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Synthesis and Reactivity of Organotin(IV) Nitrates with Heterocycles Systems

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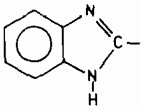
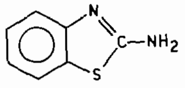
The reactions of $R_{4-n}Sn(NO_3)_n$ (R = Ph, Bu^n; n = 1,2) compounds with benzimidazole and 2-aminobenzthiazole have been made and investigated in relation to the reaction conditions. The IR, NMR and MS techniques have been used to characterize the final reaction products.

Introduction

The synthesis and the characterisation of nitrates of organotin with P, As, S, N, O containing ligands have been the object of our recent work, in which the chemical and structural properties of the compounds have been related to the coordinating and oxidising properties of the nitrate group, to the redox character of the tin-ligand system and to the number and to the nature of the organic groups σ-bonded to the tin atom [1–3].

This paper deals with the reactivity of $R_{4-n}Sn(NO_3)_n$ (R = Ph, Bu^n; n = 1, 2) compounds towards benzimidazole (BI) and 2-aminobenzthiazole (ABT) which is discussed in relation to the nature of the final products and to the reaction conditions.


BI


ABT

Experimental

All the reactions were carried out in dry nitrogen (or argon) atmosphere by use of anhydrous reagents and solvents. All the solvents were distilled before use.

Elemental C, H, N analyses were made on a Perkin-Elmer Mod. 240 automatic analyser. The quantitative determination for tin was obtained by atomic absorption spectroscopy on a Perkin-Elmer Mod. 303 spectrophotometer, using standard solutions of Ph_3SnCl.

The gas chromatographic analysis was carried out on a Perkin-Elmer Mod. 990 equipment with CARBOWAX 1500 columns. The nuclear magnetic resonance spectra were registered on a Varian EM 360 (60 MHz) equipment, using deuterated dimethylsulphoxide as solvent and tetramethylsilane as internal standard. A Varian CH5 spectrometer was used for mass spectrometry analysis.

Preparation of $R_{4-n}Sn(NO_3)_n$ (R = Ph, Bu^n; n = 1, 2)

For all the compounds the synthesis was carried out by reaction of anhydrous silver nitrate with equimolar amounts of the organotin chloride [4, 5]. With the exception of $Bu_2Sn(NO_3)_2$, acetonitrile for $AgNO_3$ and acetone for organotin chloride were used as reaction solvents. Ph_3SnNO_3 and $Ph_2Sn(NO_3)_2$ were prepared at room temperature while for $Bu_2Sn(NO_3)_2$ a water–ice bath was employed. After filtration of AgCl, small portions of acetone were added to the concentrated solution with the aim of completing the precipitation of the silver salt. From the final solution Ph_3SnNO_3 and $Ph_2Sn(NO_3)_2$, as white solids, and Bu_3SnNO_3, as colourless oil, were isolated. $Bu_2Sn(NO_3)_2$ was synthesised as white solid using a Soxhlet extracting equipment with boiling methanol solution of Bu_2SnCl_2 and solid $AgNO_3$ positioned in the filter-paper thimble.

Reactions of $R_{4-n}Sn(NO_3)_n$ with Organic Ligands

All the reactions were carried out in anhydrous solvents (acetone, chloroform or benzene) by dropping the equimolar amount of the dissolved ligand at room temperature into the stirred solution of the organotin compound. Precipitation generally occurred by slow evaporation of the solvent or by adding small portions of n-pentane (or n-hesane) to the reaction solution.

Results and Discussion

Concerning the products obtained from the reaction of the organotin compounds with the heterocyclic ligand in acetone, it can be observed that in most cases two different compounds have been isolated and, when possible, characterized (Tables I–

TABLE I. Analytical Data of Some Compounds Obtained from Reaction of $R_{4-n}Sn(NO_3)_n$ (R = Ph, Bu^n; n = 1, 2) with 2-Aminobenzthiazole (ABT) and Benzimidazole (BI).

