Easy General Method for Interhalide Conversions in Organotin Compounds

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Summary: The halides in organotin halides are easily interconverted in excellent yields using aqueous ammonium halide solutions and various organic solvents.

Introduction

Organotin halides are well-known compounds that have found extensive use within both academe and industry.[1−4] Most other functional organotin compounds such as organotin hydrides, alkoxides, amides, and carboxylates are prepared using the corresponding organotin halide as a starting material.[1]

A particular potential application of diorganotin dihalides is as antitumor agents.[2] The biological activity of diorganotin dihalides is found to vary with different halides.[2] It would therefore be extremely useful to be able to easily interconvert the halogens in an organotin compound.

Several investigations regarding the exchange of halides in organotin halides have been published. Tributyltin chloride and dibutyltin dichloride were converted into their respective bromides or iodides via a halogen exchange reaction with certain alkyl bromides or iodides (e.g., allyl bromide, dibromomethane, or iodoethane) in the presence of 5 mol % of the corresponding tetrabutylammonium halide as a catalyst.[5] Organotin bromides and iodides can also be prepared from the corresponding chlorides via metathesis with the appropriate sodium halide in acetone,[6,7] whereas the corresponding fluorides can be prepared by reaction with sodium or potassium fluoride in aqueous alcohol solution.[8]

While it is generally straightforward to exchange a lighter halogen with a heavier halogen on tin (the fluoride syntheses being a major exception), there are far fewer methods for replacing a heavy halogen with a lighter analogue. For example, organotin iodides can be converted to the corresponding chlorides via stirring with silver chloride in dry acetonitrile with the exclusion of light for 14 days.[9]

A few methods of converting some alkyltin fluorides into the corresponding chlorides and bromides have been published. Armitage and Tarassoli have reported the synthesis of tri-*n*-butyltin bromide in 88% yield via the direct reaction of triethylbromosilane and tri-*n*-butyltin fluoride.[10] Mitchell and co-workers[11] reported the use of sodium chloride or sodium bromide in anhydrous THF for the preparation of trialkyltin chlorides or bromides from the corresponding fluorides in yields ranging from 48 to 86% using reaction times between 3 and 5 days. It is noteworthy that their attempts to convert triphenyltin fluoride into the corresponding chloride or bromide were unsuccessful.

With the exception of the organotin fluoride syntheses, all of the previously described methods require the halide interconversions to be performed under anhydrous conditions, presumably to avoid hydrolysis of the organotin halides. Furthermore, some methods have the added disadvantages of involving either costly reagents[9,10] or lengthy reaction times.[9,11]

Surprisingly, there appear to be no reports concerning the use of ammonium halides nor any involving the use of aqueous conditions (other than for organotin fluoride syntheses[8]) for halogen exchange reactions at tin. We now describe a general method that enables (1) halogen interconversion within both aryl and alkyltin halides, (2) the exchange of any halide within an organotin halide with all other possible halides, and (3) performing these conversions both up and down group 17 by the use of saturated aqueous ammonium halide solutions as halide conversion agents. Of particular significance is the rapid conversion of triorganotin fluorides into the corresponding chlorides. Owing to their extremely low solubility in common organic solvents, organotin fluorides are usually formed as a means of removing organotin byproducts in both organic and organometallic syntheses. With the method reported here, it is now possible to recycle triorganotin fluorides easily and quickly via conversion into the corresponding chloride, bromide, or iodide.

Results and Discussion

While this study was performed using butyl and phenyl tin compounds as representative examples, these reactions can be utilized for most if not all other

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organotin halides. We have included three specific examples involving organotin halides containing organic groups other than butyl or phenyl (Table 1).

$$\underset{(\mathrm{R} = n\text{-Bu, Ph; X, Y = Cl, Br, I})}{\mathrm{R_3SnX + NH_4Y}} \xrightarrow[\text{rt}]{\mathrm{Et_2O/H_2O}} \mathrm{R_3SnY + NH_4X} \quad (1)$$

$$\underset{(\mathrm{R} = n\text{-Bu, Ph; Y = Cl, Br, I})}{\mathrm{R_3SnF + NH_4Y}} \xrightarrow[\text{reflux}]{\mathrm{THF/H_2O}} \mathrm{R_3SnY + NH_4F} \quad (2)$$

The reaction of triorganotin halides with saturated ammonium halide solutions in ether at room temperature affords the desired triorganotin halide in excellent yields within 2 h (eq 1). The conversion of triorganotin fluorides required a slightly different technique. The triorganotin fluoride was suspended in THF, combined with saturated ammonium halide solution, and heated to reflux until no insoluble material remained in the reaction mixture, indicating the completion of the reaction (eq 2). A reaction time of 1 h was sufficient to completely convert tributyl and triphenyltin fluoride into their respective chlorides, whereas 12 h was needed for the conversion of triphenyltin fluoride into triphenyltin bromide.

