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SHORT PAPER

The reactivity of tributyltin oxygen compounds with CCl_4: implications for its use as an extraction/reaction solvent

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A variety of tributyltin oxygen compounds, $(nC_4H_9)_3SnOX$ where $X=Sn(nC_4H_9)_3$, C_2H_5, nC_4H_9, C_8H_{17}, $CH_2C_6H_5$, $COCH_3$, have been studied in refluxing CCl_4. A reaction was observed to occur where $X=C_2H_5$, C_4H_9, C_8H_{17}, $CH_2C_6H_5$, leading to the formation of $(nC_4H_9)_3SnCl$, $CHCl_3$ and an aldehyde. Possible reaction pathways are suggested. These reactions have implications for the use of CCl_4 as an extraction/reaction solvent.

Keywords: Tributyltin oxygen compounds, CCl_4, NMR spectroscopy, solvent extraction

INTRODUCTION

Organotin compounds have achieved commercialization in a wide variety of applications.[1] In most of these uses, however, the tin compound is ultimately contained in a solid matrix. The elucidation of the chemical nature of the tin species present is therefore often difficult, due to the limitations of solid-state spectroscopic techniques, e.g. Mössbauer and infrared spectroscopies when applied to mixtures. A promising solid-state technique for studying organotin compounds appears to be cross-polarization magic-angle-spinning NMR,[2] but as yet this method is in its infancy. Consequently, in many cases chemical information is obtained by extracting the organotin derivative and subjecting the resulting solution to high-resolution NMR. In choosing an extraction solvent the following conditions should be met: the solvent should preferably not coordinate to the tin atom as this markedly affects the NMR parameters; for ^{13}C and ^{1}H NMR studies the solvent resonances should interfere as little as possible; and extraction solvents should be chosen with as low a boiling point as possible so as to avoid unwanted side-reactions. One of the most common laboratory solvents that fulfils the above criteria is carbon tetrachloride. This solvent also finds extensive use in organotin synthetic chemistry,[3] where low boiling point and polarity are prerequisites.

During the course of previous studies[4,5] into the compatibility of tributyltin fungicides with synthetic pyrethroid insecticides, a reaction was observed to occur between certain tributyltin oxygen compounds and carbon tetrachloride. This reaction has been investigated and is reported herein.

EXPERIMENTAL

Bis(tributyltin) oxide, $((nC_4H_9)_3Sn)_2O$, was obtained from Schering AG, West Germany, and was used without further purification. All other tributyltin compounds were prepared by methods described elsewhere.[3]

The tributyltin compounds were refluxed in CCl_4 in the dark under an atmosphere of nitrogen. Aliquots were withdrawn periodically prior to NMR investigations. Concentrations in each case were as given in Table 1.

NMR spectra were recorded on a JEOL FX60Q spectrometer, with field frequency lock to external D_2O. ^{119}Sn spectra were recorded under nuclear Overhauser suppressed conditions, and, to obtain quantitative results, a pulse repetition time of 10 s was used. ^{119}Sn and ^{13}C chemical shifts ($\delta^{119}Sn$ and $\delta^{13}C$) are relative to Me_4Sn and Me_4Si respectively and are accurate to ± 0.1 ppm.

Table 1 ^{119}Sn NMR chemical shifts in CCl_4 solution

Compound	Concentration (% w/v)	δ ^{119}Sn(ppm)
$[(nC_4H_9)_3Sn]_2O$	10	85.8
$(nC_4H_9)_3SnOC_2H_5$	50	90.8
$(nC_4H_9)_3SnOC_4H_9$	50	91.2
$(nC_4H_9)_3SnOC_8H_{17}$	50	92.8
$(nC_4H_9)_3SnOCH_2C_6H_5$	50	101.6
$(nC_4H_9)_3SnOC_6H_5$	50	107.2
$(nC_4H_9)_3SnOCOCH_3$	10	91.2
$(nC_4H_9)_3SnCl$	10	143.5

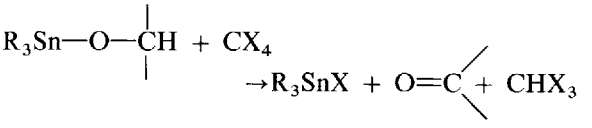
RESULTS AND DISCUSSION

Table 1 shows ^{119}Sn NMR chemical shift data of the tributyltin oxygen compounds studied.

