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INTERACTION OF AMMONIUM SALTS WITH ORGANOMETALLIC OXIDES, HYDROXIDES AND ALKOXIDES. A CONVENIENT SYNTHESIS OF ORGANOTIN HALIDES AND PSEUDOHALIDES

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SUMMARY

Organotin oxides, hydroxides, and alkoxides react with ammonium halides and ammonium thiocyanate in the presence of an inert solvent to give the corresponding organotin halides and isothiocyanates respectively in high yields. The reactivity of ammonium halides, NH_4X, has been found to be in the order of $X = I > Br > Cl$. The mechanism of the reaction of thiourea with organotin oxides has been discussed. It has been demonstrated that thiourea first rearranges to ammonium thiocyanate which then reacts with organotin oxides to yield the corresponding isothiocyanate.

INTRODUCTION

Organotin halides and pseudohalides are generally prepared from the corresponding oxides or hydroxides by treatment with an appropriate acid[1,2]. This method sometimes requires the use of corrosive acids. Organotin isocyanates[3] and isothiocyanates[4] have also been synthesized by reacting organotin oxides with urea and thiourea respectively. We wish to report a new method utilizing ammonium halides and ammonium pseudohalides for the synthesis of organotin halides and pseudohalides.

RESULTS AND DISCUSSION

Organotin oxides and ammonium halides, upon refluxing in methylcyclohexane (b.p. 101°), generated ammonia and water (eqns. 1 and 2). Ammonia escaped through the condenser and water was collected in a Dean–Stark trap. The reaction products (Table 1) were found to be organotin halides. High yields of purified products were readily obtained.

$$(R_3Sn)_2O + 2\ NH_4X \rightarrow 2\ R_3SnX + 2\ NH_3 + H_2O \qquad (1)$$

$$R_2SnO + 2\ NH_4X \rightarrow R_2SnX_2 + 2\ NH_3 + H_2O \qquad (2)$$

Organotin hydroxides, when heated with ammonium halides in the presence

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TABLE 1

INTERACTION OF AMMONIUM HALIDES WITH ORGANOTIN OXIDES

Organotin oxide	X in NH_4X	Reaction time (h)	Reaction product	M.p. (°C) or b.p. (°C/mm) (reported)^3	Yield (%)	Sn (%) found (calcd.)	X (%) found (calcd.)	M.p. Bipy adduct (°C) (reported)^2
Bu_2SnO	I	3	Bu_2SnI_2	143–147/0.25 (124–134/0.2)	92	24.40 (24.38)	52.52 (52.15)	162–163 (163)
	Br	8	Bu_2SnBr_2	130–132/0.25 (96–98/0.04)	80	30.30 (30.22)	40.87 (40.69)	176–177 (176–177)
	Cl	15	Bu_2SnCl_2	98–100/0.45 (89–91/0.2)	70	38.90 (39.07)	23.42 (23.33)	179–180 (179–180)
Me_2SnO	I	8	Me_2SnI_2	43–44 (44)	60	29.70 (29.48)	62.62 (63.05)	212–214 (214)
$(Pr_3Sn)_2O$	I	4	Pr_3SnI	128–132/2.0 (140–141/4.0)	88	31.50 (31.57)	34.2 (34.04)	
	Br	8	Pr_3SnBr	119–120/2.0 (126–127/12.0)	80	36.2 (36.19)	24.6 (24.39)	
	Cl	12	Pr_3SnCl	98–100/4.0	62	41.9 (41.87)	12.62 (12.52)	
$(Bu_3Sn)_2O$	I	2	Bu_3SnI	132–135/0.25 (168/8)	91	28.50 (28.47)	30.76 (30.44)	
	Cl	12	Bu_3SnCl	110–112/0.5 (98/0.45)	72	36.30 (36.46)	10.78 (10.89)	

of methylcyclohexane also gave organotin halides (Table 2). Organotin n-butoxides and ammonium halide in refluxing toluene yielded butanol, ammonia and the corresponding organotin halides (eqn. 3, Table 2). Toluene seemed to be a satisfactory solvent since it formed an azeotrope with n-butanol which could be removed as it was

