

THIOCYANOGEN CLEAVAGE OF CARBON-TIN BONDS

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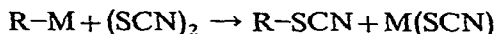
SUMMARY

A number of tetraorganotin compounds of the types $(\text{CH}_3)_3\text{SnR}$ and, to a lesser extent, $(\text{C}_6\text{H}_5)_3\text{SnR}$, where R is a group normally readily cleaved by electrophilic agents, have been demonstrated to react readily with thiocyanogen $(\text{SCN})_2$, in benzene or carbon tetrachloride solution. When R = *cis*- or *trans*-2-butenyl (crotyl), 2-propynyl or 1,2-propadienyl (allenyl), the rearranged α -methallyl, allenyl or 2-propynyl thiocyanates, respectively, are produced. The reactions are quantitative as judged by direct PMR observations. When R possesses only moderate reactivity towards electrophiles, *e.g.*, CH_3 as in $(\text{CH}_3)_4\text{Sn}$, polymerisation of $(\text{SCN})_2$ is more rapid than cleavage.

The stereochemical path in the cases of *cis*- and *trans*-styryltrimethylstannanes is shown to be retention at the vinylic carbon.

INTRODUCTION

Recently it was reported that thiocyanogen reacts with a number of metal alkyls and aryls to form organometal (or metalloidal) thiocyanates in the cases of B, Cd and Bi, and isothiocyanates in the cases of As and Sb¹. However, little information relevant to mechanism was provided, and since we judged thiocyanogen cleavage in the sense below to be potentially useful for the synthesis of organic thiocyanates as well as organometal isothiocyanates, we set out to provide some information on this cleavage reaction of carbon-metal systems.



We were also interested in the rearrangements in appropriate systems that might accompany $(\text{SCN})_2$ cleavage.

RESULTS

Thiocyanogen, in approximately known concentrations (but always less than 1 M) was generated in benzene or carbon tetrachloride in the usual way from Pb $(\text{SCN})_2$ and bromine (see Experimental). These solutions were kept chilled and pro-

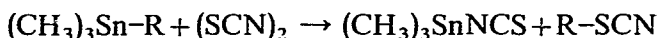
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tected from light, but in most cases the thiocyanogen solutions were freshly prepared. Since PMR spectroscopy was such a rewarding technique in our studies of the reaction of another sulfur electrophile (SO_2) with organotin systems, our approach again was based on this technique. Routinely then, a roughly known amount of organotin compound was dissolved in either CCl_4 or C_6H_6 in an NMR tube, and the spectrum was recorded. Small aliquots of $(\text{SCN})_2$ were then added, and the spectrum again was recorded. This sequence was repeated until signals of the starting compound had entirely disappeared. This approach affords a good chance of observing moderately labile intermediates or isomers, should they appear and then disappear at other than prohibitively fast rates.

Reaction of $(\text{CH}_3)_3\text{SnR}$ and $(\text{SCN})_2$

These reactions were generally conducted in CCl_4 , since our experience was that $(\text{SCN})_2$ was less prone to polymerisation in this solvent. In addition, PMR observations are not complicated by solvent absorption, and chemical shifts of organic thiocyanates were highly concentration-dependent in benzene.

On the basis of the evidence outlined below, the following equation represents the reaction under study.



Where $\text{R} = -\text{CH}_2-\text{CH}=\text{CH}_2$; $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$ (*cis* or *trans*); $-\text{CH}=\text{C}=\text{CH}_2$. (In some cases R in the product R-SCN has a rearranged structure. See below.) In the cases $\text{R} = \text{CH}_3$ or $\text{CH}_2\text{C}_6\text{H}_5$, reaction was very sluggish and no signs of reaction could be detected before polymerisation of $(\text{SCN})_2$ made further observations futile. Thus a more reactive C-Sn system was required.

