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## Synthesis of Organotin Mixed Dihalides

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A study of functional group exchange on both methylsilicon and methylgermanium residues shows it not to deviate substantially from randomness in the case of halogens,[1] except with fluorine, when the least methylated silicon residue is preferentially fluorinated.[2] Consequently yields of mixed dihalogenosilanes are less than 50%.[3] Exchange between methylsilicon and methylgermanium moieties shows the heavier halogen to prefer the heavier metalloid,[1] as would be predicted from bond energies.[4]

Mixed organotin dihalides were first reported almost a century ago. $Ph_2SnClX$ (X = Br or I) were prepared from the dichloride and the corresponding hydrogen halide. Bromination of 1,3-dichlorotetra-*n*-butylditin oxide yields di-*n*-butyltin chloride bromide in 60% yield as the only tin dihalide. This is also formed in good yield by recrystallizing or redistilling an equimolar mixture of $(n\text{-Bu})_2SnCl_2$ and $(n\text{-Bu})_2SnBr_2$.[5]

This note describes the synthesis of the dialkyltin dihalides $R_2SnXY$ (R = Me, Et, or *n*-Bu; XY = ClBr, ClI, or BrI) by the redistribution method (A) just mentioned or by the halogen exchange (B) between silicon and tin. This latter method is

$$R_2SnX_2 + R_2SnY_2 \rightarrow 2R_2SnXY$$

$$R_2SnX_2 + Me_3SiY \rightarrow R_2SnXY + Me_3SiX$$

normally exothermic for monohalogen-substituted species with the heavier halogen preferring tin and can also be used to prepare the dialkyltin dihalides $R_2SnX_2$

$$R_3SnX + Me_3SiY \rightarrow Me_3SiX + R_3SnY$$

(R = Me or *n*-Bu; X, Y = Cl, Br, or I with Y heavier than X)

$$R_3SnF + Et_3SiX \rightarrow R_3SnX + Et_3SiF$$

(R = *n*-Bu or Ph; X = Cl, Br, or I)

*e.g.*

$$(n\text{-Bu})_2SnCl_2 + 2Et_3SiI \rightarrow (n\text{-Bu})_2SnI_2 + 2Et_3SiCl$$

Though all the mixed dihalides can be prepared by one of these two methods, few can be made by both. Neither method has been found suitable for tin fluoride halides, though two such compounds have been reported, using NaF or HF as the fluorinating agent[6]

$$(R = t\text{-Bu})\ R_2SnClF \xleftarrow{NaF} R_2SnCl_2 \xrightarrow{HF} R_2SnClF\ (R = Me)$$

Table I gives the physical characteristics of the dihalides along with the method(s) of synthesis. Yields were excellent and, apart from di-*n*-butyltin bromide iodide, were crystalline solids melting sharply at temperatures near or above those of their symmetrical precursors. All analyzed well (Table II) and their Mössbauer spectra, which show the presence of only one kind of tin nucleus as a single doublet having values of the quadrupole splitting $\Delta E_Q$ ranging from 3.0 to 3.5 mm sec$^{-1}$, support the absence of mixtures.[7]

Apart from diethyltin chloride iodide, all the mixed dihalides appear to be stable pure, but in solution the $^{119}Sn$ nmr spectra show the mixed methyl and ethyl iodides to randomize.[8] Only one absorption is observed for $R_2SnClBr$ (R = Me or Et) supporting a single species or very rapid halogen exchange. This parallels the proton nmr observations on methyltin mono-, di-, and trihalide mixtures, which showed the presence of mixed species.[9] None were isolated so, apart from di-*n*-butyltin chloride bromide, all the mixed dihalides reported here are new compounds.

Details of the spectroscopic results will be reported later and it is hoped to couple this with a structural study.

## Experimental Section

Trimethylchlorosilane was purchased from Fluka while the bromide and iodide were prepared in good yield from $(Me_3Si)_2O$ and $PBr_3$ or $AlI_3$.[10] Triethylhalogenosilanes resulted from $Et_3SiH$, prepared from trichlorosilane and a Grignard reagent, using the appropriate allyl halide.

$R_3SnF$ (R = *n*-Bu, Ph) were obtained from Phase Separations Ltd. and M and T Chemicals Inc., while $Me_3SnCl$ and $Me_2SnCl_2$ resulted from the arrangement of $Me_4Sn$ with $SnCl_4$.[11] Di-*n*-butyltin dichloride was commercially available from Albright and Wilson (Mfg.) Ltd. Diethyltin dichloride (mp 85°)[12] was prepared in almost quantitative yield by warming the oxide with excess trimethylchlorosilane.

All compounds were characterized either by analysis for at least carbon and hydrogen or by comparison of their physical properties with those of reported authentic samples. Care was taken to exclude moisture from the reactions and typical among them are the following ones.