TABLE 2

INTERACTION OF AMMONIUM HALIDES WITH ORGANOTIN HYDROXIDES AND ALKOXIDES

Organotin hydroxide or alkoxide	X in NH_4X	Reaction time (h)	Reaction product	M.p. (°C) or b.p. (°C/mm) (reported)^2	Yield (%)	Sn (%) found (calcd.)	X (%) found (calcd.)	M.p. Bipy adduct (°C) (reported)^2
Ph_3SnOH	I	2	Ph_3SnI	118–120 (119–121)	90	24.70 (24.88)	26.75 (26.60)	
	Cl	10	Ph_3SnCl	104–106 (104–106)	67	30.80 (30.78)	9.32 (9.19)	
$(C_6H_{11})_3SnOH^a$	I	2	$(C_6H_{11})_3SnI$	65 (65)	94	23.9 (23.96)	25.56 (25.62)	
	Br	6	$(C_6H_{11})_3SnBr$	76–77	85	26.60 (26.48)	17.96 (17.83)	
$Bu_2Sn(OBu)_2$	I	3	Bu_2SnI_2	138–142/0.2 (124–132/0.2)	93	24.66	52.44	162–163 (163)
	Cl	24	Bu_2SnCl_2	98–100/0.4 (89–91/0.2)	73	39.20	23.52	179–180 (179–180)
Bu_3SnOBu	I	2.5	Bu_3SnI	130–135/0.3 (168/8)	94	28.47	30.2	

^{a} C_6H_{11} = cyclohexyl.

formed by careful fractionation*.

$$R_3SnOR' + NH_4X \rightarrow R_3SnX + NH_3 + R'OH \qquad R' = \text{alkyl or H} \qquad (3)$$

When organotin oxides and hydroxides were treated in refluxing methylcyclohexane with ammonium thiocyanate, the reaction products were found to be ammonia, water, and the corresponding organotin isothiocyanates:

$$R_3SnOH + NH_4SCN \rightarrow R_3SnNCS + H_2O + NH_3 \qquad (4)$$

Organotin butoxides and ammonium thiocyanate in refluxing toluene also yielded the organotin isothiocyanates:

$$R_nSn(OBu)_{4-n} + (4-n)\,NH_4SCN \xrightarrow{C_6H_5CH_3} R_nSn(NCS)_{4-n} + (4-n)\,NH_3 + (4-n)\,BuOH \qquad (5)$$

These reactions are summarized in Table 3.

Organotin halides formed in these reactions were identified by their boiling and melting points, elemental analyses, and infrared spectra. The purity of the products was estimated by GLC. In the case of dialkyltin dihalides, 2,2′-bipyridine adducts were also prepared to confirm the identity of the products.

The organotin isothiocyanates were characterized by their infrared spectra, which showed the N=C stretching band in the region 2080–2050 cm^{-1} and also a band in the region 850–890 cm^{-1}, which can be attributed to C=S stretching absorption. These data indicate that the nitrogen atom of the thiocyanate group is directly attached to tin atom[8,9]. The details of the infrared spectra of these and other pseudohalogen derivatives of tin will be described elsewhere.

Comparison of yields and the reaction times in Tables 1 and 2 show that the iodides are obtained in better yields and in shorter times than the bromides, which in turn are better than chlorides, suggesting that the order of reactivity is $I^- > Br^- > Cl^-$. This could be ascribed either to the higher solubility of ammonium iodide (the reactions are heterogeneous) or to the greater nucleophilicity of iodide ion, or both.

