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NOTE

THE CLEAVAGE OF TIN–OXYGEN AND TIN–SULFUR BONDS BY ORGANOLITHIUM REAGENTS

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INTRODUCTION

Organostannoxanes are known to be cleaved by Grignard reagents or sodium acetylide to form tin–carbon bonds[1]. Methyllithium and trimethyltin oxide are reported to react to form tetramethyltin[2]. The same reagent in the presence of trimeric dimethyltin sulfide cleaves the tin–sulfur bond to yield tetramethyltin[3]. Since no systematic study of the cleavage of tin–oxygen or tin–sulfur bonds has been carried out to date we felt it would be worthwhile to investigate the reactions of methyllithium, n-butyllithium, phenyllithium and several lithium acetylides with a series of compounds containing tin–oxygen and tin–sulfur bonds. This paper reports the results of our study.

RESULTS AND DISCUSSION

We have treated the following organotin compounds with organolithium reagents: $(R_3Sn)_2X$ and $(R_2SnX)_n$ where $R = n\text{-}C_4H_9$ and C_6H_5 and X = oxygen and sulfur. Inorganic tin dioxide and tin disulfide, which have Sn–O–Sn or Sn–S–Sn bonds in common with the organotin oxides and sulfides, were also included in this group of compounds for study. In addition organotin compounds of the types $R_{4-n}Sn(OR')_n$ where $R = n\text{-}C_4H_9$, C_6H_5 and $R' = H$, $(CH_3)_2CH$ and $CH_3C(O)$ were also studied. The results of this investigation are shown in Table 1.

The reaction of the stannoxanes and their sulfur analogues with lithium reagents can best be interpreted by a stepwise reaction:

$$R_3SnXSnR_3 + R'Li \rightarrow R_3SnR' + R_3SnXLi$$
$$R_3SnXLi + R'Li \rightarrow R_3SnR' + Li_2X$$

Several conclusions may be reached in regard to the reaction of lithium reagents with tin–oxygen and tin–sulfur bonds. The solubility of the organotin compounds in the organic solvent is an important factor determining the yield. The highly soluble starting materials gave nearly quantitative results. The reactivity of the organolithium reagents appears to have little influence. Thus, methyllithium and n-butyllithium react with di-n-butyltin oxide in diethylether to yield about 60% of the corresponding

TABLE 1

	Reagent	Ratio	Temp.[a]	Solvent	Product	Yield (%)
$(n\text{-}C_4H_9)_2SnO$	CH_3Li	1:2	RT	Et_2O	$(n\text{-}C_4H_9)_2Sn(CH_3)_2$	60
	$n\text{-}C_4H_9Li$	1:2	RT	Et_2O	$(n\text{-}C_4H_9)_4Sn$	62
	$n\text{-}C_4H_9Li$	1:2	RT	THF	$(n\text{-}C_4H_9)_4Sn$	80
	$CH_3C{\equiv}CLi$	1:2	Reflux	THF	$(n\text{-}C_4H_9)_2Sn(C{\equiv}CCH_3)_2$	47
$[(n\text{-}C_4H_9)_2SnS]_3$	$n\text{-}C_4H_9Li$	1:6	RT	Et_2O	$(n\text{-}C_4H_9)_4Sn$	92
	$CH_3C{\equiv}CLi$	1:6	Reflux	THF	$(n\text{-}C_4H_9)_2Sn(C{\equiv}CCH_3)_2$	71
	$C_6H_5(CH_2)_2C{\equiv}CLi$	1:6	Reflux	THF	$(n\text{-}C_4H_9)_2Sn[C{\equiv}C(CH_2)_2C_6H_5]_2$	60
$(C_6H_5)_2SnO$	C_6H_5Li	1:2	Reflux	THF	$(C_6H_5)_4Sn$	92
$[(n\text{-}C_4H_9)_3Sn]_2O$	CH_3Li	1:2	RT	Et_2O	$(n\text{-}C_4H_9)_3SnCH_3$	80
	$n\text{-}C_4H_9Li$	1:2	RT	Et_2O	$(n\text{-}C_4H_9)_4Sn$	94
$[(C_6H_5)_3Sn]_2O$	C_6H_5Li	1:2	RT	THF	$(C_6H_5)_4Sn$	99
$[(C_6H_5)_3Sn]_2S$	C_6H_5Li	1:2	RT	THF	$(C_6H_5)_4Sn$	95
$(C_6H_5)_3SnOH$	C_6H_5Li	1:2	Reflux	THF	$(C_6H_5)_4Sn$	85
SnO_2	C_6H_5Li	1:6	Reflux	Et_2O/C_6H_6	$(C_6H_5)_4Sn$	1.3
SnS_2 (amorphous)	C_6H_5Li	1:4	Reflux	THF	$(C_6H_5)_4Sn$	4
SnS_2 (crystalline)	C_6H_5Li	1:4	Reflux	THF	$(C_6H_5)_4Sn$	20
$(n\text{-}C_4H_9)_2Sn(OAc)_2$	$n\text{-}C_4H_9Li$	1:2	0°	Et_2O	$(n\text{-}C_4H_9)_4Sn$	80
$(iso\text{-}C_3H_7O)_4Sn$	C_6H_5Li	1:4	Reflux	THF	$(C_6H_5)_4Sn$	81

[a] RT = room temp. (20–25°); average reaction time = 4–5 h.

tetraalkyltin. The use of tetrahydrofuran increased the yield to about 80%.