This technique can also be applied to diorganotin dihalides and organotin trihalides. As examples, we were able to convert diphenyltin dichloride, phenyltin trichloride, and butyltin trichloride into their respective bromides. However, while the ammonium bromide solution was sufficiently acidic to prevent hydrolysis during the course of the reaction, care must be taken during the workup. Washing the organic layer from the diphenyltin dibromide preparation with distilled water caused hydrolysis and the formation of an insoluble distannoxane.

Experimental Section

General Procedures. Method A. Approximately 500 mg of the starting organotin halide was dissolved in 5 mL of diethyl ether, 5−10 mL of a saturated aqueous solution of the appropriate ammonium halide was added, and the resulting reaction mixture was magnetically stirred. The aqueous layer was replaced twice with fresh ammonium halide solution at 1 h intervals. The organic layer was separated and dried over sodium sulfate. After filtration the solvent was removed in vacuo to give the desired organotin halide as a pure product (as checked by ^{119}Sn NMR). ^{119}Sn{^{1}H} NMR (111.85 MHz, $CDCl_3$): Ph_3SnCl δ −44.9; Ph_3SnBr δ −61.1; Ph_3SnI δ −113.5; Bu_3SnCl δ 141.2; Bu_3SnBr δ 142.1; Bu_3SnI δ 85.6; Ph_2SnBr_2 δ −72.4; Me_3SnBr δ 126.5.

Table 1. Reaction Conditions and Yields for the Interconversion of Halides in Various Organotin Halides

starting material	product	method	reaction time, h	isolated yield, %
Ph_3SnF	Ph_3SnCl	B	1	95
	Ph_3SnBr	B	12	97
	Ph_3SnI	B	12	96
Ph_3SnCl	Ph_3SnBr	A	2	97
	Ph_3SnI	A	2	95
Ph_3SnBr	Ph_3SnCl	A	2	98
	Ph_3SnI	A	2	97
Ph_3SnI	Ph_3SnCl	A	2	98
	Ph_3SnBr	A	2	95
Bu_3SnF	Bu_3SnCl	B	1	99
	Bu_3SnBr	B	4	96
	Bu_3SnI	B	4	98
Bu_3SnCl	Bu_3SnBr	A	2	96
	Bu_3SnI	A	2	99
Bu_3SnBr	Bu_3SnCl	A	2	95
	Bu_3SnI	A	2	97
Bu_3SnI	Bu_3SnCl	A	2	96
	Bu_3SnBr	A	2	97
Ph_2SnCl_2	Ph_2SnBr_2	A	2	94
$PhSnCl_3$	$PhSnBr_3$	C	2	98
$BuSnCl_3$	$BuSnBr_3$	C	2	95
Me_3SnCl	Me_3SnBr	A	2	94
$PhLR^*SnCl$[12, a]	$PhLR^*SnBr$[a,b]	A	2	87
$(IPh_2Sn)_2(CH_2)_5$	$(ClPh_2Sn)_2(CH_2)_5$	A	2	91

[a] L = [2-(1*S*)-1-Dimethylaminoethyl]phenyl; R* = (1*R*,2*S*,5*R*)-menthyl. [b] Mp 157 °C. Anal. Calcd for $C_{26}H_{38}SnNBr$: C, 55.4; H, 6.8; N, 2.5. Found: C, 55.8; H, 7.1; N, 2.4.

Method B. Approximately 1 g of the starting triorganotin fluoride was suspended in 15 mL of THF, and 40 mL of a saturated aqueous solution of ammonium halide was added. The resulting reaction mixture was stirred at reflux until both aqueous and organic layers were clear. The organic layer was separated and dried over sodium sulfate. After filtration the solvent was removed in vacuo to give the desired triorganotin halide as a pure product (as checked by ^{119}Sn NMR). ^{119}Sn{^{1}H} NMR (111.85 MHz, $CDCl_3$): Ph_3SnCl δ −45.1; Ph_3SnBr δ −61.3; Ph_3SnI δ −113.9; Bu_3SnCl δ 143.5; Bu_3SnBr δ 142.7; Bu_3SnI δ 85.4.

Method C. Approximately 500 mg of the starting organotin trichloride was dissolved in 10 mL of chloroform, 5−10 mL of a saturated aqueous solution of ammonium bromide was added, and the resulting reaction mixture was magnetically stirred. The aqueous layer was replaced twice with fresh ammonium bromide solution at 1 h intervals. The organic layer was separated and dried over sodium sulfate. After filtration the solvent was removed in vacuo to give the desired organotin tribromide as a pure product (as checked by ^{119}Sn NMR). ^{119}Sn{^{1}H} NMR (111.85 MHz, $CDCl_3$): $BuSnBr_3$ δ −141.7; $PhSnBr_3$ δ −227.1.

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