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PREPARATION OF SOME TRIETHYLAMMONIUM CHLORIDE—*N*-SUBSTITUTED *N'*-CYANO-*O*-(TRIPHENYLSTANNYL)ISOUREA COMPLEXES

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Summary

Eleven (triphenylstannyl)cyanamide: organic isocyanate adducts were converted into anionic complexes by reaction with triethylammonium chloride. The IR spectra of the complexes indicate that the tin is bonded to oxygen rather than to nitrogen in the original adducts. The Mössbauer parameters of two of the complexes were obtained, the quadrupole splittings being consistent with trigonal bipyramidal structures. The Mössbauer parameters of the (triphenylstannyl)cyanamide: organic isocyanate adducts indicate a tin coordination number greater than four.

Introduction

We recently concluded that the tin atom in (triphenylstannyl)cyanamide: organic isocyanate adducts was bonded to oxygen rather than to nitrogen [1]. This conclusion was based on the observation that none of the adducts exhibited a band near 1660 cm^{-1} due to the carbonyl group of a urea; this band was reported to be present in the IR spectrum of the 1/1 addition compound formed between dimethylaminotrimethylstannane and phenyl isocyanate [2]. Nevertheless, the possibility still existed that a band attributed to C=N at 1515—1560 cm^{-1} in the IR spectra of the (triphenylstannyl)cyanamide: organic isocyanate adducts was actually due to a tin-coordinated carbonyl group, which would mean that the tin was bonded to nitrogen in these adducts. The purpose of the present study was to convert some (triphenylstannyl)cyanamide: organic isocyanate adducts into anionic complexes by reaction with triethylammonium chloride in order to gain information on whether the tin is bonded to nitrogen or to oxygen in the original adducts.

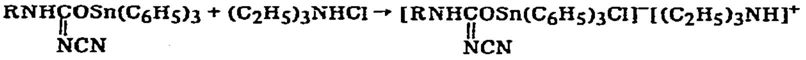
Results and discussion

Eleven (triphenylstannyl)cyanamide: organic isocyanate adducts were converted into anionic complexes by reaction with triethylammonium chloride (1 : 1 mol ratio) in tetrahydrofuran at 26°C (Table 1). In addition to their identification by elemental analysis, the compounds in Table 1 were further identified by their IR spectra (Table 2).

The IR spectra of the anionic complexes support our previous conclusion that the tin is bonded to oxygen rather than to nitrogen in (triphenylstannyl)cyanamide: organic isocyanate adducts. Significantly, the band at 1515—1560 cm^{-1} in the IR spectra of these adducts does not shift to a value anywhere near 1660 cm^{-1} when the adduct is complexed with triethylammonium chloride. If the band at 1515—1560 cm^{-1} in these adducts was due to a tin-coordinated carbonyl group, complexation of the tin with a chloride ion from triethylammonium chloride would be expected to uncoordinate the carbonyl group causing this band to shift to a considerably higher frequency. This hypothesis is supported by the observation that when *N*-acyl-*N*-(triphenylstannyl)cyanamides and *N*-alkoxycarbonyl-*N*-(triphenylstannyl)cyanamides were complexed with triethylammo-

TABLE 1

TRIETHYLAMMONIUM CHLORIDE—*N*-SUBSTITUTED *N'*-CYANO-*O*-(TRIPHENYLSTANNYL)-ISOUREA COMPLEXES



$$\mathrm{RNH\underset{\underset{NCN}{\|}}{C}OSn(C_6H_5)_3 + (C_2H_5)_3NHCl \rightarrow [RNH\underset{\underset{NCN}{\|}}{C}OSn(C_6H_5)_3Cl]^-[(C_2H_5)_3NH]^+}$$

