

REDISTRIBUTION REACTIONS WITH GROUP IV METAL
COMPOUNDS IN DIMETHYLSULFOXIDE (DMSO)

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Redistribution reactions of Group IV organometallic compounds are widely used for preparative purposes but are often complicated by undesired side reactions and not completely understood (1).

A typical example is the number of publications on the difficult preparation of trialkyltin halides (2-6).

Our initial results show clearly the retarding effect of a complexing solvent and describe a new preparative method.

EXPERIMENTAL

1. Methyltin trichloride-DMSO complex: 10.985 g $(\text{CH}_3)_2\text{SnCl}_2$ (50 mmoles) were suspended in 50 ml DMSO and cooled with ice water. To this was added dropwise a solution of 13.027 g SnCl_4 (50 mmoles) in approx. 20 ml DMSO. The mixture was refluxed for 24 hrs. and after addition of benzene to the clear solution the complex $\text{CH}_3\text{SnCl}_3 \cdot 2\text{DMSO}$ crystallized. The crude material (yield > 90%) is recrystallized from hot ethanol and chloroform or ether.

Calculated for $\text{C}_5\text{H}_{15}\text{Cl}_3\text{O}_2\text{S}_2\text{Sn}$ m.p. = 188-190°

	C 15.1	H 3.8	Cl 26.8	S 16.2	Sn 29.9
Found	14.8	3.7	25.6	15.9	28.5
	13.8	3.5	27.1	16.5	27.1

2. Triphenyllead chloride (Ph₃PbCl): 1.372 g Ph₄Pb (2.662 mmoles) and 1.151 g Ph₂PbCl₂ were stirred in 20 ml DMSO at 95° for 24 hrs. Unreacted Ph₄Pb (1.1364 g = 2.204 mmoles) was filtered off and 0.7028 g (1.194 mmoles) of Ph₂PbCl₂·2DMSO crystallized from the filtrate upon cooling. From the clear supernatant solution 0.3766 g (0.795 mmoles) Ph₃PbCl was precipitated by addition of 50 ml of water, corresponding to 15% conversion.

3. Cyclohexyltin compounds (Cy = cyclohexyl): All reactions of Table I were carried out by mixing the reactants in approx. 1/100 molar amounts and stirring the slurries under nitrogen at the indicated temperatures. Excess SnCl₄ was distilled at room temperature and ca. 10⁻² torr, together with CyCl. SnCl₂ remained insoluble after addition of benzene to the residue. The benzene was evaporated from the filtrate at room temperature. Ethanol added to the residue leaves Cy₄Sn insoluble. Cy₃SnCl crystallized from the hot alcohol solution upon cooling while Cy₂SnCl₂ was obtained after evaporation of the ethanol and recrystallization from petroleum ether.

In the presence of DMSO, Cy₃SnCl crystallized first, addition of ethanol precipitates SnCl₄·2DMSO and slow evaporation in a stream of nitrogen affects crystallization of Cy₂SnCl₂·2DMSO.

Identification of the isolated reaction products was carried out by infrared analysis and differential thermal analysis.*

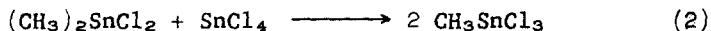
DISCUSSION

Despite an equilibrium constant (6) of

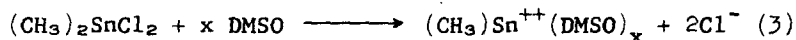
$$[(\text{CH}_3)_2\text{SnCl}_2][\text{SnCl}_4]/[\text{CH}_3\text{SnCl}_3]^2 = 7 \times 10^{-2} \quad (1)$$

*H. G. Langer and T. P. Brady, to be published.

pure CH_3SnCl_3 has never been obtained via the redistribution reaction. Kinetic effects cannot explain the successful isolation of $\text{CH}_3\text{SnCl}_3 \cdot 2\text{DMSO}$ in our laboratory. Based on previous work (1,5) the rate of the reaction



should be fast compared with the duration of the experiment. Neumann (5) postulated an enhanced reaction rate in polar solvents with increased nucleophilicity of SnCl_4 by adduct formation. Kitching (7) suggests the dissociation



which might lead to the ion pair $[(\text{CH}_3)_2\text{Sn}^{++}(\text{DMSO})_x][\text{SnCl}_6^{--}]$ with subsequent rearrangement to the product. Both effects could be important for the initial part of the reaction. The successful isolation of the complex, however, must be due to either (or both):-
 (a) a reduction of the vapor pressure of SnCl_4 in DMSO which would retard the disproportionation of CH_3SnCl_3 ; (b) the low solubility of the complex which removes it from the equilibrium and drives the reaction to completion.

