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CONVENIENT ONE-STEP SYNTHESES OF TRI-n-BUTYLTIN BROMIDE OR IODIDE AND DI-n-BUTYLTIN DIBROMIDE OR DIIODIDE FROM THE CORRESPONDING ORGANOTIN CHLORIDES

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Summary

Tri-n-butyltin bromide or iodide and di-n-butyltin dibromide or diiodide may be conveniently prepared from the corresponding organotin chlorides by tetra-n-butylammonium halide-catalyzed halogen redistribution reactions with suitable alkyl bromides or iodides. However, similar transformations are not feasible for trimethylhalosilanes.

Introduction

Several years ago it was reported [1] from our laboratory that halogen redistribution reactions between tin of tri-n-butyltin halides and carbon of non-sterically hindered alkyl halides take place readily in the presence of a quater-

$$Bu_3SnX + RX' \rightleftharpoons Bu_3SnX' + RX$$

nary ammonium halide catalyst. Mechanistic studies [2] showed that the reactions involve nucleophilic backside displacements at carbon by a pentacoordinated tri-n-butyldihalotin anion species formed by coordination of halide ion with the tri-n-butyltin halide. More recently, by measuring the equilibrium positions attained with various alkyl halides, the halogen redistribution reactions between carbon and tin were used to obtain information concerning structural effects on alkyl halide carbon—halogen bond dissociation energies [3]. Also, the process was extended in a limited way to halogen redistribution reactions between benzyl halides and trialkyl-silicon, -germanium and -lead halides [4]. We now wish to report our development of a convenient method using the halogen redistribution procedure for converting the inexpensive, readily available, tri-n-butyltin chloride and di-n-butyltin dichloride in one step into the corresponding bromides or iodides.

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Results and discussion

In the halide ion-catalyzed halogen redistribution reactions between typical alkyl halides and tri-n-butyltin halides in 1 : 1 mole ratios, the equilibrium positions reached [3] range from 50 to 70% conversions of the starting materials. To attain synthetically acceptable conversions using the process, one therefore must shift the position of equilibrium either by using an excess of one of the starting materials or by removing one of the products as it is formed. It was anticipated that the latter method could be readily employed for the conversion of organotin chlorides to the corresponding organotin bromides or iodides if an alkyl bromide or iodide is used whose chloride boils lower than the organotin chloride.

In preliminary small scale studies of the conversion of tri-n-butyltin chloride to tri-n-butyltin iodide, both ethyl iodide and methyl iodide were found to be satisfactory reagents for the halogen redistributions. Other small primary alkyl iodides should also behave similarly. However, ethyl iodide appeared to offer the best starting material for the conversions both because of its high reactivity in bimolecular nucleophilic substitutions and also because of its relatively low cost per mole of iodide.

For the conversion of tri-n-butyltin chloride to tri-n-butyltin bromide, preliminary small scale studies were done using both ethyl bromide and dibromomethane as the alkyl bromides. Based on the results, it was decided to use only the dibromomethane for further examination. This is because higher temperatures can be employed with dibromomethane, thus permitting shorter reaction times.

The Experimental section summarizes the best procedures found for preparing tri-n-butyltin bromide or iodide and di-n-butyltin dibromide or diiodide from the corresponding organotin chlorides by reaction with dibromomethane or ethyl iodide, respectively. The yields of all of the organotin bromides and iodides were high. However, those for the iodides were slightly higher than those for the bromides. Also, the times necessary for complete conversion to the iodides were shorter than those required for the bromides.

For all of the preparations 5 mole% tetra-n-butylammonium bromide or iodide was used as the halide ion catalyst. However, any source of organic soluble halide ion will suffice for the reactions. For example, *N*-alkylpyridinium halides generated in situ by reaction of pyridine with the starting dibromomethane or ethyl iodide reagents were also found to be suitable catalysts.

The halide ion-catalyzed halogen redistribution process should not be limited just to syntheses of di- and tri-n-butyltin bromides and iodides, but should also be applicable for conversions of other organotin halides as well as organogermanium and organolead halides. Although we have not actually examined any of the latter systems on preparative scales, from their behaviors in the millimole scale reactions carried out in the course of our metal—halogen bonding studies reported earlier [4], it is believed that similar conditions to those employed for the butyltin halides should be directly applicable.

Finally, in light of the current value of trimethyliodosilane or trimethylbromosilane in organic syntheses [5], it was hoped that these might be conveniently synthesized from trimethylchlorosilane via halide ion-catalyzed halogen redistribution reactions. However, various attempts to achieve this including reactions of trimethylchlorosilane with ethyliodide or allyl bromide at reflux for several days in the presence of tetra-n-butylammonium iodide or bromide or molecular iodine were unsuccessful. It is believed that this is due in part to unfavorable equilibrium positions for the carbon—silicon halogen redistribution reactions. In our earlier studies [4] of trimethylsilicon—halogen bonding, it was observed that the equilibrium positions in the 1 : 1 mole ratio reactions of trimethylchlorosilane with benzyl iodide or benzyl bromide were less than 1% and only 7% in the direction of formation of trimethyliodosilane or trimethylbromosilane, respectively.

