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Synthesis of N,N,N′-Trisubstituted *N″*-Cyanoguanidines and *N*-Aryl-*N′*-(triorganostannyl)-*N′*,*N″*-dicyanoguanidines

Eugene J. Kupchik,* Hans E. Hanke, Jack P. DiMarco, and Roy J. Chessari

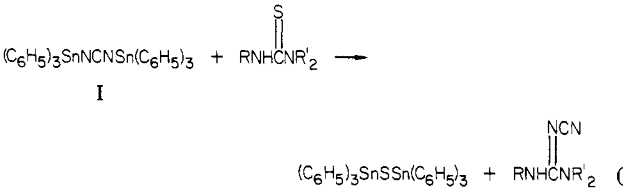
Department of Chemistry, St. John's University, Jamaica, New York 11439

Bis(triphenylstannyl)carbodiimide reacts with 1,1,3-trisubstituted thioureas to give N,N,N′-trisubstituted *N″*-cyanoguanidines. Bis(triphenylstannyl)carbodiimide and bis(trimethylstannyl)carbodiimide react separately with ethyl *N*-arylthiocarbamates to give the corresponding *N*-aryl-*N′*-(triorganostannyl)-*N′*,*N″*-dicyanoguanidines.

The reactions of bis(triphenylstannyl)carbodiimide (I) with 1,3-disubstituted thioureas to give N,N′-disubstituted *N″*-cyanoguanidines and with N-substituted thioamides to give N′-substituted *N*-cyanoamidines have been reported (*1*, *2*). We now wish to report on the reactions of bis(triphenylstannyl)carbodiimide (I) with 1,1,3-trisubstituted thioureas and with ethyl *N*-arylthiocarbamates. The reaction of bis(trimethylstannyl)carbodiimide with two *N*-arylthiocarbamates is also described.

Results and Discussion

Bis(triphenylstannyl)carbodiimide (I) was found to react with 1,1,3-trisubstituted thioureas (1/1 mole ratio) in acetonitrile at the reflux temperature to give bis(triphenyltin) sulfide (24–82%) and the corresponding N,N,N′-trisubstituted *N″*-cyanoguanidine (25–51%) (eq 1). The cyanoguanidines were identified by



$$\underset{\mathrm{I}}{\mathrm{(C_6H_5)_3SnNCNSn(C_6H_5)_3}} + \mathrm{RNH}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{NR'_2} \longrightarrow \mathrm{(C_6H_5)_3SnSSn(C_6H_5)_3} + \mathrm{RNH}\overset{\overset{\mathrm{NCN}}{\|}}{\mathrm{C}}\mathrm{NR'_2} \quad (1)$$

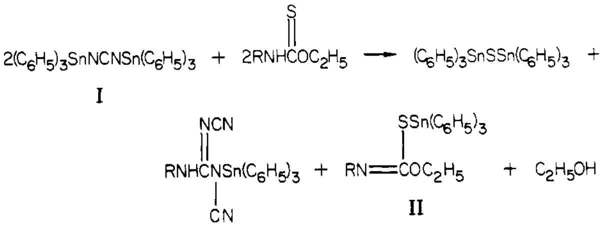
elemental analysis and by their IR spectra (Table I). In addition, one of the compounds (II, Table I) was subjected to a mass-spectral analysis. The expected parent ion at *m/e* 216 was present, and the fragmentation pattern was entirely consistent with the proposed structure. For example, a peak at *m/e* 201 is probably due to loss of $CH_3\cdot$ from the parent ion; a peak at *m/e* 187 is probably due to loss of $C_2H_5\cdot$ from the parent ion; furthermore, a peak at *m/e* 124 is probably due to loss of $C_6H_5NH\cdot$ from the parent ion. The fact that a considerable amount of I must be utilized in this reaction is no serious disadvantage, since the bis(triphenyltin) sulfide produced in the reaction can be readily converted to bis(triphenyltin) oxide in at least 70% yield by reaction with mercuric oxide in refluxing ethanol/benzene (*3*); the bis(triphenyltin) oxide is readily converted to I (*4*).

Table I. N,N,N′-Trisubstituted *N″*-Cyanoguanidines (RNHC(NCN)NR′$_2$)[a]

				IR spectra[c]		
no.	R	R′	mp,[b] °C	NH	C≡N	C=N
I	C_6H_5	CH_3	178–180	3226 m, 3165 m	2179 s	1563 s
II	C_6H_5	C_2H_5	123–125	3215 m, 3155 m	2183 s	1580 s
III	C_6H_5	$C_6H_5CH_2$	185–187	3215 m, 3185 m	2179 s	1565 s
IV	*p*-$CH_3C_6H_4$	CH_3	190–192	3145 m	2174 s	1563 s
V	*o*-$CH_3C_6H_4$	CH_3	178–180	3185 m	2179 s	1587 s

[a] Elemental analyses (C, H, and N) in agreement with theoretical values were obtained and submitted for review. [b] Refers to the analytical sample; recrystallization solvents were 95% ethanol (I, III), ethanol/water (V), ethanol/*n*-pentane (IV), and ethanol/*n*-hexane (II). [c] Values are expressed in cm^{-1}; s = strong, m = medium, w = weak.

