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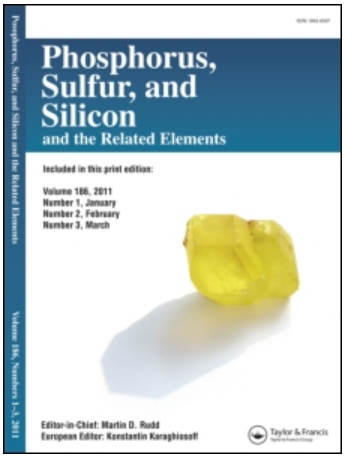

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Synthesis of Trimesitylpseudohalostannane, $(Mes)_3SnX$, (Mes=Mesityl: × =OCN, N_3, CN and SCN) by Reaction of $(Mes)_3SnCl$ with Alkaline Metal Pseudohalides in the Presence of Crown Ethers

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A solid-liquid substitution reaction of $(Mes)_3SnCl$ with MX (Mes = mesityl: × = OCN, N_3, CN and SCN: M=Na or K) was carried out in the presence of one of three crown ethers (18-crown-6, 15-crown-5, and 12-crown-4) as well as in the absence of them, using *n*- hexane as a solvent at 25°C. The reaction attained equilibrium in a shorter period in the presence of the crown ethers than in the absence of them, except the reaction with KCN. The extent of the substitution was dependent on X, but nearly independent on the kind of the three crown ethers.

Keywords: solid-liquid reaction; trimesitylpseudohalostannane; crown ethers; phase transfer catalysis

INTRODUCTION

There is a problem of dissolving together two mutually insoluble

reagents in considerable concentration to obtain rapid reaction rates in synthetic process. One solution to the problem is to find a proper solvent which can dissolve both reagents.[1] Use of phase transfer catalysis is another solution.[2] Crown ethers act not only as a good chelating agent for the alkaline metal ions but also as a phase-transfer catalysis.[3] We encountered the above problem in synthesizing trimesitylpseudohalogermanes according to the equation;

$$(Mes)_3GeCl\ (solution) + MX(solid) \rightarrow (Mes)_3GeX\ (solution) + MCl(solid)$$

However, the solid-liquid substitution reaction of $(Mes)_3GeCl$ with alkaline metal pseudohalides, MX, (M=Na or K) proceeded by using 18-crown 6-ether as a phase transfer catalysis.[4] In this paper, we describe the synthesis of the title pseudohalostannanes by a solid-liquid substitution reaction of $(Mes)_3SnCl$ with MX in the presence of crown ethers (18-crown-6, 15-crown-5 or 12-crown-4).

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EXPERIMENTAL

Preparation of chlorotrimesitylstannane, $(Mes)_3SnCl$

A dry tetrahydrofuran (THF) solution (mesityl bromide (58.1 g, 0.29 mol) +THF 50 ml) was slowly added dropwise to a mixture of Mg (9.56 g, 0.39 mol) and dry THF (180 ml) at 80 ℃ under N_2 atmosphere. The suspension was further refluxed at 80 ℃ for an hour. The resulting Grignard reagent solution was added to an ice-cooled toluene solution ($SnCl_4$ (16.0 g, 0.062 mol) + dry toluene 100 ml) without exposure to the air. The mixture was refluxed at 80 ℃ for 8 hours under nitrogen atmosphere. 6 M HCl(30 ml) was added to the mixture. The formed precipitate was separated by suction and ether(100 ml) was added to the filtrate. The ether of the separated upper layer was evaporated and the precipitate was dissolved into toluene(200 ml). The solution was allowed to stand overnight over Na_2SO_4 to remove H_2O. The toluene

was evaporated by suction after separation of Na_2SO_4. The resulting deposit was solved into toluene(200 ml) and was let stand overnight at -20 ℃ in a refrigerator, forming white crystalline solid (25.4 g). The yield was 80.5%. Anal. calcd. (%) for $C_{27}H_{33}SnCl$: C 63.37, H 6.50: found: C 64.29 , H 6.55. : m. p., 170-172 ℃.

