Journal of Organometallic Chemistry, 73 (1974) 59—66
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THE REACTION OF IODINE MONOCHLORIDE AND MONOBROMIDE WITH TETRAORGANOTINS

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(Received December 20th, 1973)

Summary

The reactions of iodine monochloride and iodine monobromide with a tetraalkyltin (butyl) and a tetraaryltin (phenyl) have been studied with a view to establishing their utility as routes to organotin chlorides and bromides respectively. Rapid high yield syntheses of the triorganotin bromides, diorganotin dichlorides and trialkyltin chloride were achieved. Some further suggestions are made on the mechanism of interhalogen fission of tin—carbon bonds.

Introduction

The halogen cleavage reactions of tetraorganotin compounds have been extensively used in the one step preparation of organotin halides [1—5] and the subsequent preparation of other organotin species. The reaction with iodine generally requires treatment at high temperature without solvent or in a boiling solvent to produce the triorganotin iodide. To produce the triorganotin bromide, reaction with bromine must be carried out at low temperature (—30 to —40°) or in some cases in pyridine at room temperature. However, at room temperature the diorganotin dibromide is generally produced. Because of the complexity of the reaction, chlorine fission is not used to produce an organotin chloride especially since the convenient redistribution reaction between tetraorganotin and tin tetrachloride is available.

The mechanism of these electrophilic substitution reactions by halogens on tetraorganotins has been thoroughly studied mainly by Nasielski and coworkers [6]. In polar solvents the reaction is first order in both reagents, but in non-polar solvents an alternative mechanism, involving two halogen molecules per molecule of tetraorganotin becomes important [7].

Despite the great amount of work both on the preparative and mechanistic aspects of the reactions of tetraorganotins with halogens, the reactions of interhalogens with tetraorganotins have only recently been the subject of brief reports, one preparative [8], the other mechanistic [9]. While our work was proceeding, the clean room temperature fission of a tin—carbon bond with iodine monochloride was used to produce 3-iodo-1,2-dihydrobenzocyclobutene and presumably a triorganotin chloride or diorganotin dichloride [8]. Earlier [9] a kinetic study of the reaction of iodine monobromide with tetramethyl- and tetrapropyltin showed that in a non-polar solvent the polar mechanism involving two molecules of the interhalogen in the rate determining step was much more important than with the halogens. In all cases the products were determined by bond polarities and not by prediction based on hard or soft properties, i.e. the reaction goes according to eqn. 1. This is in contrast to the reactions of ICl with $(CH_3)_3M—M'(CH_3)_3$ species (M, M' = C, Si, Ge, Sn) [10].

$$R_4Sn + IX \rightarrow R_3SnX + RI \quad (1$$

(X = Cl or Br)

Our interest in the preparative potential of reactions of tetraorganotins with ICl and IBr arose because we required a rapid room temperature route to pure triorganotin halides and diorganotin dihalides in connection with our studies on their complexes [11] and photoelectron spectra [12]. Secondly, at the time we were looking for a method for analysing tetraorganotin species possibly produced during the decomposition of triorganotin species [13], and had been investigating the halogens for this purpose.

Experimental

General

Tetrabutyltin, iodine and iodine monochloride were obtained from B.D.H. and were used without further purification. Iodine monobromide was obtained from B.D.H. and purified by a published procedure [14]. Carbon tetrachloride was stored over calcium chloride and distilled before use.

^1H NMR spectra were recorded on a Perkin—Elmer R12 spectrometer at 32° and infrared spectra were recorded on a PE 457 Grating Infrared Spectrophotometer.

