Experimental Section

cis- and *trans*-4-*tert*-butylcyclohexyl- and 1-menthylphosphorochloridates and -phosphorochloridothioates were prepared by phosphorylation of *cis*- and *trans*-4-*tert*-butylcyclohexanol and 1-menthol with phosphorus oxychloride or thiophosphoryl chloride in the presence of a tertiary base (*3*, *4*). The preparation of *exo*- and *endo*-norbornyl- (*7*) and bornyl- (*8*) phosphorochloridates and -phosphorochloridothioates has been described in detail elsewhere. Chloridates from 1- and 2-adamantols, 1-adamantylamine (*5*), pyrrolidine, morpholine, and piperazine (*2*) were obtained by a literature method. The various derivatives listed in Tables I-V, viz., amidates, azides, hydrazides, hydrazones, were obtained by treatment of the chloridates with amines, sodium azide, and hydrazine, as previously described (*2*, *5*, *7*, *8*).

Phosphorus NMR spectra were obtained from a Bruker HFX-90 spectrometer operating at 36.43 MHz. Chemical shifts are expressed on the δ scale with upfield shifts negative; the external standard is 85% phosphoric acid.

Literature Cited

(1) Cremlyn, R. J. "Pesticides: Preparation and Mode of Action"; Wiley: Chichester, England, 1978.
(2) Cremlyn, R. J.; Akhtar, N. *Phosphorus Sulfur* **1979**, *7*, 247 and unpublished work.
(3) Cremlyn, R. J.; Dewhurst, B. B.; Wakeford, D. H.; Raja, R. A. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1171.
(4) Cremlyn, R. J.; Dewhurst, B. B.; Wakeford, D. H. *Synthesis* **1971**, 646.
(5) Cremlyn, R. J.; Ellam, R. M.; Akhtar, N. *Phosphorus Sulfur* **1979**, *7*, 257.
(6) Cremlyn, R. J.; Ellam, R. M.; Akhtar, N. *Phosphorus Sulfur* **1978**, *5*, 1.
(7) Cremlyn, R. J.; Ellam, R. M.; Akhtar, N. *Phosphorus Sulfur* **1979**, *5*, 277.
(8) Cremlyn, R. J.; Ellam, R. M.; Akhtar, N. *Phosphorus Sulfur* **1979**, *7*, 109.
(9) Van Wazer, J. R. In "Determination of Organic Structure by Physical Methods"; Academic Press: New York, 1971; Chapter 7.

Received for review August 18, 1980. Accepted November 3, 1980.

Synthesis of Triphenyltin Halide-Diorganocyanamide Complexes

Eugene J. Kupchik* and Homayoun Naima

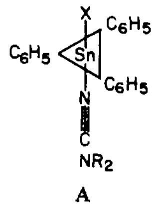
Department of Chemistry, St. John's University, Jamaica, New York 11439

Four new triphenyltin halide-diorganocyanamide complexes were synthesized by allowing triphenyltin chloride and triphenyltin iodide to react separately with dibenzylcyanamide and benzyltritylcyanamide. Their Mössbauer spectra indicate that they have a trigonal bipyramidal structure.

The synthesis of complexes of triphenyltin bromide with dibenzylcyanamide and benzyltritylcyanamide has previously been described (*1*). We now wish to describe some other triphenyltin halide-diorganocyanamide complexes.

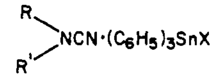
Four new triphenyltin halide-diorganocyanamide complexes were synthesized by allowing triphenyltin chloride and triphenyltin iodide to react separately with dibenzylcyanamide and benzyltritylcyanamide in refluxing acetonitrile. The new complexes were identified by elemental analysis (Table I) and by their infrared spectra (Table II).

The Mössbauer parameters of the new complexes as well as those of the previously synthesized triphenyltin bromide complexes are given in Table II. Poller and Ruddick (*2*) have concluded that large quadrupole interactions of 4.0-2.6 mm s^{-1} for triphenyltin compounds are associated with trigonal bipyramidal structures. Ensling et al. (*3*) have calculated that triphenyltin compounds in which the three phenyl groups occupy the equatorial positions of a trigonal bipyramid should exhibit a quadrupole splitting value of 3.1 mm s^{-1}. Thus, the data in Table II indicate that the complexes probably have structure A. Evidence that the nitrile nitrogen rather than the amino nitrogen is bonded to the tin has previously been given (*1*).