The mechanism of the reaction of ammonium halides with organotin compounds is not clearly understood. The possibility of the dissociation of ammonium halides into ammonia and free acid (eqn. 6), which then reacts with organotin oxide, hydroxide or alkoxide to give the final products can be ruled out on the basis[10] that such dissociations occur around 300°.

$$NH_4X \rightleftarrows NH_3 + HX \qquad (6)$$

The results can be rationalized in terms of a nucleophilic displacement on the metal by halide ion. The role of ammonium halide in this case is presumably that of a protonation of the oxygen, allowing facile departure of water, alcohol or stannol:

$$R_3SnOR' + NH_4X \xrightarrow{-NH_3} [R_3Sn\underset{H}{\overset{+}{O}}R'] \xrightarrow{X^-} R_3SnX + HOR' \qquad (7)$$
$$R' = H,\ Bu,\ \text{or } SnR_3$$

The formation of organotin isothiocyanates can also be explained on the basis of a simple nucleophilic attack by thiocyanate ion on tin with proton transfer from NH_4^+ to yield the observed products.

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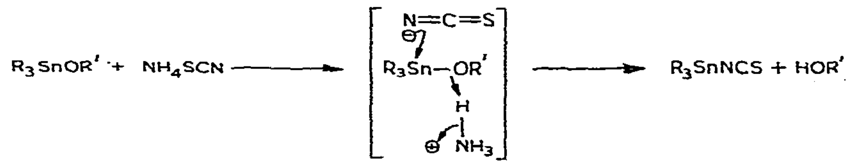
* The toluene/butyl alcohol azeotrope has b.p. 103° and contains *ca.* 28% butyl alcohol[12].

TABLE 3

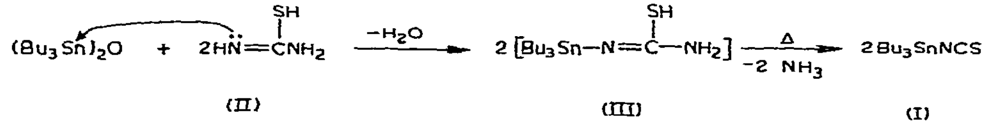
REACTIONS OF AMMONIUM THIOCYANATE WITH ORGANOTIN COMPOUNDS

Starting materials	Organotin isothiocyanate	Yield (%)	M.p. (°C) or b.p. (°C/mm) (reported)	Sn (%) found (calcd.)	C (%) found (calcd.)	H (%) found (calcd.)	S (%) found (calcd.)	N (%) found (calcd.)
Bu_2SnO	$Bu_2Sn(NCS)_2$[a]	75	145 (142.5–145)[5]	33.7 (33.9)	35.0 (34.6)	5.05 (5.18)	18.1 (18.3)	7.9 (7.99)
$Bu_2Sn(OBu)_2$	$Bu_2Sn(NCS)_2$	81	143–145					
$(Bu_3Sn)_2O$	Bu_3SnNCS	88	155/0.4 (160/0.5)[4]	34.1 (34.1)	44.9 (44.8)	7.56 (7.82)	9.1 (9.1)	4.36 (4.02)
Bu_3SnOBu	Bu_3SnNCS	75	150–152/0.3					
$(Pr_3Sn)_2O$[b]	Pr_3SnNCS[c]	30	126–128/0.2	38.8 (38.8)	39.4 (39.2)	6.95 (6.91)	14.5 (14.5)	4.48 (4.57)
Me_3SnOH	Me_3SnNCS[d]	75	105–108 (108.5)[6]	53.3 (53.3)	21.7 (21.7)	4.01 (4.09)	14.2 (14.5)	6.3 (6.32)
Ph_3SnOH	Ph_3SnNCS	90	171–172 (172–173)[7]	29.0 (29.1)	55.9 (55.9)	3.76 (3.70)	7.8 (7.86)	3.4 (3.43)
$(C_6H_{11})_3SnOH$	$(C_6H_{11})_3SnNCS$[c]	78	123	27.8 (27.8)	53.8 (53.5)	7.85 (7.86)	7.55 (7.52)	3.23 (3.28)

[a] 2,2′-Bipyridine adduct, m.p. 152–153° (lit.[5] 152.5–153°C.). [b] This reaction was carried out at room temperature. [c] New compounds. [d] Pyridine adduct, m.p. 112–114° (lit.[8] 110–113°).



