REACTIONS OF 4-PICOLINE WITH TRIMETHYLTIN CARBOXYLATES

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ABSTRACT

Two new trimethyltin carboxylate complexes of 4-picoline viz $Me_3SnOCOCHCl_2.4\text{-}Pic$ *and* $Me_3SnOCOC_6H_5.4\text{-}Pic$ *have been synthesized and characterized by i.r.* ^{119}Sn- *and* ^1H-*nmr spectroscopic methods. The compounds form five coordinate tin molecules with the pyridyl nitrogen binding to the central Sn to form a (1:1) Lewis acid: Lewis base complex. Attempt to prepare 4-picoline complexes of* $Me_3SnOCOCH_3$, $Me_3SnOCOCH_2Cl$ *and* $Me_3SnOCOCCl_3$ *by the same method of preparation could not give the desired products; this is not fully understood and therefore subject to further studies. However, solvent effect does not seem to play any significant role as, at least, one of the complexes has formed in either acetone or dichloromethane.*

INTRODUCTION

There are reports[1-3] on pyridyl complexes of organotin and several others[4-7] on the preparation of pyridine adducts of organotin halides. However, very little has been reported on pyridine complexes of organotin carboxylates. We have previously published the successful synthesis of some pyridine adducts of trimethyltintrifluoroacetate and dimethyltin bistrifluoroacetate[8]. Further investigation[9] reveals that reacting pyridine adducts of diphenyltindichloride with silver trifluoroacetate gives the phenyltin acetate rather than pyridine adduct of the compound. Our recent report was on the synthesis of 4-picoline adducts of organotin pseudo halides[10]. In our effort to study this intriguing class of compounds further, we now report the synthesis and spectroscopic characterization of adducts of $Me_3SnOCOCHCl_2$, $Me_3SnOCOC_6H_5$ and $Me_3SnOCOCCl_3$ with 4-picoline, the latter complex having been reported earlier[8].

EXPERIMENTAL

All reagents were of high grade and were used without further purification. The Me_3SnCl and 4-picoline were obtained from Aldrich. Solvents were purified based on accepted procedures[6]. Dry acetone was prepared by refluxing analytical grade acetone with p-toluene sulphonylchloride (2g/l) for 45 minutes and distilling into a bottle protected with $CaCl_2$ guard tube.

Melting temperatures were reported uncorrected (Table 1), i.r. spectra (in nujol) were run on a Perkin - Elmer RB 3100 and SP 800 i.r. spectrometers and calibrated with polystyrene. The nmr spectra were run at the Department of Chemistry, University of Sussex, England and Abubakar Tafawa Balewa University, Bauchi, Nigeria. Microanalysis of the complexes (C, H, Cl, F, N) were performed at the Microanalytical Laboratories of University of Sussex, while the Sn content was determined at the Analytical Laboratories of the Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria. Their physical data are shown in Table 1.

$Me_3SnOCOC_6H_5$ .4-Pic

Me_3SnCl (2.59g, 0.113mole) in dichloromethane (50ml), C_6H_5COOK (2.24g, 0.014mole) in dichloromethane (50ml) and 4-picoline (1.27ml)

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were mixed in a 250ml conical flask. This was stirred magnetically for 24 hours and filtered. The filtrate was concentrated at low pressure and left to stand at 50°C for 48 hours. Yellowish product obtained was washed with petroleum spirit (40 - 60°C). 62% yield was obtained.

$Me_3OCOCHCl_2$.4-Pic, $Me_3SnOCOCF_3$.4-Pic

Some quantity (0.022mole) of halo-substituted acetic acid ($CHCl_2COOH$, CF_3COOH) in acetone (50ml) and Na_2CO_3 (1.17g, 0.11mole) in acetone (25ml) were mixed in a 250ml conical flask. A vigorous reaction occurred and CO_2 was evolved. Me_3SnCl (3.99g, 0.02mloe) in acetone (50ml) and picoline (1.95ml) were added and the mixture stoppered and stirred magnetically for 24 hours. This was filtered and the filtrate concentrated at low pressure, then allowed to stand at 5°C for 72 hours. The $Me_3SnOCOCF_3$.4Pic and $Me_3SnOCOCHCl_2$.4Pic obtained were recrystallized from chloroform; 55 and 62% yields were obtained respectively.

Table 1: Physical properties and elemental analysis of trimethyltincarboxylates and trimethyltin carboxylate-4-picoline complexes.