Following refluxing in CCl_4 for increasing periods of time, ^{119}Sn NMR spectra were recorded and, in some cases, in addition to a resonance due to the refluxed compound, a peak due to $(nC_4H_9)_3SnCl$ was observed. Table 2 reports the percentage converion to $(nC_4H_9)_3SnCl$ after the appropriate reflux times.

It can be seen that $(nC_4H_9)_3SnOCH_2C_6H_5$ had been almost completely converted to $(nC_4H_9)_3SnCl$ after a refluxing time of 50 h. The ^{13}C NMR spectrum of this solution was recorded (Table 3) and by comparison with authentic samples was found to contain, in addition to the organotin compounds, chloroform and benzaldehyde.

With respect to the mechanism of this reaction it has previously been reported[6] that organotin alkoxides react with polyhalomethanes under free-radical conditions leading to the formation of corresponding carbonyl compounds according to the accompanying simplified reaction scheme (Scheme 1):



Scheme 1

In the studies outlined above, either UV light or a free-radical initiator, such as azoisobutyronitrile, was necessary to promote the reaction. In the present work neither a free-radical initiator nor UV light was present. In fact, refluxes were carried out in the dark to

Table 2 Extent of conversion of $(nC_4H_9)_3Sn—O—X$ into $(nC_4H_9)_3SnCl$[a]

X in $(nC_4H_9)_3Sn—O—X$		Reflux time[b] 0 h	4 h	10 h	25 h	50 h
$CH_2C_6H_5$	$(nC_4H_9)_3Sn—O—X$	100	60	40	15	5
	$(nC_4H_9)_3SnCl$	—	40	60	85	95
C_8H_{17}	$(nC_4H_9)_3Sn—O—X$	100	100	95	90	80
	$(nC_4H_9)_3SnCl$	—	N/D	5	10	20
nC_4H_9	$(nC_4H_9)_3Sn—O—X$	100	100	100	95	90
	$(nC_4H_9)_3SnCl$	—	N/D	N/D	5	10
C_2H_5	$(nC_4H_9)_3Sn—O—X$	100	100	95	90	85
	$(nC_4H_9)_3SnCl$	—	N/D	5	10	15
C_6H_5	$(nC_4H_9)_3Sn—O—X$	100	100	100	100	100
	$(nC_4H_9)_3SnCl$	—	N/D	N/D	N/D	N/D
$CO.CH_3$	$(nC_4H_9)_3Sn—O—X$	100	100	100	100	100
	$(nC_4H_9)_3SnCl$	—	N/D	N/D	N/D	N/D
$Sn(nC_4H_9)_3$	$(nC_4H_9)_3Sn—O—X$	100	100	100	100	100
	$(nC_4H_9)_3SnCl$	—	N/D	N/D	N/D	N/D

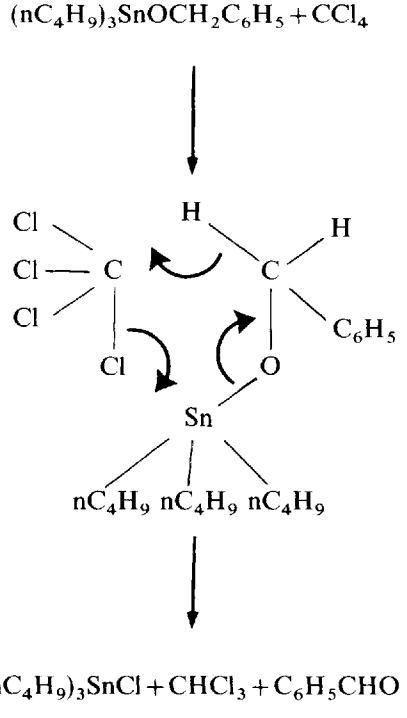
[a]Percentage compositions obtained from integration of ^{119}Sn NMR resonances. [b]N/D, not detected.