The reaction of bis(triphenylstannyl)carbodiimide (I) with ethyl *N*-arylthiocarbamates (1/1 mole ratio) in acetonitrile (17 h) at the reflux temperature gave bis(triphenyltin) sulfide and novel



$$\underset{\mathrm{I}}{\mathrm{2(C_6H_5)_3SnNCNSn(C_6H_5)_3}} + \mathrm{2RNH}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{OC_2H_5} \longrightarrow \mathrm{(C_6H_5)_3SnSSn(C_6H_5)_3} + \mathrm{RNH}\overset{\overset{\mathrm{NCN}}{\|}}{\mathrm{C}}\underset{\underset{\mathrm{CN}}{|}}{\mathrm{N}}\mathrm{Sn(C_6H_5)_3} + \underset{\mathrm{II}}{\mathrm{RN{=}}\overset{\overset{\mathrm{SSn(C_6H_5)_3}}{|}}{\mathrm{C}}\mathrm{OC_2H_5}} + \mathrm{C_2H_5OH} \quad (2)$$

N-aryl-*N′*-(triphenylstannyl)-*N′*,*N″*-dicyanoguanidines, which were identified by elemental analysis and by their IR spectra (Table II, eq 2). The yields of dicyanoguanidines based on eq 2 were 31–65%. The yields of bis(triphenyltin) sulfide based on eq 2 were greater than 100%, which suggests that some of the sulfide may have resulted from the decomposition of II; this hypothesis is supported by the observation that compounds having structure II readily decompose to give, as one of the products, bis(triphenyltin) sulfide (*3*).

Two *N*-aryl-*N′*-(trimethylstannyl)-*N′*,*N″*-dicyanoguanidines (XI and XII, Table II) were obtained by substituting bis(trimethylstannyl)carbodiimide for I in reaction 2. Their IR spectra showed both the ν_{as}(SnC) band and the ν_s(SnC) band, which indicates that the trimethyltin group may be nonplanar in these compounds (*5*).

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 Beckman IR 8 infrared spectrophotometer or Perkin-Elmer Infracord and with 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 (Nujol). The mass-spectral data were obtained with a Hitachi RMU-6D mass spectrometer by Morgan-Schaffer Corporation, Montreal 252, Quebec, Canada. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Reaction of Bis(triphenylstannyl)carbodiimide with 1-Phenyl-3,3-diethylthiourea. A mixture of bis(triphenylstannyl)carbodiimide (108.0 g, 0.146 mol), 1-phenyl-3,3-diethylthiourea (30.4 g, 0.146 mol), and acetonitrile (500 mL) was refluxed for 13 h. The mixture was cooled to 0 °C and filtered to give 88.0 g (82%) of bis(triphenyltin) sulfide: mp 143–145 °C (lit. (*14*) mp 145.5–147 °C).

The acetonitrile was evaporated from the filtrate, the residue was stirred with ethanol, and the mixture was cooled to 0 °C

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Table II. *N*-Aryl-*N*′-(triorganostannyl)-*N*′,*N*″-dicyanoguanidines ($RNHC(NCN)N(CN)SnR'_3$)[a]

				IR spectra[c]			C_6H_5 ring vibration (*6-8*)	SnC_6H_5 (*8, 9-13*)	
no.	R	R′	mp,[b] °C	NH	C≡N	C=N		ν_{as}	ν_s
VI	C_6H_5	C_6H_5	185-187	3401 m	2165 s	1563 s	451 s	277 s[d]	230 s
VII	2-naphthyl	C_6H_5	210-212	3390 m	2203 s, 2155 s	1563 s	452 s[e]	276 s[f]	226 s
VIII	*p*-FC_6H_4	C_6H_5	163-165	3378 m	2165 s	1563 s	451 s[g]	277 s[h]	232 s
IX	*p*-$C_2H_5OC_6H_4$	C_6H_5	195-196	3367 w, 3205 w	2160 s	1563 s	452 s	275 s[i]	227 s
X	*p*-$O_2NC_6H_4$	C_6H_5	210-212	3390 m	2165 s	1570 s	451 s[j]	267 s[k]	231 s
XI[l]	C_6H_5	CH_3	180-182	3245 w, 3268 m	2212 s, 2169 s	1563 s			
XII[m]	2-naphthyl	CH_3	186.5-187.5	3289 w, 3413 w	2212 s, 2169 s	1590 s			

