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Preliminary communication

A NOVEL SYNTHETIC ROUTE TO DIORGANOTIN DICHLORIDES AND DIBROMIDES

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Summary

Diorganotin dichlorides and dibromides can be prepared by a simple and convenient one-step process involving the reaction of Grignard reagent with $(Acac)_2SnX_2$ (AcacH = pentane-2,4-dione; X = Cl or Br). The yields of lower diorganotin dihalides are excellent while those of higher diorganotin dihalides are moderate.

Diorganotin dihalides and their derivatives find extensive applications in the laboratory as well as in industry especially as poly(vinyl chloride) stabilisers [1] and as fungicides and insecticides [2]. The laboratory procedure for the synthesis of diorganotin dihalides involves first the preparation of tetraorganotin compounds, R_4Sn, and then disproportionation with $SnCl_4$ at higher temperatures [3]. Although well established, this method is very time consuming. We report here a general and a very simple method for the synthesis of various diorganotin dichlorides and dibromides which involves the reaction between $(Acac)_2SnX_2$ (AcacH = pentane-2,4-dione; X = Cl or Br) and the appropriate Grignard reagent.

When a benzene solution of $(Acac)_2SnX_2$ is treated with a 2 molar proportion of a Grignard reagent in ether/benzene a mild exothermic reaction rapidly takes place to give the corresponding diorganotin dihalides, as in eq. 1.

$$(Acac)_2SnX_2 + 2\ RMgX \rightarrow R_2SnX_2 + 2\ AcacMgX \qquad (1)$$

The reaction is completed by refluxing for 2—3 hours. The precipitated AcacMgX is filtered off, solvents are removed from the filtrate by distillation, and the product is isolated by vacuum distillation. The reaction is in fact about 75% complete at room temperature, and refluxing only marginally improves the yield. The results are summarised in Table 1.

Initial experiments show that the reaction is applicable to the synthesis

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TABLE 1

SYNTHESIS OF DIORGANOTIN DIHALIDES BY THE ACTION OF RMgX ON $(Acac)_2SnX_2$.

	RMgX	$(Acac)_2SnX_2$	R_2SnX_2	Yield (%)
1	EgMgBr	$(Acac)_2SnBr_2$	Et_2SnBr_2	93
2	n-PrMgCl	$(Acac)_2SnCl_2$	n-Pr_2SnCl_2	74.5
3	i-PrMgCl	$(Acac)_2SnCl_2$	i-Pr_2SnCl_2	57
4	n-PrMgBr	$(Acac)_2SnBr_2$	N-Pr_2SnBr_2	87
5	n-PrMgBr	$(Acac)_2SnBr_2$	n-Pr_2SnBr_2	69 [a]
6	i-PrMgBr	$(Acac)_2SnBr_2$	i-Pr_2SnBr_2	69
7	n-BuMgCl	$(Acac)_2SnCl_2$	n-Bu_2SnCl_2	52
8	i-BuMgBr	$(Acac)_2SnBr_2$	i-Br_2SnBr_2	60
9	PhMgBr	$(Acac)_2SnBr_2$	Ph_2SnBr_2	60

[a] Yield at room temperature.

of dialkyl- and diaryltin dichlorides and dibromides. The yields of alkyltin compounds are generally higher than those of aryl derivatives. Lower alkyl-Grignards give almost quantitative yields of R_2SnX_2 but lower yields are obtained from the higher alkyl-Grignards. Similarly, n-alkyl-Grignards give better yields of dialkyltin dihalides than branched alkyl-Grignards. Finally, the yields of diorganotin dibromides are better than those of the dichlorides.

Exchange of halide between MgX and SnX′ takes place when X and X′ are different. Thus, EtMgBr reacts with $(Acac)_2SnCl_2$ to give Et_2SnBr_2 and $Et_2SnClBr$. The products were identified in the mixture without isolation by NMR and mass spectra; the absence of Et_2SnCl_2 is noteworthy. Similarly, Ph_2SnBr_2 and $Ph_2SnClBr$ are formed in the reaction between PhMgBr and $(Acac)_2SnCl_2$.

The easy availability of $(Acac)_2SnX_2$ (X = Cl, Br) [4] and its hydrolytic stability in contrast to $SnCl_4$ make it a very useful starting material for the synthesis of various organotin compounds. It should also be noted that the reaction between SnX_4 and RMgX in 1/2 molar ratio gives only a mixture of $R_nSnX_{(4-n)}$ (n = 1—4) [5], whereas the reaction reported herein gives a single product in a clean reaction.

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