CH_3)_3SnI$ and CH_3SnI_3 and of $(CH_3)_2SnI_2$ in $Sn(CH_3)_4$.

In the first case, we observed that redistribution started only above 140°. At this temperature, redistribution to $(CH_3)_2SnI_2$ was complete after 12 h. In the second-case, we observed the beginnings of redistribution after 24 h at 120°, and only after several days at the same temperature, had all the reactants disappeared with formation of $(CH_3)_3SnI$.

CONCLUSION

The proposed reaction mechanism for the formation of R_3SnX and R_2SnX_2 compounds by the reaction of R_4Sn with SnX_4 ($X = Cl, Br$) was followed and confirmed by means of changes in the NMR spectra.

The rate of redistribution decreases in the sequence: chlorides > bromides > iodides. Combined with the investigations on the redistribution of ethyltin and butyltin chlorides these results show that the rate of redistribution between alkyltin halides decreases with increasing radius of the halogen atom and increasing length of the carbon chain in the alkylgroup.

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SUMMARY

Redistribution reactions were studied by PMR methods for mixtures of $Sn(CH_3)_4$ with SnX_4($X = Cl, Br, I$), for different molar ratios. Reaction mechanisms were proposed and could be confirmed by studying other mixtures containing, apart from the starting material, also one of the reaction products $(CH_3)_nSnX_{4-n}$. The rate of redistribution decreases in the sequence: chlorides > bromides > iodides.

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