Reaction of tetraphenyltin with iodine monochloride (molar ratio 1/2)

ICl (0.87 g; 0.0053 mole) in 50 ml CCl_4 was added dropwise with vigorous stirring to 1.07 g Ph_4Sn (0.0025 mole) in 250 ml CCl_4 at 0°. The blood red color of the ICl solution disappeared after the addition of each drop and the addition was completed in half-an-hour, when a pink colour persisted and all of the Ph_4Sn had dissolved. After carefully distilling off the carbon tetrachloride, the residue was extracted with 10 ml 40—60° petroleum ether and on removal of this solvent 0.8 g of a liquid, shown by infrared and NMR to be iodobenzene (0.004 mole), was obtained. The remaining solid was dissolved in 25 ml CCl_4 and was treated with 10 ml aqueous 0.1 *M* NaOH to convert any phenyltin chlorides to hydroxides. The resulting precipitate was washed with cold water, ethanol and ether. It was then treated with boiling toluene to dissolve any Ph_3SnOH present. The insoluble product (0.62 g) was shown to be pure

Ph_2SnO (Found: C, 49.50; H, 3.25. Calcd.: C, 49.88; H, 3.46%). The yield of Ph_2SnO based on Ph_4Sn is 86%.

The toluene solution yielded a hardly significant trace of a white solid. The quantity was too small to establish whether it was Ph_3SnOH or not.

When the experiment was repeated without the NaOH treatment, evaporation of the CCl_4 solution, after removal of iodobenzene, gave 0.80 g Ph_2SnCl_2 (0.0023 mole; 92% yield), recrystallised from $CHCl_3$/petroleum ether. The reaction can also be carried out by shaking both solutions together at room temperature and over 80% yields of Ph_2SnCl_2 are always obtained, even with excess ICl. In this way the total working time can be as little as three hours.

Reaction of tetraphenyltin with iodine monochloride (molar ratio 1/1)

The reaction was repeated as above except that only 0.44 g (0.0027 mole) ICl in 50 ml CCl_4 was used. Following the addition, the solution was colourless and a white precipitate remained. After removing half of the solvent, the precipitate was filtered off, washed with cold CCl_4 and dried. 0.51 g (0.0012 mole) $(C_6H_5)_4Sn$ [confirmed by IR, m.p. 223°; lit. 224–225° and analysis (Found: C, 66.90; H, 4.42. Calcd.: C, 67.50; H, 4.69%)] was obtained. On evaporating the CCl_4 solution to dryness and extracting with petroleum ether as above, 0.40 g (0.002 mole) iodobenzene was obtained. Treatment of a CCl_4 solution of the solid residue with 0.1 *M* NaOH then hot toluene produced 0.34 g (1.18×10^{-3} mole) of Ph_2SnO (80% yield). A trace of a white solid was obtained from the toluene extract. From a melting point determination it appeared to be Ph_3SnOH or $(Ph_3Sn)_2O$. [M.p. 119° (Lit. [1] 119–120°)].

Reaction of tetraphenyltin with iodine monobromide (molar ratio 1/1)

When a solution of IBr (0.56 g, 0.0027 mole) in 50 ml CCl_4 was added dropwise to 1.05 g (0.0025 mole) Ph_4Sn in 250 ml at room temperature (30°), the colour change took place slowly. Therefore all of the IBr solution was added and the mixture was stirred for half an hour, when a pale pink colour persisted. On carrying out the same treatment as above, 0.35 g (0.0018 mole) iodobenzene was recovered, but on treatment with hot toluene almost all of the solid residue dissolved. Recrystallisation from this solvent produced 0.77 g (0.0021 mole) Ph_3SnOH [identified by IR and analysis (Found: C, 59.42; H, 4.26. Calcd.: C, 59.01; H, 4.37%)]. The yield in this reaction is 84% based on Ph_4Sn and this yield of pure Ph_3SnBr (Found: C, 50.82; H, 3.65; Br, 17.92. Calcd.: C, 50.34; H, 3.50; Br, 18.65%) can be obtained by omitting the NaOH treatment.

