Tetrahedron Letters No.1, pp. 43-47, 1967. Pergamon Press Ltd.
Printed in Great Britain.

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

Horst G. Langer
The Dow Chemical Company
Eastern Research Laboratory
Wayland, Massachusetts

(Received 5 October 1966)

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 $(CH_3)_2SnCl_2$ (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 $CH_3SnCl_3\cdot 2DMSO$ crystallized. The crude material (yield > 90°/₀)is recrystallized from hot ethanol and chloroform or ether.

Calculated for $C_5H_{15}Cl_3O_2S_2Sn$ m.p. = 188-190°

	C	H	Cl	S	Sn
Calculated	15.1	3.8	26.8	16.2	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 (Ph_3PbCl): 1.372 g Ph_4Pb (2.662 mmoles) and 1.151 g Ph_2PbCl_2 were stirred in 20 ml DMSO at 95° for 24 hrs. Unreacted Ph_4Pb (1.1364 g = 2.204 mmoles) was filtered off and 0.7028 g (1.194 mmoles) of $Ph_2PbCl_2 \cdot 2DMSO$ crystallized from the filtrate upon cooling. From the clear supernatent solution 0.3766 g (0.795 mmoles) Ph_3PbCl was precipitated by addition of 50 ml of water, corresponding to 15°/o 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 $SnCl_4$ was distilled at room temperature and ca. 10^{-2} torr, together with CyCl. $SnCl_2$ 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 Cy_4Sn insoluble. Cy_3SnCl crystallized from the hot alcohol solution upon cooling while Cy_2SnCl_2 was obtained after evaporation of the ethanol and recrystallization from petroleum ether.

In the presence of DMSO, Cy_3SnCl crystallized first, addition of ethanol precipitates $SnCl_4 \cdot 2DMSO$ and slow evaporation in a stream of nitrogen affects crystallization of $Cy_2SnCl_2 \cdot 2DMSO$.

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

DISCUSSION

Despite an equilibrium constant (6) of

$$[(CH_3)_2SnCl_2][SnCl_4]/[CH_3SnCl_3]^2 = 7 \times 10^{-2} \qquad (1)$$

---

[*] 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 $CH_3SnCl_3 \cdot 2DMSO$ in our laboratory. Based on previous work (1,5) the rate of the reaction

$$(CH_3)_2SnCl_2 + SnCl_4 \longrightarrow 2\ CH_3SnCl_3 \qquad (2)$$

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

$$(CH_3)_2SnCl_2 + x\ DMSO \longrightarrow (CH_3)Sn^{++}(DMSO)_x + 2Cl^- \qquad (3)$$

which might lead to the ion pair $[(CH_3)_2Sn^{++}(DMSO)_x][SnCl_6^{--}]$ 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°/₀ 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

$$[Ph_4Pb][Ph_2PbCl_2\ \ldots\ x\ DMSO]\ [Ph_3PbCl\ \ldots\ x\ DMSO]^2 > 1 \qquad (4)$$

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		Temp. [°C.]	Time [hrs.]	Moles			
Cy_4Sn	$+SnCl_4$	→		Cy_4Sn	$+Cy_3SnCl$	$+Cy_2SnCl_2$	$+SnCl_2$
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
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 $CySnCl_3$ strongly affects the yield and composition of the final reaction products. The course of the reaction between Cy_4Sn and $SnCl_4$ is clearly demonstrated by the fifth experiment in Tablê I which proceeds according to:

$$2Cy_4Sn + 2SnCl_4 \longrightarrow 2Cy_3SnCl + 2CySnCl_3 \qquad (5)$$

$$Cy_3SnCl + SnCl_4 \longrightarrow Cy_2SnCl_2 + CySnCl_3 \qquad (6)$$

$$3CySnCl_3 \longrightarrow 3SnCl_2 + 3CyCl \qquad (7)$$

$$2Cy_4Sn + 3SnCl_4 \longrightarrow Cy_3SnCl + Cy_2SnCl_2 + 3SnCl_2 + 3CyCl \qquad (8)$$

The presence of Cy_3SnCl and $SnCl_4$ 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 Cy_2SnCl_2 in experiments 3 and 4 and the large amount of $SnCl_2$ formed is conclusive evidence for (6) and (7) to proceed at elevated temperatures.

TABLE II
REACTION YIELDS (DMSO)

Moles		Temp. [°C.]	Time [hrs.]	Moles	
Cy_4Sn	$+SnCl_4$			Cy_3SnCl	$+Cy_2SnCl_2$
1	1	200	120		0.3
1	3	170	72	very little	

TABLE III
SOLVENT EFFECTS

Moles		Temp. [°C.]	Time [hrs.]	Solvent	Result
Cy_2SnCl_2	$+SnCl_4$				
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 $(C_2H_5)_2SnCl_2$, 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.

ACKNOWLEDGEMENT - The experimental work carried out by Mrs. A. H. Blut and Mr. T. F. Brady is gratefully acknowledged.

REFERENCES

1. K. Moedritzer, Organometal. Chem. Rev., 1, 179 (1966).
2. W. J. Jones, W. C. Davies, S. T. Bowden, C. Edwards, V. E. Davis, and L. H. Thomas, J. Chem. Soc., 1947, 1446
3. K. A. Kozeschkow, Ber., 66, 1661 (1933).
4. J. G. A. Luijten, and G. J. M. van der Kerk, "Investigation in the Field of Organotin Chemistry", Tin Research Institute, Middlesex (England), 1955, pp. 48, 103.
5. W. P. Neumann, and G. Burkhardt, Ann., 663, 11 (1963).
6. D. Grant and J. R. van Wazer, J. Organometal. Chem., in press.
7. W. Kitching, Tetrahedron Letters, 31, 3689 (1966).
8. P. R. Austin, J. Am. Chem. Soc., 54, 3287 (1932).