**Reaction of $Me_3SiI$ with $Me_3SnCl$ and with $Me_2SnCl_2$.** The iodide (4.10 g, 1 mol) was added dropwise to trimethyltin chloride (4.06 g, 1 mol) with cooling. An exothermic reaction occurred, and after the addition was completed, the mixture was heated overnight. Volatile constituents were pumped off, trapped, and fractionated giving trimethylchlorosilane (1.6 g, 73%), bp 57°, $n^{22}D$ 1.3884,[10] while distillation of the residue yielded trimethyltin iodide (4.7 g, 80%), bp 59° (12 mm), mp 4°, $n^{22}D$ 1.5682 (4.7 g, 80%).[13]

**Table I.** Physical Characteristics of Dialkyltin Dihalides $R_2SnXY$ and $R_2SnX_2$ [mp, °C (bp, °C (*P*, mm)]

| | XY | | | | | |
|---|---|---|---|---|---|---|
| R | ClBr | ClI | BrI | $Cl_2$ | $Br_2$ | $I_2$ |
| Me | 81 (A[a]) | 35 (B) | 48–49 (A, B) | 106–107 | 77–78 | 36<br>(62 (1)) |
| Et | 62–63 (B[a]) | *b* | 47–48 (B) | 85 | 62–64 | 45–46 |
| *n*-Bu | 33–34 (A, B)<br>(88 (0.04)) | 25 (A, B)<br>(86 (0.01))<br>$n^{28}D$ 1.5378 | (104 (0.04)) (A)<br>$n^{28}D$ 1.5635 | 41–42 | 22–23 | (110 (0.01))<br>$n^{25}D$ 1.6044 |

[a] Method of preparation of mixed dihalides: A, redistribution; B, halogenosilane exchange. [b] $Et_2SnClI$ appeared to be labile, even as a solid.

**Table II.** Analysis of Dialkyltin Dihalides $R_2SnXY$

| | % found (calcd) | | |
|---|---|---|---|
| | C | H | Total halogen ($R_2SnClBr$) |
| $Me_2SnClBr$ | 8.65 (9.09) | 2.51 (2.28) | 43.3 (43.6) |
| $Me_2SnClI$ | 7.38 (7.72) | 2.06 (1.94) | 40.9 (40.8)[a] |
| $Me_2SnBrI$ | 6.68 (6.75) | 1.71 (1.70) | *b* |
| $Et_2SnClBr$ | 16.82 (16.44) | 3.42 (3.45) | 38.9 (39.4) |
| $Et_2SnBrI$ | 12.94 (12.52) | 2.67 (2.62) | *b* |
| $(n\text{-Bu})_2SnClBr$ | 28.07 (27.64) | 5.25 (5.18) | 32.6 (33.2) |
| $(n\text{-Bu})_2SnClI$ | 24.76 (24.33) | 4.53 (4.56) | 31.8 (32.2)[a] |
| $(n\text{-Bu})_2SnBrI$ | 21.88 (21.84) | 4.16 (4.12) | *b* |

[a] Iodine only. [b] The analysis figures for total halogen in bromide iodides were unreliable.

Dimethyltin diiodide was prepared similarly (8.3 g, 85%), bp 62° (1 mm), mp 36°. *Anal.* Calcd for $C_2H_6SnI_2$: C, 5.96; H, 1.50; I, 63.5. Found: C, 6.16; H, 1.52; I, 63.6.

**Reaction of Tri-*n*-butyltin Fluoride with Triethylbromosilane.** The bromide (11.44 g, 1 mol) was slowly added, with cooling, to the tin fluoride (18.10 g, 1 mol). The reaction was exothermic and after heating for 6 hr, the mixture was carefully fractionated giving triethylfluorosilane (5.1 g, 68%), bp 109°, $n^{20}D$ 1.3905,[10] and tri-*n*-butyltin bromide (19.1 g, 88%), bp 104° (0.5 mm), $n^{28}D$ 1.5015.[12]

**Reaction of $Me_3SiBr$ and $Et_2SnCl_2$.** The additon of the components in equimolar quantities led to a mildly exothermic reaction. After heating overnight, the chlorosilane was pumped off and distilled (1.1 g, 86%), bp 57°, $n^{18}D$ 1.3900, while the residual diethyltin chloride bromide was recrystallized from dry pentane (3.5 g, 92%), mp 62–63°. *Anal.* Calcd for $C_4H_{10}SnClBr$: C, 16.42; H, 3.45; total halogen, 39.40. Found: C, 16.82; H, 3.42; total halogen, 38.9.

**Reaction of Di-*n*-butyltin Dichloride and Di-*n*-butyltin Diiodide.** The dichloride (1.68 g, 1 mol) and diiodide (2.7 g, 1 mol) were mixed and warmed. Vacuum distillation yielded di-*n*-butyltin chloride iodide (3.2 g, 73%), bp 88–89° (0.01 mm), mp 25°, $n^{28}D$ 1.5380. *Anal.* Calcd for $C_8H_{18}SnClI$: C, 24.33; H, 4.56; I, 32.2. Found: C, 24.76; H, 4.53; I, 31.8.