Cummins and Dunn[4] have reported that the reaction of thiourea with bis(tributyltin)oxide at 200° yields bis(tributyltin)sulphide (70%) and tributyltin isothiocyanate (I) (15%). They postulated that the formation of (I) proceeded by attack of the tautomer (II) of thiourea on tin to yield the intermediate, (III), followed by loss of ammonia.



Evidence against the possibility that our reaction proceeds in a similar manner lies in the probable necessity of higher temperatures (*ca.* 175°)[11] for the conversion of ammonium isothiocyanate to thiourea than those which we employed (100–110°).

$$(NH_2)_2C{=}S \overset{ca.\ 175^\circ}{\rightleftharpoons} NH_4SCN$$

We have observed that ammonium thiocyanate remains unchanged in boiling methylcyclohexane for two hours, and indeed, stirring a mixture of tri-n-propyltin oxide with ammonium thiocyanate in methylcyclohexane at *room temperature* for four hours was found to yield a substantial amount of the tri-n-propyltin isothiocyanate. In contrast, in none of our reactions was there found evidence for sulphide formation as observed at higher temperatures[4].

In view of the above, it would seem reasonable that the isothiocyanate formation described by Cummins and Dunn[4] actually proceeds by prior equilibration of the thiourea with ammonium thiocyanate, followed by simple nucleophilic displacement as we have proposed above (we have confirmed the appearance of the thiocyanate[11] upon heating thiourea in tetralin for two hours at 175°). This explanation is also compatible with the observation that *N,N'*-disubstituted thioureas, which cannot rearrange to thiocyanates, give only the sulphides[4].

The generality of this reaction has been extended to other organometallic oxides, alkoxides and metal alkoxides. Also, preliminary work has shown that other ammonium salts such as acetates, azides and isocyanates give excellent yields of the corresponding organometallic and other metal alkoxy derivatives. These results will be published at a later date.

EXPERIMENTAL SECTION

General comments

Elemental analyses were performed by Mr. L. E. Swim (Dow's Analytical Laboratory). Infrared spectra were recorded on a Perkin–Elmer Grating Spectrophotometer (Model No. 337). Gas–liquid partition chromatography (GLC) was carried out isothermally using F&M instrument (Model 500) on a 10 ft. column packed with Apiezon L on chromosorb W.

Starting materials

The organotin oxides and hydroxides were purchased from Alpha Inorganics, Inc. and were used without further purification. Di-n-butyltin di-n-butoxide (b.p. 142°/0.1 mm) and tri-n-butyltin n-butoxide (b.p. 135°/0.2 mm) were prepared from the corresponding organotin oxides and n-butanol[2]. Reagent grade ammonium halides and thiocyanate (Fisher Scientific Co.) were used.

Reactions of ammonium halides with organotin oxides and hydroxides

Typically, a mixture of organotin oxide or hydroxide (0.1 mole) and ammonium halide (0.24 moles for oxides and 0.12 mole for hydroxides) in dry methyl cyclohexane (250 ml) in a flask equipped with a Dean–Stark trap connected to a condenser, and magnetic stirring assembly was heated (with fast stirring) at reflux for a varying degree of time (Tables 1 and 2). During this period, ammonia gas escaped through the condenser and the water formed and was collected in the trap. After distilling the water out, most of the solvent was also removed through the Dean–Stark trap. The reaction mixture was cooled and the unreacted ammonium halide was filtered off. The filtrate was fractionated to yield the corresponding organotin halides.

The distilled products were checked for purity by GLC and the retention times were compared with the retention times of authentic samples. Infrared spectra were also recorded as thin film in the case of liquids and as solution in carbon tetrachloride for solids. The spectra were also checked with the infrared spectra of authentic samples.