In each of the above cases, trimethyltin isothiocyanate was produced quantitatively and was identified by the coincidence of its PMR parameters [chemical shift and $J(^{119}\text{Sn}-\text{CH}_3)$ in both CCl_4 and benzene] with those of authentic samples under the same conditions. The following summarises the information on $(\text{CH}_3)_3\text{SnNCS}$: m.p. $106-108^\circ$; PMR (C_6H_6): $\delta(\text{CH}_3)$ 0.08 ppm, $J(^{119}\text{Sn}-\text{CH}_3)$ 60 Hz; PMR (CCl_4): $\delta(\text{CH}_3)$ 0.68 ppm, $J(^{119}\text{Sn}-\text{CH}_3)$ 61.5 Hz*.

The IR spectrum was in agreement with that previously reported. It should be pointed out that trimethyltin thiocyanate, $(\text{CH}_3)_3\text{SnSCN}$, is unknown.

The PMR data for the allyl, crotyl and allenyl trimethylstannanes has been previously reported² in detail and will not be repeated here. We will focus on the product data.

Reaction of $\text{CH}_2=\text{CH}-\text{CH}_2\text{Sn}(\text{CH}_3)_3$ and $(\text{SCN})_2$

Reaction was rapid and a set of resonances at ca. $\delta 5.5$ (complex) (3H) and $\delta 3.60$ ppm (doublet, J 7.0 Hz, 2H) appeared. Although a structure for the product other than $\text{CH}_2=\text{CH}-\text{CH}_2\text{SCN}$ (or NCS) is barely conceivable, it is of crucial importance to prove the nature of the pseudo-halogen linkage.

A mixture (ca. 50/50) of allylthiocyanate and allylisothiocyanate was prepared from allylbromide and potassium thiocyanate, and had the reported physical proper-

* In more polar solvents such as acetonitrile and methanol, $J(^{119}\text{Sn}-\text{CH}_3)$ in $(\text{CH}_3)_3\text{SnNCS}$ is increased to ca. 68 Hz as expected.

ties³. The salient point about the PMR spectrum of this mixture is that the CH₂ resonances occurred at δ 3.60 ppm (clear doublet, J 7.0 Hz) and at δ 4.3 ppm, which is a more complex signal. Data of a most convincing nature are available for the resonances of α -protons, i.e., >CH(SCN) in organic thiocyanates and iso counterparts, and has been summarised by Mathias⁴.

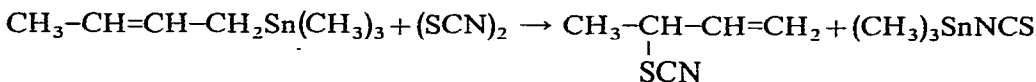
TABLE I

Compound	Chemical shift δ (ppm) of H _x		$\Delta\delta$ (ppm)
	X=SCN	X=NCS	
CH ₃ -X	2.61	3.37	0.76
CH ₃ CH ₂ -X	2.98	3.64	0.66
CH ₃ -CH(CH ₃)-X	3.48	3.95	0.47
CH ₃ -CH=CH-CH ₂ -X	3.55	4.04	0.49
CH ₂ =CH-CH ₂ -X		4.18	
CH ₂ =CH-CH(CH ₃)-X		4.35	

Clearly, a larger δ value is associated with the isothiocyanate and therefore the δ 3.60 ppm signal in the above mixture must be assigned to the thiocyanate* After the solution had been left to stand for several weeks at room temperature, the δ 3.60 ppm signal entirely disappeared in favor of the δ 4.3 ppm signal, in line with the known isomerisation of thiocyanate to isothiocyanate. Infrared evidence was entirely consistent. Deliberate addition of the synthetic isomeric mixture caused an increase in intensity of the δ 3.60 ppm signal in the spectrum of the original reaction mixture. Therefore, it is virtually certain that CH₂=CH-CH₂SCN is the kinetic product of (SCN)₂ cleavage**.

Reaction of CH₃-CH=CH-CH₂Sn(CH₃)₃ (cis and trans) and (SCN)₂

An approximately 1/1 mixture of the crotylstannane isomers also reacted very rapidly with (SCN)₂ to produce [along with (CH₃)₃SnNCS] a homogeneous product having PMR absorptions at δ 1.62 (doublet, J 7.0 Hz, 3H); δ 3.95 (unsymmetrical "quintet" J ~ 7.0 Hz, 1H) and ca. δ 5.5 ppm (complex, 3H). These data definitely rule out a 2-butenyl (crotyl) structure for the product, but are wholly in accord with the rearranged α -methallyl grouping.