Experimental

General

GLC analyses were carried out on an Aerograph A90P3 instrument, and ^1H NMR spectra were run on a Varian EM-360 instrument. Ethyl iodide, dibromomethane, allyl bromide, tetra-n-butylammonium bromide, tetra-n-butylammonium iodide and trimethylchlorosilane were obtained commercially and used without further purification. Tri-n-butyltin chloride was redistilled, b.p. 130°C/3 mmHg, n_D^{22} 1.4902 (lit. [6,7] b.p. 146°C/5 mmHg, n_D^{25} 1.4903) and di-n-butyltin dichloride was recrystallized from diethylether, m.p. 39—41°C (lit. [8] m.p. 39.5—40°C) before use.

Tri-n-butyltin iodide

A mixture of 33 g (0.10 mol) of tri-n-butyltin chloride, 23 g (0.15 mol) of ethyl iodide and 1.8 g (0.0049 mol) of tetra-n-butylammonium iodide contained in a 100 ml round-bottomed flask fitted with an air condenser and protected by a drying tube was heated slowly in an oil bath to 140°C over a period of 2.5 h. At this point it appeared that no more ethyl chloride was being evolved by the reaction mixture, and GLC examination on an SE-30 column showed that all of the starting chloride had been converted to the corresponding iodide. Purification of the latter was accomplished by vacuum distillation through a short path apparatus to give 37 g (89% yield) of material, b.p. 148—152°C/5 mmHg, n_D^{22} 1.5268 (lit. [9,10] b.p. 172°C/10 mmHg, n_D^{23} 1.5245).

Di-n-butyltin diiodide

A mixture of 9.1 g (0.030 mol) of di-n-butyltin dichloride, 12 g (0.077 mol) of ethyl iodide and 0.70 g (0.0018 mol) of tetra-n-butylammonium iodide contained in a 50 ml round-bottomed flask fitted with an air condenser and protected by a drying tube was heated slowly in an oil bath to 150°C over a period of 5 h. At this point it appeared that the reaction was complete. Vacuum distillation through a short-path apparatus gave 13 g (86% yield) of the desired diiodide, b.p. 130—137°C/0.3 to 0.4 mmHg, n_D^{21} 1.6036 (lit. [11,12] b.p. 124—134°C/0.2 mmHg, n_D^{25} 1.6020).

Tri-n-butyltin bromide

A mixture of 33 g (0.10 mol) of tri-n-butyltin chloride, 11 g (0.063 mol) of dibromomethane and 1.7 g (0.0053 mol) of tetra-n-butylammonium bromide contained in a 100 ml round-bottomed flask fitted with a short Vigreaux column and distilling head and protected by a drying tube was heated gradually to 180°C over a period of 4 h while making certain that the temperature at the distilling head never exceeded 40°C. Vacuum distillation through a short-path apparatus gave 29 g (78% yield) of material, b.p. 137—140°C/4 mmHg, n_D^{22} 1.5052 (lit. [7] b.p. 120—122°C/2 mmHg, n_D^{25} 1.5022). The purity of the product was shown to be greater than 99% by GLC examination on an SE-30 column.

Di-n-butyltin dibromide

A mixture of 7.6 g (0.025 mol) of di-n-butyltin dichloride, 7.6 g (0.044 mol) of dibromomethane, and 0.40 g (0.0012 mol) of tetra-n-butylammonium bromide contained in a 50 ml round-bottomed flask fitted with a distilling head and protected by a drying tube was heated gradually to 200°C over a period of 15 h while making certain that the temperature at the distilling head never exceeded 40°C. Vacuum distillation through a short-path apparatus gave 8.2 g (84% yield) of material, b.p. 112—114°C/2 mmHg, n_D^{23} 1.5405 (lit. [11,13] b.p. 119—120°C/3 mmHg, n_D^{25} 1.5400).

Attempted synthesis of trimethyliodosilane

A mixture of 10 g (0.091 mol) of trimethylchlorosilane, 17 g (0.11 mol) of ethyl iodide and 3.3 g (0.0090 mol) of tetra-n-butylammonium iodide contained in a 50 ml round-bottomed flask equipped with a reflux condenser, drying tube and magnetic stirrer was heated at reflux (oil bath temp. 74°C) for 48 h. Examination of an aliquot of the mixture by NMR showed that no observable reaction had taken place.

Since the tetra-n-butylammonium iodide catalyst which did not dissolve at the beginning of the reaction still appeared to be largely undissolved, 20 ml of acetonitrile was added and the mixture was refluxed for an additional 24 h. There was still no observable conversion of the trimethylchlorosilane to the iodide or the ethyl iodide to the chloride.

Attempted synthesis of trimethylbromosilane

Into a 100 ml round-bottomed flask fitted with a short Vigreaux column was added 22 g (0.20 mol) of trimethylchlorosilane, 12 g (0.10 mol) of allyl bromide and 3.3 g (0.0090 mol) of tetra-n-butylammonium bromide. The mixture was heated at reflux in the air cooled Vigreaux column for 2 days (oil bath temperature about 90°C). During this period some trimethylchlorosilane and allyl bromide were lost by distillation. However, NMR examination of the material in the reaction vessel showed no significant formation of trimethylsilicon bromide.

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