No.	R	Yield [a] (%)	M.p. [b] (°C)	Analysis found (calcd.) (%)			
				C	H	N	Sn
I	C_2H_5	83	105—106	56.27 (56.07)	6.41 (6.22)	9.46 (9.34)	19.50 (19.79)
II	n-C_3H_7	67	124—125	57.05 (56.75)	6.55 (6.40)	9.65 (9.13)	18.94 (19.35)
III	n-C_4H_9	68	124—125	57.65 (57.39)	6.50 (6.58)	9.17 (8.92)	19.24 (18.90)
IV	cyclo-C_6H_{11}	86	133—134	59.07 (58.78)	6.75 (6.63)	8.84 (8.57)	18.05 (18.15)
V	$CH_2{=}CHCH_2$	71	93—95	56.99 (56.94)	6.02 (6.09)	9.40 (9.16)	19.70 (19.40)
VI	C_6H_5	84	141—143	59.59 (59.33)	5.93 (5.76)	8.63 (8.65)	18.16 (18.32)
VII	*m*-$CH_3C_6H_4$	88	110—114	60.08 (59.89)	6.02 (5.94)	8.30 (8.47)	17.94 (17.93)
VIII	*p*-$C_2H_5OC_6H_4$	72	127—130	59.83 (59.02)	6.07 (5.97)	8.19 (8.10)	18.06 (17.15)
IX	*p*-FC_6H_4	80	151—153	57.80 (57.73)	5.55 (5.45)	8.64 (8.41)	17.64 (17.82)
X	*p*-ClC_6H_4	80	129—131	56.20 (56.34)	5.48 (5.32)	8.44 (8.12)	17.42 (17.40)
XI	*m*-$O_2NC_6H_4$	78	101—105	55.22 (55.48)	5.35 (5.24)	10.35 (10.11)	15.30 (17.13)

[a] Based on material that melts within 5°C of the analytical sample. [b] Analytical sample.

TABLE 2

IR SPECTRA OF TRIETHYLAMMONIUM CHLORIDE—*N*-SUBSTITUTED *N'*-CYANO-*O*-(TRIPHENYLSTANNYL)ISOUREA COMPLEXES [a]

No.	NH	C≡N	C=N [b]	C_6H_5 ring vibrations [12—14]	$Sn(C_6H_5)_3$ [14—18] ν_{as}	ν_s
I	3280w	2174s	1587s	451s	275s	228s [c]
II	3300w	2174s	1587s	451s	286s	248s [d]
III	3280w	2174s	1587s	451s	276s	230s [e]
IV	3268w	2174s	1550s	452s	274s	227s [f]
V	3268w	2174s	1592s	449s	274s	225s [g]
VI	3268w	2174s	1615s	455s	278s	233s [h]
VII	3247w	2170s	1610s	454s	275s	232s [i]
VIII	3257w	2169s	1600s	456s	274s	234s [m]
IX	3268w	2179s	1615s	453s	274s	230s [j]
X	3268w	2180s	1613s	451s	274s	236s [k]
XI	3280w	2180s	1618s	454s	270s	234s [l]

[a] Values are expressed in cm^{-1}; s = strong, m = medium, w = weak. [b] This assignment is somewhat uncertain due to the presence of aromatic C=C bands in this region. [c] A band was also present at 208s cm^{-1}. [d] A band was also present at 212s cm^{-1}. [e] A band was also present at 198m cm^{-1}. [f] A band was also present at 206s cm^{-1}. [g] A band was also present at 208s cm^{-1}. [h] Also present were bands at 204s and 252s cm^{-1}. [i] Also present were bands at 200s and 256s cm^{-1}. [j] A band was also present at 206s cm^{-1}. [k] A band was present at 197s cm^{-1}. [l] Also present were bands at 200m and 248m cm^{-1}. [m] Also present were bands at 208m and 194m cm^{-1}.

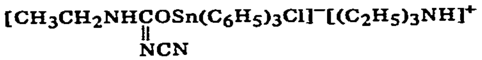
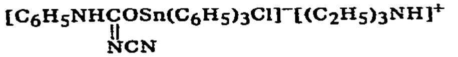
nium chloride, the tin-coordinated carbonyl group frequency in these compounds was raised by about 100 cm^{-1} [3,4].

The frequency of the C=N band in the IR spectra of the *N*-substituted *N'*-cyano-*O*-(triphenylstannyl)isoureas and the triethylammonium chloride—*N*-substituted *N'*-cyano-*O*-(triphenylstannyl)isourea complexes is considerably lower than in trialkylisoureas [5] which suggests that the C=N group is conjugated with the C≡N group in these compounds.