* We have noted that solvent and concentration effects are important in determining chemical shifts in these compounds, and the difference between δ 4.3 ppm (our figure) and δ 4.18 ppm (reported) above is almost certainly attributable to such factors.

** We noted substantial isomerisation of our product after several hours to that one having a CH₂ resonance at δ 4.3 ppm. This is in line with the general observation that allylic isothiocyanates are thermodynamically preferred over the thiocyanates. IR analysis of products, though complicated by the problem of achieving complete separation of R-SCN from (CH₃)₃SnNCS, was entirely consistent with the above (and later) conclusions.

Authentic α -methallyl isothiocyanate was synthesised (the thermal isomerisation of crotyl thiocyanate yields α -methallyl isothiocyanate) in the reported fashion⁵ and exhibited PMR resonances at δ 1.52 (doublet J 6.5 Hz, 3H); δ 4.35 ("quintet", $J \sim 6.5$ Hz, 1H) and complex vinyl absorption δ 5.5 ppm (3H). This resembles the data for the cleavage product above except that the methine proton resonance *i.e.* >CH-NCS at δ 4.35 is some 0.4 ppm to lower field, and these signals were clearly separate by this amount on admixture. Thus the α -methallyl thiocyanate is the cleavage product, and as far as we are aware, this is the first information available on this compound. Heating the CCl_4 solution of the reaction product at 65° for a few minutes caused nearly complete isomerisation to the known crotyl isothiocyanate^{4,5}, as judged by the PMR data (Fig. 1 and Table 1). α -Methallyl thiocyanate is also the sole organic product from the reaction of crotylmercuric bromide and $(\text{SCN})_2$.

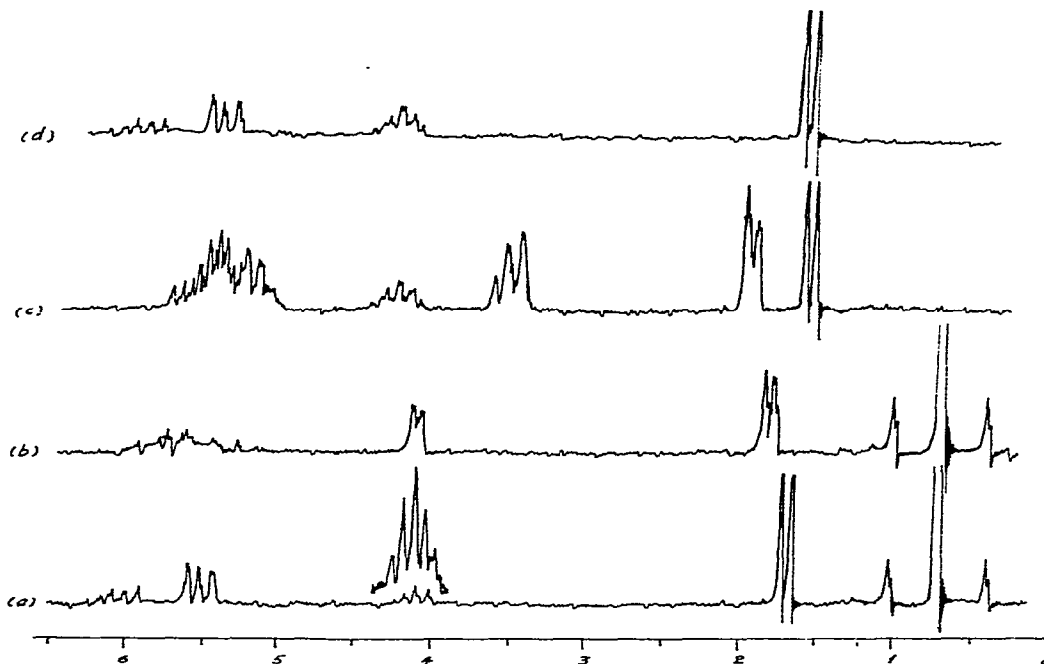
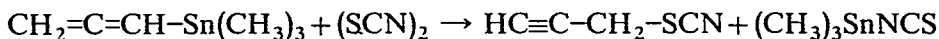