Reaction of tetraphenyltin with iodine monobromide (molar ratio 1/2)

The room temperature reaction of Ph_4Sn (1.05 g, 0.0025 mole) with a 2/1 excess of IBr (1.10 g, 0.0053 mole) produced mixtures of Ph_3SnOH and $[Ph_2SnO]_n$. Typically after three hours at 30° the products were 0.48 g (0.003 mole) Ph_3SnOH and 0.29 g (0.001 mole) $(Ph_2SnO)_n$.

Refluxing in CCl_4 for three hours still produced some Ph_3SnOH. It was necessary to reflux 1.65 g (0.008 mole) IBr with 1.05 g (0.0025 mole) Ph_4Sn in 250 ml CCl_4 for four hours, followed by the NaOH treatment to produce conversion to $(Ph_2SnO)_n$ (0.53 g, 0.002 mole). An 80% yield of Ph_2SnBr_2 can be produced using this reaction without the base treatment.

Reaction of tetrabutyltin with iodine monochloride

ICl (3.89 g; 0.024 mole) in 25 ml CCl_4 was added dropwise, rapidly with stirring to 3.47 g (0.010 mole) Bu_4Sn in 25 ml CCl_4 at 30°. At each drop the colour change was rapid and at the end of the addition a pink color remained. After removal of more than half of the solvent and stands at 0° for several hou white crystals were obtained and recrystallised from CCl_4. The infrared and NMR spectra and melting point, 40—41° (lit. 40.5°) confirmed this solid as *dibutyltin dichloride. The first crop was 2.03 (0.0067 mole) and 0.8 g (0.002* mole) was recovered from the mother liquors to give a total yield of 93% Bu_2SnCl_2. The other (liquid) reaction product, recovered after the removal of all of the solvent, was identified as butyl iodide by IR and NMR spectroscopy.

Reactions of tetrabutyltin with ICl and IBr followed by ^1H NMR spectrometr

Because of the possibility of mixtures being formed it was decided to follow these reactions by ^1H NMR to evaluate their potential as preparative route to the butyltin halides. The method of analysis is as follows.

Although the ^1H NMR spectra of Bu_4Sn, Bu_3SnX, Bu_2SnX_2 ($A_3B_2C_2D$ system) and BuX ($A_3B_2C_2X_2$ system) are very complex and have not been ful analysed to our knowledge, it was possible to use the spectra to obtain the proportions of each species in mixtures.

This analysis was based on the integrated intensities in four regions of the spectra, (a) 6.50-6.90 τ, (b) 7.85-8.30 τ, (c) 8.30-8.80 τ, and (d) 8.80-9.30 τ. The intensity ratio of all the model compounds in these regions were as follow (sum of intensities = total no. of protons per molecule).

Compound	Region (a)	(b)	(c)	(d)
$(CH_3CH_2CH_2CH_2)_4Sn$	0	0	18	18
$(CH_3CH_2CH_2CH_2)_3SnX$	0	$\underbrace{4.2 \quad 13.8}_{(18)}$		9
X = Cl, Br				
$(CH_3CH_2CH_2CH_2)_2SnX_2$	0	$\underbrace{6.4 \quad 5.6}_{(12)}$		6
X = Cl, Br				
$CH_3CH_2CH_2CH_2I$	2	2.2	2	2.8

Standard mixtures were made up and it was found that the relative concentrations could be measured to within 10%. This error was all in the measurement of the integrated intensity.

For a reaction mixture the intensity due to butyl iodide was first remove since it is determined uniquely by region (a), then the following equations wer solved, to give the molar proportions of Bu_2SnX_2 (x) Bu_3SnX (y) and Bu_4Sn (z).

$$\begin{aligned} 6.4x + 4.2y \quad &= (b) \\ 5.6x + 13.8y + 18z &= (c) \\ 6x + 9y + 18z \quad &= (d) \end{aligned}$$

where b, c and d are the τ value ranges, 7.857-8.30 τ, 8.30-8.80 τ and 8.80-9.3 respectively. x, y and z are the molar proportions of Bu_2SnX_2, Bu_3SnX and Bu_4Sn respectively. (See Table).

