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.

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Synthesis of Three [(Trifluoroethyl)amino]pyridines

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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			
$\delta(CH_2)$	4.1 M (2)	3.8 M (2)	3.91 Q (2)[b]
J			9
$\delta(NH)$	5.0 S (1)	5.5 M (1)	
$\delta(ArH_\beta)$	6.5 M (2)		6.69 D (2)
$\delta(ArH_\gamma)$	7.4 T (1)		
$\delta(ArH_\alpha)$	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

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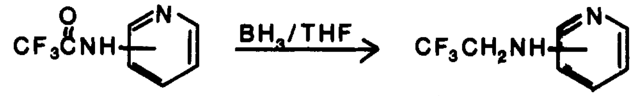
Scheme I



made on a Varian EM360 NMR spectrometer; shifts (δ) are given in ppm relative to internal Me_4Si with S = singlet, D = doublet, T = triplet, Q = quartet, M = complex multiplet; the value in parentheses is the relative area. Elemental analyses on all new compounds were submitted for review and were within ±0.3% of the expected values.

2,2,2-Trifluoro-N-(4-pyridyl)acetamide. Trifluoroacetic anhydride (21.0 g, 0.1 mol) was added dropwise to a rapidly stirred solution of 9.41 g (0.1 mol) of 4-aminopyridine in 100 mL of diethyl ether. The reaction mixture was held overnight at room temperature and then decomposed by addition of 150 mL of saturated aqueous sodium bicarbonate. The aqueous phase was extracted with additional ether, and the combined ether layers were dried over anhydrous magnesium sulfate, filtered, and evaporated. The slightly yellow residue was recrystallized from benzene to yield 10.1 g (53.1%) of colorless solid melting at 139 °C. Vacuum sublimation raised the melting point to 143.7 °C.

Diborane Reduction. A solution of 9.51 g (0.05 mol) of the trifluoroacetamide in 50 mL of tetrahydrofuran (dried over sodium–lead alloy) was added under argon over a period of 20–30 min to a stirred, 1 M solution of diborane in tetrahydrofuran (200 mL) (see Scheme I). The reaction mixture was stirred at room temperature for 2 h, then refluxed for 20–25 h, and finally cooled to room temperature. Excess diborane was destroyed by careful addition of 5 mL of absolute ethanol followed by 1 mL of water. Concentrated aqueous hydrochloric acid (15 mL was added, and ~180 mL of the tetrahydrofuran was removed by distillation. The residue was poured into 100 mL of water. This solution was extracted with three 50-mL portions of ether which were discarded. The aqueous phase was made strongly basic by addition of 15 mL of 50% aqueous sodium hydroxide and again extracted with three 50-mL portions of ether. Drying over anhydrous magnesium sulfate, filtering, and evaporating yielded the desired product. Yields, properties, and analytical data are given in Table I.

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