Reactions of ammonium halides with organotin n-butoxides

Ammonium halide (0.24 mole) was heated at reflux in dry toluene (250 ml) in a flask (with stirring) connected to a fractionating column with a variable take-off still head. The first few ml (*ca.* 25 ml) of toluene was discarded (this operation was carried out to remove any water from ammonium halide). It was then cooled, organotin n-butoxide (0.20 mole for monobutoxide and 0.10 mole for dibutoxide) was now introduced into the flask. The reaction was stirred and refluxed, toluene n-butanol azeotrope (b.p. 103°)[12] was first collected. During this period ammonia gas was evolved from the reaction mixture. Most of the toluene was then distilled off. After filtering the unreacted ammonium halide, the crude organotin halide was distilled to yield the pure product.

Preparation of di-n-butyltin diisothiocyanates

(*a*) *From di-n-butyltin oxide.* Di-n-butyltin oxide (11.0 g) and ammonium thiocyanate (7 g) were suspended in methylcyclohexane (400 ml). The reaction mixture slowly heated to reflux with vigorous stirring and refluxed for approximately 10 h. During this period, ammonia was evolved and water produced was collected in a Dean–Stark trap. Methyl cyclohexane (*ca.* 300 ml) was then distilled and an insoluble white mass settled out. This was suspended in boiling chloroform (250 ml) and then filtered hot to remove unreacted ammonium thiocyanate. The filtrate was concentrated to about 100 ml and then allowed to crystallize. Impure di-n-butyltin diisothiocyanate (11.5 g) precipitated as white, shiny crystals, m.p. 140–145°. A small portion of this was recrystallized from ether to yield pure material.

(*b*) *From di-n-butyltin di-n-butoxide.* Ammonium thiocyanate (5.0 g) was dried by refluxing with stirring in toluene (350 ml) and removing 50 ml of distillate. This was then cooled to room temperature and di-n-butyltin di-n-butoxide (7.5 g) was added. The reaction mixture was refluxed for 5 h, during which period the n-butanol/toluene azeotrope was removed by distillation. After evaporating the excess toluene a white powder was obtained, which was refluxed with chloroform (175 ml) and filtered hot to remove unreacted ammonium thiocyanate. On concentrating the filtrate, fine crystals of di-n-butyltin diisothiocyanate (6.0 g) precipitated out.

Preparation of tri-n-butyltin isothiocyanate

(*a*) *From bis-tri-n-butyltin oxide.* A mixture of bis(tri-n-butyltin) oxide (41 g) and ammonium thiocyanate (12 g) in methylcyclohexane (125 ml) was refluxed with stirring for 4 h. Ammonia was evolved and water was removed as above. Methylcyclohexane (80 ml) was then distilled, leaving a white slurry. This was filtered and the filtrate fractionated to give pure tri-n-butyltin isothiocyanate (42 g).

(*b*) *From tri-n-butyltin n-butoxide.* Ammonium thiocyanate (11.5 g) was dried by refluxing with stirring toluene (350 ml), and then distilling about 50 ml of the toluene. To this was added tri-n-butyltin n-butoxide (17.5 g) and the reaction mixture was refluxed with stirring for 4 h, during which period the n-butanol/toluene azeotrope was fractionated out. On evaporating toluene from the reaction mixture, a white solid with some viscous liquid was obtained. This was diluted with water and extracted with methylene chloride. The organic layer was dried ($MgSO_4$), and on fractionation yielded pure tri-n-butyltin isothiocyanate (12.0 g).

Preparation of tricyclohexyltin isothiocyanate

This compound (22.0 g) was prepared from tricyclohexyltin hydroxide (27 g), ammonium thiocyanate (5.4 g) and methylcyclohexane (125 ml) in the manner described above for the preparation of di-n-butyltin diisothiocyanate.

Preparation of triphenyltin isothiocyanate

Triphenyltin hydroxide (3.7 g) and ammonium thiocyanate (1.4 g) was refluxed in methylcyclohexane (75 ml). Water was removed and then most of the methylcyclohexane was distilled. The insoluble mass was refluxed with chloroform (30 ml) and the filtrate yielded the needle-shaped crystals of triphenyltin isothiocyanate (4 g), m.p. 168–170.5°. Recrystallization gave the pure product.