The low yield of Ph_3PbCl from Ph_4Pb and Ph_2PbCl_2 in DMSO compared with an 86% yield obtained in 18 hours with refluxing butanol by Austin (8) also indicates that thermodynamic rather than kinetic factors are important, even though one might invoke a decreased nucleophilicity of Ph_2PbCl_2 by complex formation in DMSO. It is more reasonable to assume a shift in the equilibrium

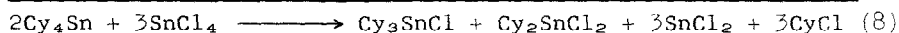
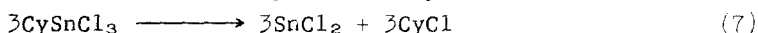
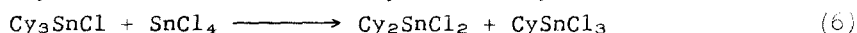
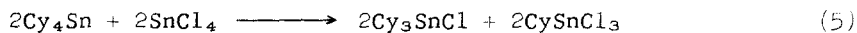
$$[\text{Ph}_4\text{Pb}][\text{Ph}_2\text{PbCl}_2 \dots x \text{DMSO}] [\text{Ph}_3\text{PbCl} \dots x \text{DMSO}]^2 > 1 \quad (4)$$

because of a weak interaction between DMSO and Ph_3PbCl (weaker acidity or possibly steric hindrance) and a much stronger interaction between DMSO and Ph_2PbCl_2 . This interaction might be a solvate formation, but does not necessarily require the existence of a stable complex in solution.

TABLE I
REACTION YIELDS (neat)

Moles Cy ₄ Sn+SnCl ₄		Temp. [°C.]	Time [hrs.]	Moles Cy ₄ Sn+Cy ₃ SnCl+Cy ₂ SnCl ₂ +SnCl ₂		
1	1	190	20	0.5	0	>0.5
1	1	120	20	0.5	0.2	0.8
3	1	140	20	2	1	0
1	3	140	20		0.8	1.6
1	6	100	1			
		140	2			
		25	16	0.5	0.5	1.5

Steric effects, if important, should be even more pronounced for cyclohexyl compounds. Thermal decomposition of CySnCl₃ strongly affects the yield and composition of the final reaction products. The course of the reaction between Cy₄Sn and SnCl₄ is clearly demonstrated by the fifth experiment in Table I which proceeds according to:



The presence of Cy₃SnCl and SnCl₄ at the termination of the experiment clearly points out that the two compounds react very slowly at room temperature if at all. The presence of Cy₂SnCl₂ in experiments 3 and 4 and the large amount of SnCl₂ formed is conclusive evidence for (6) and (7) to proceed at elevated temperatures.

TABLE II
REACTION YIELDS (DMSO)

Moles Cy ₄ Sn+SnCl ₄		Temp. [°C.]	Time [hrs.]	Moles Cy ₃ SnCl+Cy ₂ SnCl ₂	
1	1	200	120	0.3	
1	3	170	72	very little	

TABLE III
SOLVENT EFFECTS

Moles Cy ₂ SnCl ₂ +SnCl ₄		Temp. [°C.]	Time [hrs.]	Solvent	Result
1	1	135	48	DMSO	No reaction
1	1	150	24	TMSO	No reaction
1	1	120	72	POCl ₃	No reaction
1	3	120	72	SnCl ₄	No reaction

Whereas, Neumann (5) finds that POCl_3 promotes the reaction between SnCl_4 and $(\text{C}_2\text{H}_5)_2\text{SnCl}_2$, we find (Tables II and III) that polar, ionizing, or complexing solvents apparently inhibit the nucleophilic attack of SnCl_4 on Cy_4Sn and Cy_2SnCl_2 . No reaction whatsoever between Cy_4Sn and SnCl_4 in DMSO was observed below 170° . In tetramethylenesulfoxide (TMSO) at 150° and in a mixture of xylene and DMSO at 140° also no reaction took place.

No evidence was found that Cy_2SnCl_2 and SnCl_4 react in any solvent including POCl_3 . Even if only small amounts of CySnCl_3 had been formed and immediately decomposed it would have been detected by the presence of SnCl_2 or CyCl .

In summary DMSO can play an important role in the preparation of organometallic compounds via the redistribution reaction. Care should be taken, however, to differentiate between the effects of complexing solvents on the kinetics and those on the thermodynamics of such reactions.

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