[a] Elemental analyses (C, H, N, F, and Sn) in agreement with theoretical values were obtained and submitted for review. [b] Refers to the analytical sample; recrystallization solvents were ethyl acetate (VI-VIII), acetonitrile (X-XII), and benzene (IX). [c] Values are expressed in cm^{-1}; s = strong, m = medium, w = weak. [d] Bands were present at 375 w and 342 cm^{-1}. [e] A band was present at 476 m cm^{-1}. [f] A band was present at 340 w cm^{-1}. [g] A band was present at 482 m cm^{-1}. [h] Bands were present at 377 w, 361 m, and 316 w cm^{-1}. [i] A band was present at 376 cm^{-1}. [j] A band was present at 490 w cm^{-1}. [k] Bands were present at 180 s, 202 m, 330 s, and 377 s cm^{-1}. [l] Bands were present at 551 s [ν_{as}(SnC)], 617 m, 500 m [(ν_s(SnC)], 380 w, 352 s, 284 s, and 208 m cm^{-1}. [m] Bands were present at 550 s [ν_{as}(SnC)], 597 w, 513 w, 499 w [ν_s(SnC)], and 468 s cm^{-1}.

and filtered to give 8.64 g (24%) of pure *N*-phenyl-*N*′-diethyl-*N*″-cyanoguanidine (II, Table I), mp 123-125 °C. The ethanol was evaporated from the filtrate, the residue was stirred with ethyl acetate, and the mixture was filtered to give 8.08 g (27%) of additional II, mp 123-125 °C (total yield of II, 51%).

Reaction of Bis(triphenylstannyl)carbodiimide with Ethyl N-(p-Ethoxyphenyl)thiocarbamate. A mixture of bis(triphenylstannyl)carbodiimide (14.80 g, 0.02 mol), ethyl *N*-(*p*-ethoxyphenyl)thiocarbamate (4.51 g, 0.02 mol), and acetonitrile (250 mL) was refluxed for 17 h. The acetonitrile was evaporated from the filtrate, the residue was stirred with carbon tetrachloride (200 mL), and the mixture was filtered to give 3.78 g of material, mp 138-140 °C. This material was stirred with hot ethanol, and the mixture was filtered to give 1.77 g (31%) of *N*-(*p*-ethoxyphenyl)-*N*′-(triphenylstannyl)-*N*′,*N*″-dicyanoguanidine (IX, Table II), mp 193-195 °C. A single recrystallization from benzene raised the melting point to 195-196 °C.

The carbon tetrachloride was evaporated from the original filtrate, the residue was stirred with hot ethanol (75 mL), and the mixture was cooled and filtered to give 10.69 g of bis(triphenyltin) sulfide, mp 140-141 °C.

Preparation of N-Phenyl-N′-(trimethylstannyl)-N′,N″-dicyanoguanidine (XI, Table II). A mixture of bis(trimethylstannyl)carbodiimide (7.35 g, 0.02 mol), ethyl *N*-phenylthiocarbamate (3.63 g, 0.02 mol), and acetonitrile (250 mL) was refluxed for 15 h. The mixture was allowed to cool to 25 °C and then was filtered. The solvent was evaporated from the filtrate, the residue was stirred with carbon tetrachloride (250 mL), and the mixture was filtered to give 2.88 g of material, mp 145-150 °C. Recrystallization of this material from acetonitrile afforded 1.46 g (42%) of crude *N*-phenyl-*N*′-(trimethylstannyl)-*N*′,*N*″-dicyanoguanidine, mp 168-170 °C. A second recrystallization from acetonitrile gave 1.15 g (33%) of pure product, mp 180-182 °C.

Preparation of N-(2-Naphthyl)-N′-(trimethylstannyl)-N′,N″-dicyanoguanidine (XII, Table II). A mixture of bis(trimethylstannyl)carbodiimide (7.35 g, 0.02 mol), ethyl *N*-(2-naphthyl)thiocarbamate (4.63 g, 0.02 mol), and acetonitrile (250 mL) was refluxed for 15 h. The acetonitrile was evaporated, the residue was stirred with carbon tetrachloride (250 mL) for 2 h, and the mixture was filtered to give 4.11 g of material, mp 130-145 °C. Recrystallization of this material from ethyl acetate/diethyl ether afforded 0.183 g (5%) of pure *N*-(2-naphthyl)-*N*′-(trimethylstannyl)-*N*′,*N*″-dicyanoguanidine, mp 184.5-185.5 °C. Recrystallization from acetonitrile gave the analytical sample, mp 186.5-187.5 °C.

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Studies on Cycloimmonium Ylides. Synthesis of Some 2,4,6-Triaryl-Substituted Pyridines via Picolinium Ylides

Ram. S. Tewari,* Ajay K. Dubey, Naresh K. Misra, and Priya D. Dixit

Department of Chemistry, H. B. Technological Institute, Kanpur-208002, India

A wide variety of 2,4,6-triaryl-substituted pyridines have been synthesized by the interaction of aroylmethylenepicolinium ylides with different α,β-unsaturated ketones. The structural assignments were based on microanalytical and spectral data.

Introduction

Extensive studies have been carried out in the reactions of pyridinium ylides and isoquinolinium ylides with α,β-unsaturated ketones following the first reports of Krohnke et al.[1-9] Almost no work has been done on picolinium ylides, and we therefore

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