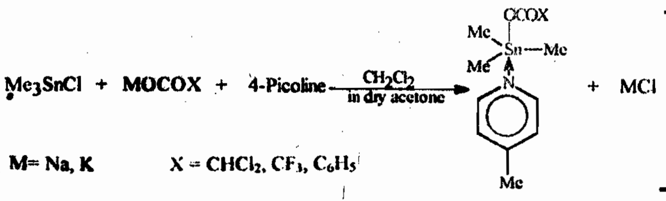
	Medium of preparation	Physical appearance	Melting point (°C)	Elemental Analysis found (calc.)			
				C	H	N	Sn
$Me_3SnOCOCHCl_2$	Acetone	Light brown crystals	97				
$Me_3SnOCOCHCl_2$.4Pic	Acetone	Colourless crystals	61-62	34.33 (34.25)	4.45 (4.51)	3.64 (3.65)	30.84 (30.63)
$Me_3SnOCOCF_3$	Dichloromethane	White crystals	74				
$Me_3SnOCOCF_3$4.Pic	Dichloromethane	Light yellow crystals	57	35.71 (35.62)	3.81 (3.97)	3.79 (3.82)	32.08 (32.32)
$Me_3SnOCOC_6H_5$	Acetone	Colourless crystals	124				
$Me_3SnOCOC_6H_5$.4Pic	Acetone	Yellow crystals	76-78	47.56 (47.74)	4.53 (4.58)	3.71 (3.68)	31.40 (31.51)

RESULTS AND DISCUSSION

The elemental analyses and spectral data obtained have shown that indeed some trimethyltin carboxylates do form adducts with the 4-picoline. The process used in this work to prepare these compounds involves simple substitution reaction using alkali metal carboxylate salts.

Table 1 shows a clear trend in the relationship of the melting points of the parent trimethyltin carboxylates and their 4-picoline complexes. Generally the parent trimethyltin carboxylates show higher melting temperatures than their 4-picoline complexes. This could suggest either elements of polymerization in the parent carboxylates[11,12] or reduced stability of the complexes compared with the parent trimethyltin carboxylates.

The rationale in preparing the various trimethyltin carboxylates reported in this paper is to find if there could be any noticeable effect of the electron withdrawing ability of the halogen substituents of the nucleophiles on the stability of the pyridine complexes they form. At this stage, it does not seem that a clear relationship exists between the melting points of the complexes and the



electron withdrawing ability of the carboxylate nucleophile.

Infrared spectroscopy is used to determine whether the trimethyltin carboxylate-4-picoline complexes are formed. The Sn-Me stretch is usually noted around 770-790cm^{-1} and if the carboxylate is present in the compound, it shows appropriately. For instance characteristic bands for C=O and OCO, C-O and Sn-O-C are shown at about 1650-1750cm^{-1} region as in Table 2. Ligation with 4-picoline indicates pyridyl aromatic C-H and C=C bands around 3050 and 1580cm^{-1} regions, which have been observed for our compounds. P.m.r. spectroscopy has shown that SnMe protons appear between 0.0 - 1.0ppm, the Me group of picoline at about 2.40ppm, the pyridyl-hydrogens at meta positions at about 7.40ppm and the pyridyl-hydrogens at ortho positions at about 8.50ppm. Indeed n.m.r. spectra indicated the existence of these bands thereby confirming the presence of pyridine in the complexes (Table 3). The up - field

Table 2: Ir spectral (cm^{-1}) data for trimethyltincarboxylate-4-picoline complexes.

	C-H (aromatic)	C=C and OCO	C=C (Py)	C-O	C-Hal	Sn-CH$_3$ rock	Sn-O-C
$(CH_3)_3SnOCOCHCl_2.4Pic$	3080w	1635m	1560m,b	*	1190m	785m	1075w
$(CH_3)_3SnOCOCF_3.4Pic$	3060w	1614s	1588w	1415m	1195s,b	785s,b	1050w
$(CH_3)_3SnOCOC_6H_5.4Pic$	3180w	1620s	1580m	1420w	-	780m	1050w

* Nujol peak, w = weak, m = medium, s = strong, b = broad.

Table 3: Nmr Chemical shifts of trimethyltin carboxylate-4-picoline complexes (δ-values in ppm)

	$Me_3SnOCOCHCl_2.4Pic$ (in DMSO- d_6)	$Me_3SnOCOCF_3.4Pic$ (in DMSO- d_6)	$Me_3SnOCOC_6H_5.4Pic$ (in benzene- d_6)	$N(C_6H_4)CH_3$ (4-Picoline)
Sn-CH$_3$	0.68Sm	0.81Svs	0.67Sm	-
CH$_3$	2.72Sm	2.58Svs	1.92Sm	2.0Sm
Pyridyl-*m*-H	8.62-8.870Dm	7.4-7.5Dm	6.67 – 6.7 Dm	6.7 – 6.9Dvs
Pyridyl-*o*-H	9.67Dm	8.36- 8.46Dm	8.57qm	8.3 – 8.5Dvs

Sm = Singlet, medium; Dm = Duplet, medium; Dvs = Duplet, very strong; qm = Quartet, medium.

and down-field shifts in the pyridyl hydrogens at ortho and meta positions in these complexes clearly signify the binding of the pyridyl ring albeit datively through the N.

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