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**Registry No.** $Me_2SnClBr$, 54182-25-1; $Me_2SnClI$, 54182-26-2; $Me_2SnBrI$, 54182-27-3; $Me_2SnCl_2$, 753-73-1; $Me_2SnBr_2$, 2767-47-7; $Me_2SnI_2$, 2767-49-9; $Et_2SnClBr$, 54182-28-4; $Et_2SnBrI$, 54182-29-5; $Et_2SnCl_2$, 866-55-7; $Et_2SnBr_2$, 1655-81-8; $Et_2SnI_2$, 2767-55-7; $(n\text{-Bu})_2SnClBr$, 54182-30-8; $(n\text{-Bu})_2SnClI$, 28339-79-9; $(n\text{-Bu})_2SnBrI$, 54182-31-9; $(n\text{-Bu})_2SnCl_2$, 683-18-1; $(n\text{-Bu})_2SnBr_2$, 996-08-7; $(n\text{-Bu})_2SnI_2$, 2865-19-2; $Me_3SiI$, 16029-98-4; $Me_3SnCl$, 1066-45-1; $(n\text{-Bu})_3SnF$, 1983-10-4; $Et_3SiBr$, 1112-48-7; $Me_3SiBr$, 2857-97-8; $Me_3SiCl$, 75-77-4.

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# Photochemical Reaction Pathways of Ruthenium(II) Complexes.[1] Ultraviolet Irradiation of the Pyridine Complex $Ru(NH_3)_5py^{2+}$

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Previously, we have reported[3] on the photochemistry resulting when aqueous pentaamminepyridineruthenium(II), $Ru(NH_3)_5py^{2+}$, is irradiated with visible light. The prominent visible range absorption of this complex is a metal-to-ligand charge transfer (MLCT) band ($\lambda_{max}$ 407 nm, $\epsilon$ 7.78 × $10^3$ $M^{-1}$ $cm^{-1}$). However, the principal photoreactions observed are substitutional, and ligand field excited states of this $4d^6$ complex have been invoked[3,4] to explain the photoreactivity pattern. Qualitative experiments[5] have shown that ultraviolet irradiation of this complex leads not only to ligand photoaquation but also to photooxidation of ruthenium(II) to ruthenium(III). Reported here is a quantitative study of the photosubstitution and photooxidation quantum yields for the uv photolyses of this complex.

## Experimental Section

**Photolysis Procedures.** Irradiations at 334, 313, and 303 nm were carried out with an apparatus described previously.[3] This apparatus uses a 200-W, short-arc, high-pressure mercury lamp source and a Jarrell-Ash 0.25-m monochromator. Average intensities (*I*) at the respective wavelengths were 3.0 × $10^{-7}$, 1.4 × $10^{-7}$, and 0.7 × $10^{-7}$ einstein/(l. sec). Irradiations at 253.7 nm used a Philips medium-pressure mercury lamp source and an Oriel 253.7-nm mercury line interference filter ($I$ = 4.3 × $10^7$ einstein/(l. sec)). Each of these apparatus was equipped with a cell holder thermostated at 25°. Ferrioxalate actinometry was used to measure light intensities. The photolysis solutions were prepared by dissolving $[Ru(NH_3)_5py](BF_4)_2$ in argon-deaerated, aqueous solution ($\mu$ = 0.2 *M* NaCl). Ru(II) concentrations were varied from 0.4 × $10^{-4}$ to 2.3 × $10^{-4}$ *M* and no relationship between complex concentrations and measured quantum yields was obvious.

Quantum yields were determined by evaluating spectral changes in the reaction solutions as a function of light absorbed.[3] A number of the photolysis runs were analyzed by a difference method where two 2-cm spectrometer cells of the same Ru(II) solution were filled, and one was placed in the sample cell compartment (25°) of a Cary 14 spectrometer while the other was used as photolysis solution. Periodically, irradiation was interrupted, the photolysis solution placed in the reference cell compartment, and the spectrum recorded. Since the photolysis solution is placed in the reference compartment, the difference spectra recorded (Figure 1) show a positive deflection from the $t$ = 0 base line at wavelengths where the optical density of the photolysis is decreased relative to the dark control solution. The difference-spectra method has the advantage of automatically compensating for small spectral changes resulting from the very slow dark reactions. All quantum yields were evaluated as initial quantum yields by extrapolating plots of overall quantum yield values *vs.* per cent reaction back to 0% reaction.[3]

## Results and Discussion

Photolysis of aqueous $Ru(NH_3)_5py^{2+}$ at 405 nm leads principally to photoaquation of coordinated $NH_3$ and pyridine, although a very low-yield photoexchange of pyridine protons with solvent protons has also been detected.[3] Pyridine aquation (eq 1) leads to major spectral changes since the dominant

$$Ru(NH_3)_5py^{2+} + H_2O \xrightarrow{h\nu} Ru(NH_3)_5H_2O^{2+} + py \qquad (1)$$