Two samples of tin disulfide of different origin were treated with phenyllithium. The amorphous form gave only a 4% yield of tetraphenyltin whereas the crystalline form ("mosaic gold") under the same conditions resulted in a yield of 20%. Tin dioxide reacted with phenyllithium, to give a small amount of tetraphenyltin. An attempt to enhance the reactivity of phenyllithium using *N,N,N',N'*-tetramethylethylenediamine[4] and thus to obtain higher yields, was not successful.

In conclusion it can be seen that the reaction of organolithium reagents with organotin oxides and sulfides is a convenient route to a large variety of tetrasubstituted organotin compounds. Organotin oxides are readily available as starting materials and thus it is not necessary to use organotin halides using this route. This synthetic procedure also can be applied to the synthesis of organoalkynyltin compounds, a series of compounds which we have currently under study.

EXPERIMENTAL

All reactions were carried out under argon and anhydrous conditions. The chemicals used are commercially available and were purified by established methods. Gas chromatograms were recorded on an Aerograph Model A-700 with a six foot column packed with 30% SE-30. IR spectra were obtained with a Perkin–Elmer 137 spectrophotometer and NMR data on a Varian A-60. An Abbe 3L-Bausch and Lomb refractometer was used to determine the refractive indices. Molecular weights were determined with a Mechrolab Vapor pressure osmometer Model 301-A. Melting points (uncorrected) were obtained on a Thomas Hoover melting point apparatus.

General procedure

The organolithium reagent (n-butyllithium, 1.5 *M* in hexane; methyllithium, 1.7 *M* in diethyl ether or phenyllithium, 2.1 *M* in ether/benzene 30/70) was added at 0° or room temperature to the solution or suspension of the organotin oxide or sulfide and stirred for several hours. Reaction time, temperature and solvent are given in Table 1. The reaction mixture was filtered under argon through a glass frit and washed with ether. In cases where a large excess of organolithium reagent was used or where the reaction did not go to completion, the mixture was hydrolyzed and the organic layer dried with magnesium sulfate. The filtrate was concentrated and the crude product either distilled under reduced pressure or purified on a chromatographic column (neutral alumina), with a mixture of low boiling petroleum ether and benzene as eluent. The phenyllithium solution used in these reactions contained approximately 15% mineral oil. This oil could be separated from the product on the column by eluting first with low boiling petroleum ether. The products were identified by carbon and hydrogen analysis, molecular weight and comparison of their physical constants with those of authentic samples.

Bis(1-propynyl)di-n-butyltin, $(n\text{-}C_4H_9)_2Sn(C{\equiv}CCH_3)_2$

(*a*) *From di-n-butyltin sulfide.* Di-n-butyltin sulfide (13.3 g, 0.05 mole) was added dropwise to a stirred suspension of propynyllithium (4.6 g, 0.1 mole) at 0° in 250 ml anhydrous THF. The reaction mixture was allowed to come to room temperature and then heated to reflux for 3 h. The lithium sulfide was filtered under argon, washed

with 250 ml of anhydrous petroleum ether (b.p. 30°–60°) and the filtrate concentrated The remaining liquid was distilled under vacuum yielding 10.9 g (71%) of a colorless liquid b.p. 103° (0.3 mm), n_D^{27} 1.4920. (Found: C, 54.07; H, 7.97; mol.wt. (benzene), 309. $C_{14}H_{24}Sn$ calcd.: C, 54.06; H, 7.78%; mol.wt., 310.8.)

(*b*) *From di-n-butyltin oxide.* The reaction of propynyllithium with di-n-butyltin oxide in THF gave 47% bis(1-propynyl)di-n-butyltin. Reaction time: 17 h stirring at room temperature and 7 h at reflux temperature. All other conditions were similar to (*a*).

Bis(4-phenyl-1-butynyl)di-n-butyltin, $(n\text{-}C_4H_9)_2Sn[C{\equiv}C(CH_2)_2C_6H_5]_2$

A 4-phenyl-1-butynyllithium suspension was obtained by dropwise addition of 4-phenyl-1-butyne (2.68 g, 0.02 mole) to a stirred solution of 0.02 mole methyllithium in 150 ml diethyl ether at −70°. The mixture was then allowed to come to room temperature and diethyl ether was replaced with THF by distillation. To the resulting suspension, (2.75 g, 0.01 mole) di-n-butyltin sulfide in 150 ml THF was added at 0°. Reaction time: 22 h at room temperature and 4 h at reflux temperature. The lithium sulfide was filtered under argon after treatment with activated charcoal and washed with diethyl ether. The filtrate was concentrated and the remaining liquid distilled, 145° (0.2 mm). The yield was 3.05 g (60%); n_D^{25} 1.5444. (Found: mol.wt. (benzene), 478. $C_{28}H_{36}Sn$ calcd.: mol.wt., 491.) Satisfactory carbon-hydrogen analyses could not be obtained due to difficulties in purification and thermal instability. Repeated distillation did not improve the purity of this compound. The mol.wt., NMR and IR spectrum are in agreement with the assigned structure. For additional evidence, bis(4-phenyl-1-butynyl)di-n-butyltin was also synthesized from the lithium acetylide and di-n-butyltin dichloride and the product thus obtained had the same physical constants as the compound described above.

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