Fig. 1. 100 MHz Spectra (CCl_4) of: (a), Reaction product of (*cis* and *trans*) $\text{CH}_3\text{-CH=CH-CH}_2\text{Sn}(\text{CH}_3)_3$ and $(\text{SCN})_2$, *i.e.* α -methallylthiocyanate and $(\text{CH}_3)_3\text{SnNCS}$: (b), Isomerisation of solution in (a), yielding $\text{CH}_3\text{-CH=CH-CH}_2\text{NCS}$ identical (PMR) with reported values. See Text: (c), 60/40 Mixture of $\text{CH}_3\text{-CH=CH-CH}_2\text{-SCN}$ (*cis* and *trans*) and α -methallylisothiocyanate (from crotyl bromide and potassium thiocyanate): (d), Pure α -methallylisothiocyanate [the result of isomerisation of solution in (c)].

Reaction of $\text{CH}_2=\text{C}=\text{CH-Sn}(\text{CH}_3)_3$ and $(\text{SCN})_2$

Reaction was rapid, and two groups of signals, lacking tin satellites and considerably to higher field than those of the starting allene, were produced at δ 3.77 (doublet, J 2.5 Hz, 2H) and δ 2.5 ppm (triplet, J 2.5 Hz, 1H). These parameters are characteristic of the 2-propynyl ($\text{HC}\equiv\text{C-CH}_2\text{-}$) group. Confirmation that 2-propynyl thiocyanate had been formed was obtained by comparing the PMR and VPC behaviour with that of separately synthesised authentic material (See Experimental).

Thus the reaction is:

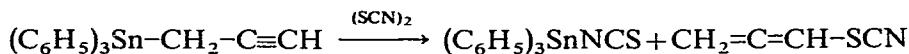
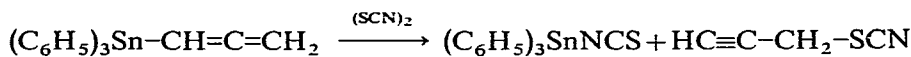


Reactions of (C₆H₅)₃Sn-CH₂-C≡CH and (C₆H₅)₃Sn-CH=C=CH₂ with (SCN)₂

A 2/1 mixture of the above isomers also reacted quite rapidly, and incremental addition of (SCN)₂ resulted in the decrease in intensity of the propargyl or allene signals and their replacement by new signals in the same regions. The non-appearance of signals ascribable to (C₆H₅)₂Sn(CH₂-C≡CH)NCS or (C₆H₅)₂Sn(CH=C=CH₂)-NCS indicated no significant cleavage of phenyl groups*.

The new sets of signals appeared at δ 2.51 (triplet, *J* 2.5 Hz, 1H) and δ 3.78 ppm (doublet, *J* 2.5 Hz, 2H), shown above to be due to HC≡C-CH₂SCN, and at δ 5.32 (doublet, *J* 6.5 Hz, 2H) and δ 5.84 ppm (triplet, *J* 6.5 Hz, 1H), such patterns being quite consistent in coupling constant and chemical shifts for CH₂=C=CH-SCN. This latter compound was moderately unstable at room temperature towards polymerisation, such behaviour being similar to that reported for the cyanoallenes, which polymerise fairly rapidly at 25°.⁶

The point of importance is that the intensities of the 2-propynyl and allene patterns due to the thiocyanate products are reversed from those of the starting tin compounds, *i.e.*, CH₂=C=CH-SCN/HC≡C-CH₂SCN 2/1. We have already demonstrated the clear allene → 2-propynyl rearrangement accompanying (SCN)₂ cleavage of (CH₃)₃Sn-CH=C=CH₂, and the results in the (C₆H₅)₃Sn series are best rationalised in terms of:



i.e. rearrangement also accompanies cleavage of (2-propynyl)triphenyltin**.