Reagents	Reaction Products	C%		H%		N%		Sn%	
		calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
$Bu_2Sn(NO_3)_2$; ABT	$ABT{\cdot}HNO_3$	39.4	39.3	3.3	3.3	19.7	19.7	–	–
	$Bu_2Sn(NO_3)_2(ABT)$	35.5	37.2	4.8	4.5	11.1	11.3	23.4	23.0
Bu_3SnNO_3; ABT	$ABT{\cdot}HNO_3$	39.4	39.3	3.3	3.5	19.7	19.1	–	–
	$Bu_3SnNO_3(ABT)$	45.4	46.1	6.6	6.8	8.4	8.8	23.6	25.0
$Ph_2Sn(NO_3)_2$; ABT	$ABT{\cdot}HNO_3$	39.4	39.4	3.3	3.4	19.7	19.6	–	–
	$[Ph_2Sn(OH)]_2O$	48.4	49.0	3.7	3.6	–	–	39.8	40.4
$Bu_2Sn(NO_3)_2$; BI	$BI{\cdot}HNO_3$	46.4	46.2	3.9	3.9	23.2	22.8	–	–
	$[Bu_2Sn(NO_3)]_2O$	31.7	32.2	6.0	5.8	4.6	4.9	39.2	40.2
Bu_3SnNO_3; BI	$(BI)_2HNO_3$	56.6	56.5	3.7	4.3	23.6	23.2	–	–
	$Bu_3SnNO_3(BI)$	48.5	48.4	7.1	7.5	8.9	9.3	25.2	26.0
$Ph_2Sn(NO_3)_2$; BI	$(BI)_2HNO_3$	56.6	55.9	3.7	4.2	23.6	22.9	–	–
	$[Ph_2Sn(OH)]_2O$	48.4	48.6	3.7	3.9	–	–	39.8	41.0
Ph_3SnNO_3; BI	$Ph_3SnNO_3(BI)$	56.6	56.6	4.0	4.0	7.9	7.9	22.4	23.5

TABLE II. Selected Vibrational Bands (cm^{-1}) Involving the Tin Atom.

Compound	Frequency	Assignment
$Bu_2Sn(NO_3)_2(ABT)$	595m	ν(Sn–C)
	300mw	ν(Sn–N)
$Bu_3SnNO_3(ABT)$	585m	ν(Sn–C)
$Bu_3SnNO_3(BI)$	605m sh	ν(Sn–C)
$[Bu_2Sn(NO_3)]_2O$	595m	ν(Sn–C)
	530sh	
	564m	ν(Sn–O–Sn)
$[Ph_2Sn(OH)]_2O$	571s	ν(Sn–O–Sn)
	300m	ν(Sn–C)
$Ph_3SnNO_3(BI)$	590m	ν(Sn–N)
	290sh	ν(Sn–C)
	270m	ν(Sn–C)

III). One of these compounds was found to correspond to the formula $L{\cdot}HNO_3$ (L = benzimidazole; 2-aminobenzthiazole), while the other compound showed to be a distannoxane type derivative such as $[R_2SnNO_3]_2O$ or as $[R_2Sn(OH)]_2O$. These tin products are not always purified and easily separated from small amounts of the ligand–organotin adduct. The identification of all the compounds was made by C, H, N, Sn chemical analyses, and by infrared and nuclear magnetic resonance spectra; particularly, the nature of $L{\cdot}HNO_3$ was confirmed by the analogy of the spectroscopic data shown by the products isolated from the reaction of BI or ABT with dilute nitric acid. The initial choice of acetone, as reaction solvent, was based on the good solubility that both organotin and heterocyclic ligand showed in it.

The formation of the two afore-mentioned compounds can be explained as a result of an hydrolysis process on the parent organotin compound with development of nitric acid, followed by the reaction of HNO_3 with the basic organic ligand to form the nitrate derivative as indicated in the following scheme:

$$2R_2Sn(NO_3)_2 + H_2O \rightleftharpoons [R_2SnNO_3]_2O + 2HNO_3$$

$$L + HNO_3 \rightleftharpoons L{\cdot}HNO_3$$

Since all the solvents and the inert gases (nitrogen or argon) were completely anhydrified before use, the mechanism of reaction must be justified on the basis of the reaction conditions alone. On the other hand, the same results were successively obtained after rigorous control of all the reaction equipments.

By a gas chromatographic analysis carried out on the reaction solution, mesityl oxide was detected in good yield which permits to formulate the probable mechanism of the reaction, as is schematized for a generic $R_2Sn(NO_3)_2$ compound:

$$2R_2Sn(NO_3)_2 + 2L + 2Me_2CO \rightleftharpoons$$

$$[R_2SnNO_3]_2O + 2L{\cdot}HNO_3 + Me_2CCHC(O)Me$$

It is well known that mesityl oxide is formed by a preliminary aldol addition of two acetone molecules under catalytic action of acid (or basic) medium and the successive conversion of diacetone-alcohol form by dehydrating agents [6, 7]. In our

TABLE III. Vibrational Absorptions (cm^{-1}) of the Nitrate Group.