A

Table I. Triphenyltin Halide-Diorganocyanamide Complexes[a]


$RR'NCN\cdot(C_6H_5)_3SnX$

compd	R	R′	X	reaction time,[b] h	yield,[c] %	mp,[d] °C
I	$C_6H_5CH_2$	$C_6H_5CH_2$	Cl	20	95	85-87
II	$C_6H_5CH_2$	$C_6H_5CH_2$	I	72	92	83-85
III	$C_6H_5CH_2$	$(C_6H_5)_3C$	Cl	18	44	143-144
IV	$C_6H_5CH_2$	$(C_6H_5)_3C$	I	144	38	141-142

[a] Elemental analyses (C, H, N, X, and Sn) in agreement with theoretical values were obtained and submitted for review. [b] The triphenyltin halide and diorganocyanamide (1/1 mole ratio) were refluxed in acetonitrile for the indicated reaction time. [c] Based on material that melts within 5 °C of the analytical sample. [d] Refers to the analytical sample.

Experimental Section

Melting points were determined with a Mel-Temp capillary melting-point apparatus and are uncorrected. The infrared data (4000-400 cm^{-1}) were obtained by using KBr pellets with a Perkin-Elmer Infracord, 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 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, TX. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Preparation of Triphenyltin Chloride-Dibenzylcyanamide Complex (I). A mixture of triphenyltin chloride (1.11 g, 0.002 88 mol), dibenzylcyanamide (*12*) (0.64 g, 0.0029 mol), and acetonitrile (10 mL) was refluxed for 20 h. Evaporation of the clear solution left 1.658 g (95%) of I, mp 85-87 °C. A single recrystallization from petroleum ether (bp 30-60 °C) gave

0021-9568/81/1726-0233$01.25/0

Table II. IR Spectra[a] and Mössbauer Parameters[b] of Triphenyltin Halide-Diorganocyanamide Complexes

compd	C≡N	C_6H_5 ring vibration (*4-6*)	ν_{as} SnC_6H_5 (*6, 7-11*)	other	δ	ΔE
I	2237s	451s	272s	374m, 350m, 326w, 230s	1.37	3.23
II	2227s	447s	272s	217s, 208m, 194s	1.48	3.32
III	2227s	449s	272s	358s, 340m, 314m, 224s	1.49	3.11
IV	2232s	447s	272s	222s, 208m, 188m	1.54	3.26
$R = R' = C_6H_5CH_2$, X = Br[c]					1.48	3.33
$R = C_6H_5CH_2$, $R' = (C_6H_5)_3C$, X = Br[c]					1.49	3.20

[a] Values are expressed in cm^{-1}; s = strong, m = medium, w = weak. [b] Units of δ (isomer shift) and ΔE (quadrupole splitting) are mm s^{-1}; isomer shifts are relative to $BaSnO_3$. The experimental error limits of δ and ΔE are ±0.03 mm s^{-1}. [c] Reference *1*.

1.5 g (91%) of the analytical sample, mp 85-87 °C.

Preparation of Triphenyltin Iodide-Dibenzylcyanamide Complex (II). A mixture of triphenyltin iodide (1.27 g, 0.002 67 mol), dibenzylcyanamide (0.64 g, 0.0029 mol), and acetonitrile (10 mL) was refluxed for 72 h. Evaporation of the clear solution left 1.858 g (92%) of II, mp 80-85 °C. A single recrystallization from petroleum ether (bp 30-60 °C) gave 1.73 g (86%) of the analytical sample, mp 83-85 °C.

Preparation of Triphenyltin Chloride-Benzyltritylcyanamide Complex (III). A mixture of triphenyltin chloride (0.67 g, 0.0017 mol), benzyltritylcyanamide (*13*) (0.65 g, 0.0017 mol), and acetonitrile (10 mL) was refluxed for 18 h. Evaporation of the pale-yellow solution left a tacky solid which was recrystallized from ethanol to give 0.59 g (44%) of III, mp 141-146 °C. Further recrystallization from ethanol gave the analytical sample, mp 143-144 °C.

Preparation of Triphenyltin Iodide-Benzyltritylcyanamide Complex (IV). A mixture of triphenyltin iodide (0.827 g, 0.001 73 mol), benzyltritylcyanamide (0.65 g, 0.0017 mol), and acetonitrile (10 mL) was refluxed for 144 h. Evaporation of the pale-yellow solution left a tacky solid which was recrystallized from ethanol to give 0.56 g (38%) of IV, mp 142-145 °C. A second recrystallization from ethanol gave the analytical sample, mp 141-142 °C.