A solid-liquid substitution reaction of $(Mes)_3SnCl$ with MX (X= OCN, N_3, CN and SCN)

Chlorotrimesitylstannane(102mg, 0.2 mmol) was added to *n*- hexane(50 ml) containing MX (2 mmol) and one of the crown ethers (0.1 mmol). The suspension was mixed mechanically at 25 ℃ and an aliquot of it (1 ml) was withdrawn from the suspension in1, 2, 3, 4, 5 and 24 hours. The crown ether, MX and MCl were separated from the sample solution by extraction with water(5 ml). The sample solution treated above was subjected to high- performance liquid chromatography(HPLC) to determine $(Mes)_3SnX$ and $(Mes)_3SnCl$. An HPLC apparatus used was a Schimadzu LC-10A. The conditions were as given below: column, Inert SIL, 5 μ m, 150 mm x 4.6 mm i.d.; mobile phase, THF/*n*-hexan, (5/95); flow rate, 0.5 ml/min; temperature, 40 ℃; detection, UV(240 nm).

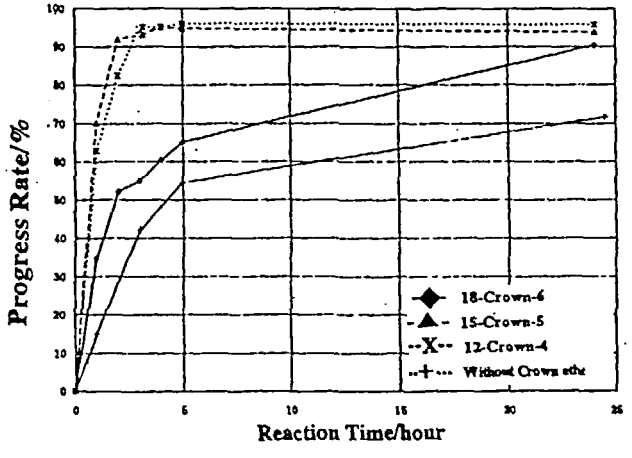

FIGURE 1. Reaction of $(Mes)_3SnCl$ with KOCN

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RESULTS AND DISCUSSION

The retention times of five stannanes, $(Mes)_3SnCl$ and $(Mes)_3SnX$ (X= OCN, N_3, CN and SCN) were 5.65, 6.13, 6.40, 7.51 and 6.20 min, respectively, under the conditions used in the measurement of HPLC. This permits the exact measurement of peak areas of the reactant and the product. The five stannanes were found to have the nearly equal value of a molar absorption coefficient at 240 nm in the used effluent. Therefore, the relative concentration of the reactant and the product can be estimated on the basis of the peak area of the chromatogram. The chromatogram of the reaction solutions had two peaks of $(Mes)_3SnCl$ and one of four $(Mes)_3SnX$'s. This suggests that no side reaction occurred in the solid-liquid substitution reaction.

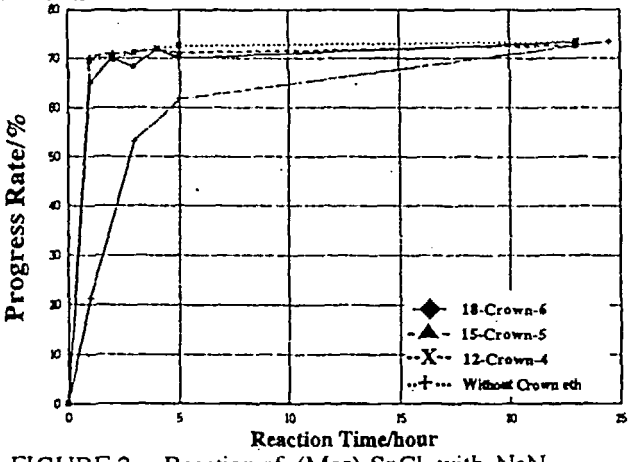

FIGURE 2. Reaction of $(Mes)_3SnCl$ with NaN_3

The solid-liquid substitution reaction of $(Mes)_3SnCl$ with MX (X= OCN, N_3, CN and SCN) was carried out in the presence of one of three crown ethers(18-crown-6,15-crown-5 and12-crown-4) as well as in the absence of the crown ethers. In the course of the reaction, an aliquot of the reaction solution was taken and the concentration of the reactant and the product was determined by HPLC. Figures1-4 show the relationship

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between the reaction time and progress rate of the reaction. The progress rate of the reaction was calculated according to the following equation;

The progress rate=peak area of $(Mes)_3SnX$/(peak area of$(Mes)_3SnX$ + peak area of $(Mes)_3SnX$) x 100.