The Mössbauer parameters for two *N*-substituted *N'*-cyano-*O*-(triphenylstannyl)isoureas and two triethylammonium chloride—*N*-substituted *N'*-cyano-*O*-

TABLE 3

MÖSSBAUER PARAMETERS OF *N*-SUBSTITUTED *N'*-CYANO-*O*-(TRIPHENYLSTANNYL)ISOUREAS AND TRIETHYLAMMONIUM CHLORIDE—*N*-SUBSTITUTED *N'*-CYANO-*O*-(TRIPHENYLSTANNYL)ISOUREA COMPLEXES [a]

No.	Compound	δ	ΔE	ΔE/δ
I	 $[CH_3CH_2NH\underset{\underset{NCN}{\Vert}}{C}OSn(C_6H_5)_3Cl]^-[(C_2H_5)_3NH]^+$	1.31	3.11	2.37
VI	 $[C_6H_5NH\underset{\underset{NCN}{\Vert}}{C}OSn(C_6H_5)_3Cl]^-[(C_2H_5)_3NH]^+$	1.31	3.11	2.37
XII	 $CH_3CH_2NH\underset{\underset{NCN}{\Vert}}{C}OSn(C_6H_5)_3$	1.43	3.51	2.45
XIII	 $C_6H_5NH\underset{\underset{NCN}{\Vert}}{C}OSn(C_6H_5)_3$	1.32	3.51	2.68

[a] Units of δ (isomer shift) and ΔE (quadrupole splitting) are mm sec^{-1}; isomer shifts refer to $BaSnO_3$.

(triphenylstannyl)isourea complexes are given in Table 3. While the data does not resolve the question of whether the tin is bonded to nitrogen or to oxygen in (triphenylstannyl)cyanamide: organic isocyanate adducts, the data does provide some additional structural information about the adducts and their complexes. Poller and Ruddick [6] have concluded that large quadrupole interactions of ≈4.0—2.6 mm sec^{-1} for triphenyltin compounds are associated with trigonal bipyramidal structures. Ensling et al. [7] have calculated that anionic triphenyltin complexes in which the three phenyl groups occupy the equatorial positions of a trigonal bipyramid should exhibit a quadrupole splitting value of 3.12 mm sec^{-1}. Thus, the phenyl groups in compounds I and VI very probably occupy the equatorial positions of a trigonal bipyramid. A ratio of quadrupole splitting to isomer shift of greater than 2.1 is usually associated with a tin coordination number greater than four [8,9,10]. It has been further suggested that a quadrupole splitting value of greater than 2.5 mm sec^{-1} is unlikely to be observed unless tin has a coordination number greater than four [11]. Thus, the data indicate that all of the compounds in Table 3 have a tin coordination number greater than four. In the case of compounds XII and XIII this may be due to inter- or intramolecular coordination between tin and the nitrogen of the CN group.

Experimental

Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. The infrared data (4000—265 cm^{-1}) were obtained using KBr pellets with a Beckman IR 8 infrared spectrophotometer and a Perkin—Elmer Model 21 double beam infrared spectrophotometer which was fitted with a cesium bromide prism and purged with nitrogen. The far infrared data (400—140 cm^{-1}) were obtained with a Perkin—Elmer Model FIS-3 far infrared spectrophotometer (CsI pellets). The Mössbauer spectral data were obtained at 77 K relative to $BaSnO_3$ by Austin Science Associates, Inc., Austin, Texas. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Preparation of triethylammonium chloride—N-ethyl-N'-cyano-O-(triphenylstannyl)isourea (I)

A mixture of *N*-ethyl-*N'*-*O*-(triphenylstannyl)isourea (4.621 g, 0.01 mol), triethylamine hydrochloride (1.3765 g, 0.01 mol), and tetrahydrofuran (300 ml) was stirred at 26°C for 20 h. The solvent was evaporated, and the residue was recrystallized from ethyl acetate to give 5.002 g (83%) of compound I, m.p. 105—106°C. A second recrystallization from ethyl acetate gave the analytical sample, m.p. 105—106°C.

The other compounds in Table 1 were prepared in a similar manner.

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