Compound	Frequency	Assignment
$Bu_2Sn(NO_3)_2$ (ABT)	1765w	$\nu_1 + \nu_4$
	1380vs	$\nu(NO)$
	1018w	$\nu_s(NO_2)$
	825m	$\delta(NO_2)$
Bu_3SnNO_3(ABT)	1765w	$\nu_1 + \nu_4$
	1380vs	$\nu(NO)$
	1005w	$\nu_s(NO_2)$
	810sh	$\delta(NO_2)$
Bu_3SnNO_3(BI)	1765w	$\nu_1 + \nu_4$
	1450–1350br	$\nu_{as}(NO_2)$
	1010w	$\nu_s(NO_2)$
	835sh	$\delta(NO_2)$
	830m	$\delta(NO_2)$
$[Bu_2Sn(NO_3)_2]O$	1620s	$\nu_{as}(NO_2)$
	1600sh	
	1380s	$\nu(NO)$
	1300s	$\nu_s(NO_2)$
	1030w	$\nu_s(NO)$
	1010sh	
	830m	$\delta(NO_2)$
Ph_3SnNO_3(BI)	1768w	$\nu_1 + \nu_4$
	1720vw	
	1390vs	$\nu(NO)$
	1018w	$\nu_s(NO)$
	830w	$\delta(NO_2)$

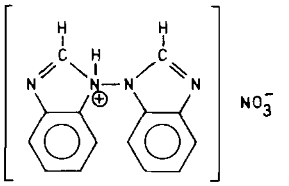
case the high dehydrating character of the organotin compounds is the responsible agent for the formation of mesityl oxide. However, the further condensation product, phorone, was not found in the reaction mixture. The autocondensation of acetone molecules involves the formation of water molecules which produce nitric acid from the organotin compound. It is not possible to exclude that the basic character of the organic ligand plays an important role in the reaction mechanism, forming the ligand–nitrate derivative. However, nitric acid formation is not a consequence of the basicity of the ligand, since in the acetone solutions of only organonitratotin compounds after some time a small amount of mesityl oxide has been also detected.

When Ph_3SnNO_3 was reacted with benzimidazole, only a very small amount of mesityl oxide was found, while the main reaction product was the adduct $Ph_3SnNO_3 \cdot BI$; this fact can be explained with the lower dehydrating character that Ph_3SnNO_3 shows with respect to the other organotin compounds.

The influence of the solvent on the reaction mechanism and on the final products of the reaction was also recently observed by Harrison and Molloy for some organotin–thiazole systems in almost similar conditions [8].

The effect of acetone on the reaction mechanism has been confirmed by the results obtained when chloroform (or benzene) was used. In these cases the main reaction product is always the adduct with metal–ligand 1:1 molar ratio.

From the reactions of $Bu^n_3SnNO_3$ and $Ph_2Sn(NO_3)_2$ with benzimidazole (in acetone solution), an organic microcrystalline product (hereafter $(BI)_2 \cdot HNO_3$) was isolated for which C, H, N analytical data suggested a molar ratio of two benzimidazole moieties for one nitrate group. The vibrational bands of benzimidazole and nitrate systems are both evident in the infrared spectrum, but these absorptions differ in several small features from those observed in $BI \cdot HNO_3$ spectrum. The identification and the characterization of this product have been made by NMR spectroscopy and mass spectrometry. The NMR spectrum, registered in deuterated dimethylsulphoxide solvent, shows some resonance values which made clearer the nature of the compound. The single resonance peak at about $\delta = 9$, whose intensity is in the 1:4 ratio with the phenyl resonance value (near $\delta = 7.6$), is assigned to the CH groups of the heterocycle ring. Another broad resonance at about $\delta = 6.7$ is observed, which is attributed to the NH^+ group [9, 10]. From the mass spectrometry data (the main mass values are 296, 118, 91, 63 m/e) it can be concluded that the more probable structure for the $(BI)_2HNO_3$ compound is the following:



Unfortunately, it was not possible to confirm the exact nature of the compound by means of X-ray diffraction owing to the poor quality of the crystals.

The tin adducts, isolated in chloroform (or benzene) solution, together with the other organotin products obtained in acetone solution, have been examined by infrared spectroscopy and the main vibrational bands, involving the tin atom [11–16] (Table II) and the nitrate group [17–19] (Table III), are reported. The NO_3^- anion seems to be covalently bonded to the metal atom only in $[Bu_2SnNO_3]_2O$, where probably it behaves as a bidentate ligand. In all the other compounds the nitrate group shows an ionic character.

The coordination of ABT or BI molecule towards tin atom is essentially evidentiated by the small shifts which some vibrational bands (mainly those involving the NH group) undergo with respect to those in the free ligand; only for $Bu_2Sn(NO_3)_2(ABT)$ and $Ph_3SnNO_3(BI)$ is the attribution of the ν(Sn–N) band possible on the basis of the Sn–N stretching assignments as given in the literature for analogous compounds [20–23].

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