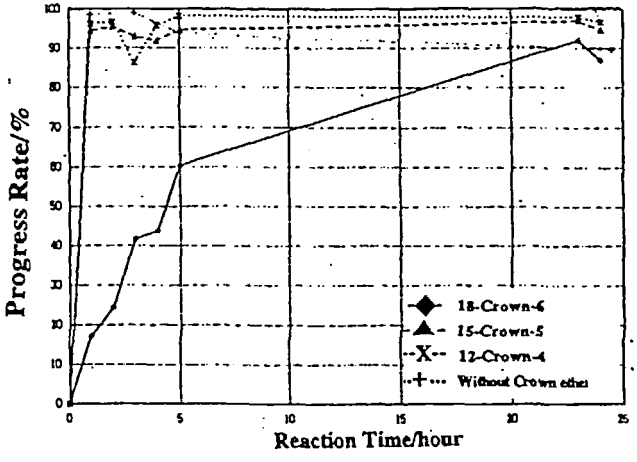

FIGURE 3. Reaction of $(Mes)_3SnCl$ with KCN

As Figs.1 and 2 show, in the case of the reactions with KOCN and NaN_3 each reaction attained equilibrium in a shorter period in the presence of the three crown ethers than in the absence of them. The reaction proceeded rapidly not only in the presence of 15-crown-5 and 12-crown-4 but also in the absence of them and slowly in the presence of 18-crown-6 in the case of the reaction with KCN, as shown in Fig.3. As Fig.4 shows, the reaction of $(Mes)_3SnCl$ with KSCN proceeded to a lesser extent even in the presence of the crown ethers. The progress rate of each reaction was found to be dependent on the pseudohalide, X, and to be nearly independent on the kind of the three crown ethers. Table 1 summarizes the best progress rate of each reaction along with that of the reaction of $(Mes)_3GeCl$ with MX.[4] The latter reaction was carried out in the presence of 18-crown-6 only.

Since stability constants of K^+ ion with the three crown ethers and those of Na^+ ion in methanol become greater as their ring sizes

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TABLE 1 The best progress rate of $(Mes)_3SnX$and $(Mes)_3GeX$

Compound	Progress rate(%)	Catalysis	Compound	Progress rate(%)	Catalysis
$(Mes)_3SnOCN$	96	12-crown-4	$(Mes)_3GeOCN$	86	18-crown-6
$(Mes)_3SnN_3$	72	12-crown-4	$(Mes)_3GeN_3$	90	18-crown-6
$(Mes)_3SnCN$	96	no use	$(Mes)_3GeCN$	91	18-crown-6
$(Mes)_3SnSCN$	28	12-crown-4	$(Mes)_3GeSCN$	91	18-crown-6

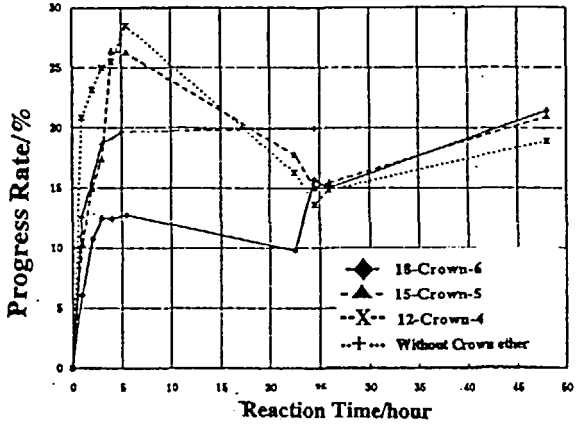

FIGURE 4. Reaction of $(Mes)_3SnCl$ with KSCN

increase, 18-crown-6 is expected to function most effectively.[3] On the contrary, 12-crown-4 acted rather better than the other crown ethers in the reaction of $(Mes)_3SnCl$ with MX (X=OCN, N_3 and SCN). This may be responsible for a difference in polarity of solvents since *n*-hexane used in the reaction is much less polar than methaol.

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