Reactions of trans- and cis-C₆H₅-CH=CH-Sn(CH₃)₃ with (SCN)₂

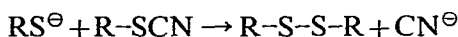
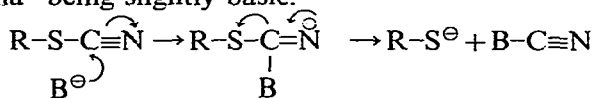
These compounds were prepared according to the method of Seyferth, Vaughan and Suzuki⁷, and the product was a mixture of *cis* and *trans* isomers. One fraction was more than 95% *trans*, and signals for the *cis* were barely detectable in the PMR spectrum. The vinyl protons in the *trans* isomer have identical chemical shifts at 60 MHz, at δ 6.70 ppm. The *cis* isomer, however, gave the characteristic AB pattern (*J*_{AB} 14.0 Hz) at δ 7.50 and δ 6.10 ppm.

Reaction of the mixture very rich (>95%) in *trans*, yielded a new AB pattern at δ 6.86 and δ 6.54 ppm (*J* 15.5 Hz). Another fraction being ca. 66% *trans* and 33% *cis* was also reacted, and besides the AB pattern just described, another at δ 6.95 and δ 6.38 ppm (*J* 10.0 Hz) also appeared, and was one-half as intense. Utilising the criterion that *J*_{AB} (*trans*) > *J*_{AB} (*cis*), it follows from the above data that *trans*-styryltin

* Such signals would be expected to have chemical shifts different from those of the starting tetraorganotin, but more importantly, would have associated tin satellites of different coupling constants.

** These reactions were quantitative as written, and the phenyl pattern in the PMR spectrum was identical with that of authentic triphenyltin isothiocyanate (δ 7.5 ppm broad), *v*_{sym}(NCS) at 1095 cm⁻¹.

compound yields *trans*-styryl thiocyanate, and likewise *cis* yields *cis* product, with no stereochemical leakage detectable by PMR spectroscopy. Thus cleavage proceeds with stereochemical retention at the vinylic carbon. Attempts to isolate the predominantly *trans* styryl thiocyanate have not been straightforward, and distillation does not clearly separate the $(\text{CH}_3)_3\text{SnNCS}$. Chromatography on neutral alumina did effect separation, but the solid compound isolated (m.p. 37–39°) lacked $-\text{SCN}$ absorption in the IR, and analysed satisfactorily for distyryl disulfide*, which was almost exclusively *trans* on the basis of its PMR spectrum. The following appears to account well for the conversion of the thiocyanate to the disulfide, and depends on the "neutral alumina" being slightly basic.



This scheme is strongly supported by our observations on the reaction product of phenyltrimethyltin and $(\text{SCN})_2$, which (besides Me_3SnNCS) is $\text{C}_6\text{H}_5\text{-SCN}$ (*vide infra*). Again column chromatography on "neutral alumina", resulted in the production of diphenyl disulfide, identical in m.p., IR and PMR spectra with authentic material. The conversion of organic thiocyanates to disulfides in the presence of base has been recorded previously, and appears to be quite characteristic of the thiocyanate structure^{8,9}.

Chromatography on a more acidic silica-gel column, produced the authentic¹⁰ phenyl thiocyanate, free from $(\text{CH}_3)_3\text{SnNCS}$, and no diphenyl disulfide was detected. In contrast to $\text{C}_6\text{H}_5\text{NCS}$, which shows a *very intense broad* band [$\nu_{\text{asym.}}(\text{SCN})$] centred at ca. 2100 cm^{-1} , phenyl thiocyanate exhibits a *moderately intense*, but very *sharp* band at 2165 cm^{-1} . This difference between $\nu(\text{SCN})$ for $-\text{NCS}$ and $-\text{SCN}$ groups is well documented^{11,12}.

In covalent compounds $\nu_{\text{asym.}}(\text{NCS})$ is generally 50–100 times more intense than $\nu_{\text{asym.}}(\text{SCN})$ ¹². Both $\text{C}_6\text{H}_5\text{NCS}$ and $\text{C}_6\text{H}_5\text{SCN}$ show similar complex proton resonance patterns at ca. $\delta 7.50\text{ ppm}$.

Attempts to discern the stereochemical course at typical secondary carbon centers *e.g.* 4-alkylcyclohexyl were thwarted by the comparatively rapid polymerisation of the $(\text{SCN})_2$.

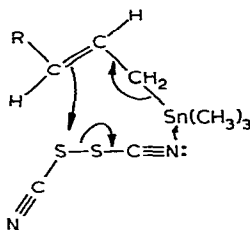
DISCUSSION

The cleavage of carbon-metal bonds by $(\text{SCN})_2$ is consistent with its pseudohalogen character, but it seems less active in this regard than the regular halogens such as bromine.