Reaction of tetrabutyltin with iodine monochloride (molar ratio 1/2)

Solutions were made in 25 ml of CCl_4 of ICl (3.89 g, 0.024 mole), added dropwise with stirring to 3.47 g (0.010 mole) Bu_4Sn in 25 ml CCl, at 30°. 1.31 g of iodine was added to prevent ICl dissociation. 1 ml each of the solutions of Bu_4Sn (4.0×10^{-4} mole) and iodine monochloride (9.0×10^{-4} mole) were shaken together in an NMR tube. The initial spectrum 2 min after mixing showed no significant amount of Bu_4Sn, 3.05×10^{-4} mole Bu_2SnCl_2, 0.95×10^{-4} mole Bu_3SnCl and 7.05×10^{-4} mole BuI. The NMR spectrum was repeated every 15 min and at the end of half an hour the reaction was seen to be complete with 8×10^{-4} mole butyl iodide and 4×10^{-4} mole Bu_2SnCl_2. $BuSnCl_2$ was recovered by the same method as for Ph_2SnBr_2 (see p. 61).

Reaction of tetrabutyltin with iodine monochloride (molar ratio 1/1)

All quantities in this experiment were the same as in the previous one except that only 1.92 g (0.012 mole) ICl was used. In this case the initial NMR spectrum (5 min) contained 0.6×10^{-4} mole Bu_4Sn, 3.3×10^{-4} mole Bu_3SnCl, 0.1×10^{-4} mole Bu_2SnCl_2 and 3.4×10^{-4} mole BuI. After 35 min, the proportion of Bu_2SnCl_2 had increased and the quantities were now 0.4×10^{-4} mole Bu_4Sn, 3.2×10^{-4} mole Bu_3SnCl, 0.45×10^{-4} Bu_2SnCl_2 and 4.1×10^{-4} mole BuI. After 3 h reaction was complete with 3×10^{-4} mole Bu_3SnCl, 0.95×10^{-4} mole Bu_2SnCl_2 and 4.8×10^{-4} mole BuI.

Using an exactly 1/1 ratio and dropwise addition of the ICl solution over 30 min, pure Bu_3SnCl could be recovered after fractional distillation b.p. 155—160°/15 mm (lit. b.p.: 140—152°/10 mm).

Reaction of tetrabutyltin with iodine monobromide (molar ratio 1/2)

The previous two experiments were repeated using the same quantities of Bu_4Sn and CCl_4 with 4.6 g (0.022 mole) of IBr. The initial quantities in the NMR tube (0.5 cm of each solution) were 2.00×10^{-4} mole Bu_4Sn and 4.40×10^{-4} mole IBr. The ^1H NMR spectrum was run 5 min after mixing and then at 15 min intervals. The initial spectrum showed no Bu_4Sn, 1.46×10^{-4} mole Bu_3SnBr, 0.34×10^{-4} mole Bu_2SnBr_2, and 2.14×10^{-4} mole BuI. After another hour, the quantities were 1.15×10^{-4} mole Bu_3SnBr, 0.65×10^{-4} mole Bu_2SnBr_2 and 2.45×10^{-4} mole BuI. However, even after 20 h, the expected reaction was not completed and the solution contained 0.52×10^{-4} mole Bu_3SnBr, 1.28×10^{-4} mole Bu_2SnBr_2, 3.0×10^{-4} mole BuI and 1.32×10^{-4} mole IBr (by difference).

Reaction of tetrabutyltin with iodine monobromide (molar ratio 1/1)

1 ml each from the solutions of 3.2 g (0.009 mole) Bu_4Sn in 50 ml CCl_4 and 2.05 g (0.010 mole) IBr (with 1.31 g I_2) in 50 ml were introduced into an NMR tube. The spectrum showed that after 5 min the reaction solution contained a 50/50 mixture of Bu_3SnBr and BuI. No further change was observed and the reaction was complete.