Table 3 ^{13}C NMR chemical shifts[a] (assignments in brackets)

Compound	$\delta^{13}C$ (ppm)									
$(nC_4H_9)_3SnOCH_2C_6H_5$	144.9 (C_6H_5)	127.6 (C_6H_5)	126.3 (C_6H_5)	126.2 (C_6H_5)	68.1 (OCH_2)	27.8 (nC_4H_9)	26.9 (nC_4H_9)	14.2 (nC_4H_9)	13.5 (nC_4H_9)	—
$(nC_4H_9)_3SnOCH_2C_6H_5$ after 50 h reflux in CCl_4	191.2 (HC=O)[b]	136.4 (C_6H_5)[b]	134.2 (C_6H_5)[b]	129.6 (C_6H_5)[b]	128.8 (C_6H_5)[b]	77.5 (CH)[c]	27.8 (nC_4H_9)[d]	26.8 (nC_4H_9)[d]	17.3 (nC_4H_9)[d]	13.6 (nC_4H_9)[d]
C_6H_5CHO[e]	191.4 (HC=O)	136.6 (C_6H_5)	134.0 (C_6H_5)	129.5 (C_6H_5)	128.8 (C_6H_5)	—	—	—	—	—
$CHCl_3$[e]	—	—	—	—	—	77.5	—	—	—	—
$(nC_4H_9)_3SnCl$[e]	—	—	—	—	—	—	27.8	26.7	17.1	13.6

[a]Recorded as 50% w/v solutions in CCl_4. [b]i.e. C_6H_5CHO. [c]i.e. $CHCl_3$. [d]i.e. $(nC_4H_9)_3SnCl$. [e]Standard samples.

prevent light-induced reactions. Therefore, since free radicals should not be generated thermally from either CCl_4 or the organotin under the mild reaction conditions employed, we believe that one of two reaction mechanisms is occurring. The first involves the formation of a cyclic transition state (Scheme 2).

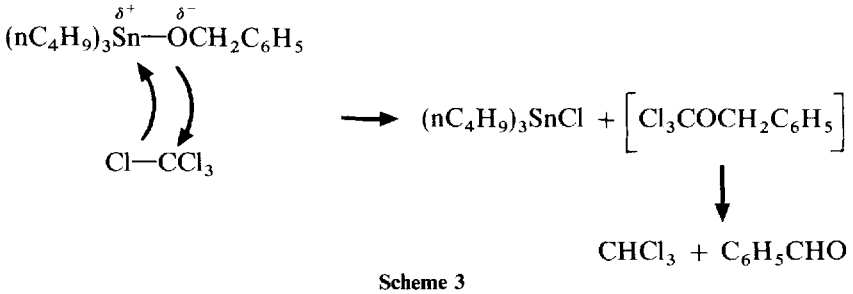


Scheme 2

The second reaction mechanism involves an addition reaction of the alkoxide and CCl_4 (Scheme 3).

^{13}C NMR spectra were recorded for the 50 h-refluxed solutions of the tributyltin alkoxides, $(nC_4H_9)_3SnOX$ where $X = C_2H_5$, nC_4H_9, C_8H_{17}, and in each case the presence of $CHCl_3$ was observed. Unfortunately, other organic species such as aldehydes were not positively identified due to the reduced conversion of organotin compounds to $(nC_4H_9)_3SnCl$ except in the case of $(nC_4H_9)_3SnOCH_2C_6H_5$. However, it is suggested that a similar reaction mechanism operates.

From the available information, it is difficult to ascertain the true reaction pathway. However, the presence of the $O—CH_2—X$ structure in the substrate appears to be necessary for the conversion to occur, since $(nC_4H_9)_3SnOC_6H_5$, $(nC_4H_9)_3SnOCOCH_3$ and $((nC_4H_9)_3Sn)_2O$ were stable in refluxing CCl_4. This observation may indicate that the reaction proceeds by the former mechanism, i.e. the formation of a cyclic transition state, since this is the only one that depends on the presence of the $O—CH_2—X$ feature. It is known[7] that, for tributyltin alkoxides, $(nC_4H_9)_3SnOR$, the alkoxide (—OR) moiety undergoes exchange between tin centres, the rate of exchange being dependent upon the steric requirements of the hydrocarbyl (R) group. Therefore, this may provide an explanation for the greater reactivity of $(nC_4H_9)_3SnOCH_2C_6H_5$ with respect to the linear aliphatic alkoxides, since it may have a slower exchange rate and so increases the probability of forming the cyclic transition state.



Scheme 3

CONCLUSION

A reaction has been observed to occur between certain tributyltin alkoxides and CCl_4 under reflux conditions leading to the formation of $(nC_4H_9)_3SnCl$, $CHCl_3$ and an aldehyde. This has obvious implications for the use of this solvent as an extraction/reaction medium, since these unwanted side-reactions lead to impurities in the solution.

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