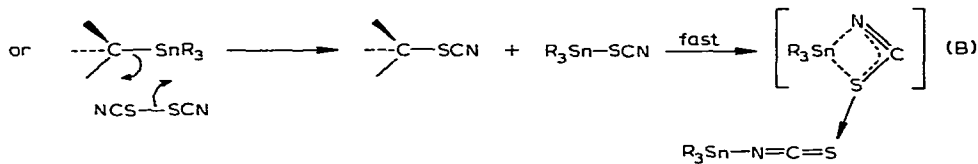
The observed order of reactivities of organic groups on tin is similar to that reported for SO_2 insertion and other electrophilic cleavages, *e.g.*, protic acid. The rearrangements reported herein are likewise similar to the rearrangements accompanying acid and SO_2 cleavage of allylic and allenic carbon-tin systems, and mechanisms

* Found: C, 70.86; H, 5.57. $\text{C}_{16}\text{H}_{14}\text{S}_2$ calcd.: C, 71.15; H, 5.18%. PMR data: *trans* AB system; δ_A 6.93, δ_B 6.87 ppm, J_{AB} 15.3 Hz; *cis* AB system; δ_A 6.69, δ_B 6.51, J_{AB} 10.8 Hz.

of the S_E type (perhaps $S_{Ei'}$) can be pictured, although the favored linear form^{13,14} for thiocyanogen ($N\equiv C-S-S-C\equiv N$) may demand substantial distortions in the transition state to achieve a cyclic array.



The formation of $(CH_3)_3SnNCS$ may be accounted for either as the kinetic product (A) or it could be formed by rapid isomerisation (B) of initially formed $(CH_3)_3SnSCN$.



Pathway (B) (to yield $M-SCN$) may be important for metals where $M-S$ bonding is preferred, e.g., Hg.

The stereochemical result in the case of styryltrimethyltin is also in line with the S_E description of the reaction, and would indicate a non-radical pathway in this case, since vinyl radicals appear to lose configuration quite rapidly even at -150° .¹⁵ For the highly reactive allyl and allenyl systems, we favor the S_E description, but cleavage of typical saturated alkyl groups under forcing conditions and where polymerisation of $(SCN)_2$ can be minimised, could conceivably have a radical component, in non-polar and radical supporting solvents such as CCl_4 .

From a synthetic point of view this cleavage of groups highly reactive in typical S_E reactions could be quite useful, and perhaps circumvents problems associated with mixtures of isothiocyanates and thiocyanates.

EXPERIMENTAL

The organotin compounds used in this study have been previously described² and thiocyanogen was generated as a CCl_4 solution in the reported manner¹⁶.

Allyl thiocyanate, uncontaminated with its iso relative, was prepared according to Foster¹⁷ in 72% yield, b.p. 35–37°/2.5 mm. $\nu_{\text{asym.}}(\text{SCN})$ at 2160 cm^{-1} . On standing this isomerised to the isothiocyanate.

A mixture of crotyl thiocyanate and α -methallyl isothiocyanate was prepared⁵ in 68% yield (both isomers), b.p. range 55–75°/760 mm. The mixture became progressively richer in the iso compound on standing.

2-Propynyl thiocyanate was prepared from 2-propynyl bromide and silver thiocyanate (in equimolar amounts) in methanol, the mixture being stirred for 24 h at room temperature. The product was extracted with ether and distilled at 82–85°/25 mm. It was a clear liquid with a pungent odour which turned brown over several days, $\nu(\text{H}-\text{C}\equiv\text{C})$ 3280 cm^{-1} ; $\nu(\text{C}-\text{H})$ at 2960 cm^{-1} , $\nu_{\text{asym.}}(\text{SCN})$ at 2155 cm^{-1} . The PMR spectrum is discussed in the text.

PMR spectra were obtained with a Varian A-60 or JEOL MH-100 spectrometers, on CCl_4 solutions with internal TMS standard. IR spectra were obtained either as neat liquids, nujol mulls or KBr discs on a Perkin-Elmer grating 247 IR.

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