Pure Bu_3SnBr in 80% yield can be obtained from the above reaction (without iodine) by simply shaking the reactants together until the color disappears and distilling off CCl_4 and BuI (130°) and vacuum distilling Bu_3SnBr (b.p. 160°/10 mm, lit. [1], b.p. 145°/5 mm).

Attempted reaction of tetrabutyltin with iodine

Using the same quantities of Bu_4Sn and CCl_4 and the same conditions as in the experiments above with the iodine alone, no evidence of reaction was obtained after 20 h. However, using four times the quantity of iodine (0.02 mole), at the end of 20 h a weak signal due to CH_2—I (of n-BuI) was observed at the higher sensitivity. The reaction of iodine with Bu_4Sn is therefore extremely slow and does not affect the reactions of iodine monochloride and bromide with Bu_4Sn.

Discussion

The main aim of this work was to evaluate the reactions of tetraorganotins with iodine monobromide and monochloride as simple synthetic routes to triorganotin halides and diorganotin dihalides. In addition this would form a preliminary analysis for further mechanistic studies to predict the products of an I—X fission of a Sn—C bond on a thermodynamic basis. However, as in the previous studies, the reactions of Bu_4Sn and Ph_4Sn with ICl and IBr always produce products with a C—I bond and Sn—X bond and never the reverse. In the NMR study there was no evidence for butyl bromide or chloride at any stage of the reactions.

No matter what molar ratio is used in the reaction between tetraphenyltin and iodine monochloride at 0°, diphenyltin dichloride is always formed. Disubstitution [1—5] is always obtained in the reaction of bromine with tetraaryltin compounds even at —30 to —40°. As shall be seen below, ICl generally undergoes the same reactions as Br_2 under the same conditions, so that, under any circumstances when bromine can be used to produce an organotin bromide, the corresponding chloride can be obtained with ICl. Thermodynamically the bond energy changes for the fission of Sn—C bonds by Br_2 and ICl respectively are about the same ($\Delta H = -28$ kcal/mole).

In contrast to the reaction of Ph_4Sn with ICl, the reaction with IBr can be easily controlled so that only monosubstitution takes place and triphenyltin bromide is produced in good yield. This reactions is probably general for all tetraaryltins and it should be a useful synthetic route and serve as an alternative to the usually recommended redistribution reaction followed by a separation procedure [17].

Fission of the second bond seems to be relatively very much slower with IBr than ICl and this conforms with the pattern already observed with I_2 and Br_2. However although the second fission step in the reaction between Ph_4Sn and I_2 and IBr is much slower than the first, the non-appearance of a monosubstituted species in the reaction between Ph_4Sn and Br_2 and ICl may indicate that in these cases the second step is relatively much quicker or that both steps are equally fast. However, we are not aware of any kinetic studies which have been carried out on this second fission reaction in tetraaryltins. In contrast the thermodynamics of the two step reaction of Ph_4Sn with Br_2 in CCl_4 solution gives a value of —78 kcal/mole for the whole reaction and —37 kcal/mole for the second step [18]. This indicates that the first step is actually more favourable thermodynamically. For tetraalkyltins (see below) the second step is always much slower.

The reactions of tetraalkyltins with halogens are known [2, 6] to be somewhat slower than the reactions of tetraaryltins. In our present study this can be clearly seen in the reaction of ICl with tetrabutyltin. With ICl/Bu_4Sn ratio of 1/1, Bu_3SnCl can be isolated and in the NMR experiment the Bu_2SnCl_2 produced can be accounted for completely by the slight excess of ICl. Even in the reaction with an ICl/Bu_4Sn ratio of 1/2 the formation and reaction of intermediate Bu_3SnCl can be observed despite the fact that the disubstitution to produce Bu_2SnCl_2 is compelte in one hour. Clearly, a two step reaction is involved to produce Bu_2SnCl_2, and the rate of the second fission reaction at least appears to be measurable by conventional slow reaction techniques whereas this does not appear to be the case with Ph_4Sn.