Preparation of tri-n-propyltin isothiocyanate

A mixture of bis(tri-n-propyltin)oxide (26 g) and ammonium thiocyanate (8 g) in benzene (100 ml) was stirred at room temperature (27°) for approximately 4 h. Ammonia was evolved and water formed. The reaction mixture now poured into water (200 ml) and extracted with more benzene (75 ml). The organic layer after drying ($MgSO_4$) was fractionated to yield a colorless liquid, b.p. 110–130°/0.2 mm (27 g). Infrared spectrum of this showed a sharp band at 2080 cm^{-1} (characteristic for organotin isothiocyanates) and another sharp band at 2248 cm^{-1} due to some unidentified impurity. Careful refractionation of the above liquid gave a low boiling fraction (8 g) b.p. 115–122°/0.2 mm (infrared spectrum of this showed a band at 2248 cm^{-1}) and pure tri-n-propyltin isothiocyanate (17 g).

Rearrangement of thiourea to ammonium thiocyanate

Thiourea (10 g) was heated for 2 h with stirring in tetralin (60 ml) and temperature was kept between 175–178°. The reaction mixture turned yellow and gave some ammonia. After cooling it to room temperature, the insoluble mass (8.9 g) was filtered and washed with cyclohexane and dried. The infrared of this displayed a sharp band at 2055 cm^{-1} corresponding to thiocyanate structure. This product gave off ammonia when treated with an aqueous solution of sodium hydroxide (thiourea does not give ammonia under these conditions). An aqueous solution of the above mass gave an intense violet color with an aqueous solution of ferric chloride; which was indicative of the presence of ammonium thiocyanate (thiourea did not give this test).

Treatment of ammonium thiocyanate in refluxing methylcyclohexane

Ammonium thiocyanate (8.0 g) was heated at reflux with stirring for 4 h. Some ammonium thiocyanate sublimed and was collected at the walls of the condenser. After cooling, the insoluble mass (7.4 g) was filtered and dried. This was found to melt at 148–150°. The m.p. did not change when mixed with an authentic sample of ammonium thiocyanate.

Preparation of 2,2'-bipyridine adducts

An ethanol solution (5 ml) of organotin dihalide or organotin diisothiocyanate (0.25 g) was added to a solution of 2,2'-bipyridine (0.25 g) in ethanol (10 ml). On shaking, a crystalline white precipitate was formed, which was filtered and recrystallized from n-butanol to yield the pure products.

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REFERENCES

1 R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Rev.*, 60(1960) 459.
2 R. W. Weiss, *Organometallic Compounds, Methods of Synthesis, Physical Constants and Chemical Reactions*, Vol. II, Springer-Verlag New York, 1967, pp. 268–286 and 302–320.
3 W. Stamm, *J. Org. Chem.*, 30 (1965) 693.
4 R. A. Cummins and P. Dunn, *Aust. J. Chem.*, 17 (1964) 411.
5 D. L. Alleston, A. G. Davies, M. Hancock and R. F. M. White, *J. Chem. Soc.*, (1963) 5469.
6 D. Seyferth and N. Kahlen, *J. Org. Chem.*, 25 (1960) 809.
7 T. N. Srivastava and S. K. Tondon, *Indian J. Appl. Chem.*, 26 (1963) 171.
8 M. Wada and R. Okawara, *J. Organometal. Chem.*, 8 (1967) 261.
9 M. Wada, M. Nishino and R. Okawara, *J. Organometal. Chem.*, 3 (1965) 70.
10 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 2nd Ed., 1966, p. 334.
11 E. E. Reid, *Organic Chemistry of Bivalent Sulphur*, Vol. V, Chemical Publishing Co., New York, 1963 p. 12.
12 L. H. Horsley, *Azeotropic Data*, A.C.S. Monograph No. 6, p. 125.