Literature Cited

(1) Cardona, R. A.; Kupchik, E. J. *J. Organomet. Chem.* **1972**, *43*, 163.
(2) Poller, R. C.; Ruddick, J. N. R. *J. Organomet. Chem.* **1972**, *39*, 121.
(3) Ensling, J.; Gutlich, Ph.; Hasselbach, K. M.; Fitzsimmons, B. W. *J. Chem. Soc. A* **1971**, 1940.
(4) Cattenach, C. J.; Mooney, E. F. *Spectrochim. Acta, Part A* **1968**, *24*, 407.
(5) Verdonck, L.; van der Kelen, G. P. *J. Organomet. Chem.* **1972**, *40*, 135.
(6) Poller, R. C. *Spectrochim. Acta* **1966**, *22*, 935.
(7) May, J. R.; McWhinnie, R. W.; Poller, R. C., *Spectrochim. Acta, Part A* **1971**, *27*, 969.
(8) Srivastava, T. N.; Tandon, S. K. *Spectrochim. Acta, Part A* **1971**, *27*, 593.
(9) Srivastava, T. S. *J. Organomet. Chem.* **1969**, *16*, 53.
(10) Wharf, I.; Lobos, J. Z.; Onyszchuk, M. *Can. J. Chem.* **1970**, *48*, 2787.
(11) Dance, N. S.; McWhinnie, W. R.; Poller, R. C. *J. Chem. Soc., Dalton Trans.* **1976**, 2349.
(12) Traube, W.; Engelhardt, A. *Chem. Ber.* **1911**, *44*, 3149.
(13) Bredereck, H.; Reif, E. *Chem. Ber.* **1948**, *81*, 426.

Received for review October 22, 1980. Accepted December 24, 1980.

Synthesis of Three [(Trifluoroethyl)amino]pyridines

Eugene R. Bissell* and Rosalind W. Swansiger

Lawrence Livermore National Laboratory, Livermore, California 94550

The synthesis of *o*-, *m*, and *p*-[(trifluoroethyl)amino]pyridine by diborane/tetrahydrofuran reduction of the corresponding trifluoroacetamide is described. The yields were 52%, 83%, and 76%, respectively. The synthesis, in 53% yield, of 2,2,2-trifluoro-*N*-(4-pyridyl)acetamide is also described.

Recently we reported (*1*) an improved synthesis of substituted *N*-(trifluoroethyl)anilines by the reduction of the corresponding trifluoroacetamides with diborane in tetrahydrofuran solution (*2*). This method is particularly advantageous for anilines bearing electron-withdrawing substituents which cannot be easily alkylated by previously used methods (*3*, *4*). Aminopyridines, like electronegatively substituted anilines, are resistant to alkylation, and fluoroalkyl derivatives of them have not been reported. We have, therefore, applied our new reduction method to the synthesis of the three isomers of [(trifluoroethyl)amino]pyridine. The results and physical and spectral properties are reported in Table I. The required trifluoroacetamides were prepared by treating the amine in ether solution with trifluoroacetic anhydride. The ortho and meta acetamides were prepared as described by Pailer and Huebsch (*5*); the para isomer appears to be new.

Table I. Yield and Properties of the Three Isomers of [(Trifluoroethyl)amino]pyridine

	ortho	meta	para
yield, %	52.1	82.5	75.5
mp, °C	59.5	73.8	159.8
recrystallization solvent	75-110 °C petroleum ether	none[a]	toluene
NMR spectrum			
δ(CH_2)	4.1 M (2)	3.8 M (2)	3.91 Q (2)[b]
J			9
δ(NH)	5.0 S (1)	5.5 M (1)	
δ(ArH_β)	6.5 M (2)		6.69 D (2)
δ(ArH_γ)	7.4 T (1)		
δ(ArH_α)	8.1 D (1)	8.1 M (2)	8.09 D (2)
J			7

[a] Sublimed at 70 °C and 4 Pa. [b] In deuterated methanol.

Experimental Section

Melting points, taken on a Mettler Model FP1 apparatus at 2 °C/min, are corrected. Nuclear magnetic resonance (NMR) measurements, in deuterated chloroform except as noted, were