The reaction of excess ICl with Bu_4Sn has a fast first step to produce Bu_3SnCl (complete in under five minutes) then a somewhat slower second step to produce Bu_2SnCl_2 (complete in $\approx$ 60 min). The slow second step is also observed with the fissions with the halogens [19]. However, with IBr, even though the first step is again fast, the second step to produce Bu_2SnBr_2 is extremely slow. As a result this is an extremely good preparative route to Bu_3SnBr and a good reaction to study if one wishes to look at the kinetics of the fission of one tin—carbon bond.

The slower second step in the IBr and ICl fissions of Bu_4Sn and the IBr fission of Ph_4Sn is probably dominated by the reduced nucleophilic character of the tin—carbon bond in the triorganotin halides compared to the tetraorganotins. In addition to the reasons for which Br_2 reacts faster with tetraorganotins than I_2, the ICl reactions may be accelerated compared to the IBr reaction due to the more polar character of the former. It will act as a better nucleophile through the Cl atom and a better electrophile through the more positively charged I atom.

The kinetics of the reactions of Me_4Sn and Pr_4Sn with IBr indicate the presence of concurrent 2nd and 3rd order reactions with the 3rd order mechanism dominating [9]. It seems likely that this will also hold for the reactions of tetrabutyltin. The ICl reactions, because of the more polar nature of ICl, are likely to be even more dominated by the third order mechanism involving complex formation between ICl and Bu_4Sn then fission of the tin—carbon bond with another molecule of ICl. With tetraphenyltin, the third order mechanism, involving a π complex with the interhalogen, proposed by Bott, Eaborn and Waters [7] is expected.

We believe that we have shown that the reactions given in the following equations are synthetically useful.

$$\mathrm{Ph_4Sn + 2ICl \xrightarrow[CCl_4]{30^\circ/5\ min} Ph_2SnCl_2 + 2PhI} \tag{1}$$

$$\mathrm{Ph_4Sn + IBr \xrightarrow[CCl_4]{30^\circ/30\ min} Ph_3SnBr + PhI} \tag{2}$$

$$\mathrm{Ph_4Sn + 2IBr \xrightarrow[CCl_4]{77^\circ/4\ h} Ph_2SnBr_2 + 2PhI} \tag{3}$$

$$\mathrm{Bu_4Sn + ICl \xrightarrow[CCl_4]{30^\circ/30\ min} Bu_3SnCl + BuI} \tag{4}$$

$$Bu_4Sn + 2ICl \xrightarrow[CCl_4]{30^\circ/15\ min} Bu_2SnCl_2 + 2BuI \qquad (5)$$

$$Bu_4Sn + IBr \xrightarrow[CCl_4]{30^\circ/5\ min} Bu_3SnBr + BuI \qquad (6)$$

Reactions (2) and (4) appear to take an unexpectedly long time compared to (6). However, this is because the interhalogen must be added slowly dropwise to prevent the formation of the dihalotin species. Boue, Gielen and Nasielski [20] also have a useful synthetic route to the trialkyltin bromide by taking advantage of the much slower reaction of bromine with tetraalkyltin in non-polar solvents. We believe that the controlled ICl reaction with tetraalkyltins (eqn. 4) will be generally satisfactory for the production of the corresponding trialkyltin chlorides which were previously inaccessible by halogen fission reactions. Eaborn et al. [8] have discovered the importance for organic synthesis of the ICl fission reaction.

Acknowledgement

We are grateful for financial support from the Research Committee of the University of Ife, and the National Research Council of Canada. We thank Miss O. Akanro for preparing some of the tetraphenyltin used.

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