29.78. Found: C, 50.12; H, 6.13; N, 6.41; O, 7.58; S, 29.69.

***tert*-Butyl *N*-(2-Thienyl)dithiocarbamate (19).** A slurry of lithium *tert*-butylmercaptide (682 mg, 7.1 mmol), **5** (1.0 g, 7.1 mmol), and 10 ml of *tert*-butyl mercaptan was heated under reflux for 5 min and then stirred at room temperature in a foil-covered flask for 20 h under anhydrous conditions. The mercaptan was evaporated under a stream of nitrogen and the pasty residue was neutralized with hydrochloric acid. The resultant oil was extracted with ether and evaporation of the ether gave a crystalline product. This was chromatographed on a dry-packed 40 g silica gel 60 (EM Laboratories, 70–230 mesh) column and eluted with carbon tetrachloride. Unreacted 2-thienyl isothiocyanate comes with the solvent front and the product comes a little later. The product was recrystallized from petroleum ether with decolorization by acid-washed Norit A charcoal, yielding 1.42 g (86%) of yellow needles: mp 87.5–88.5 °C dec; NMR (CCl_4) δ 1.63 (s, 9, CH_3), 6.80–7.01 (m, 3, thienyl H), 9.17 (br band, 1, NH).

Anal. Calcd for $C_9H_{13}NS_3$: C, 46.71; H, 5.66; N, 6.05; S, 41.57. Found: C, 46.82; H, 5.56; N, 6.06; S, 41.72.

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Registry No.—**1**, 2046-39-1; **3**, 61528-47-0; **4**, 61528-48-1; **5**, 61528-49-2; **6**, 61528-50-5; **7**, 61528-51-6; **8**, 61528-52-7; **9**, 61528-53-8; **10**, 61528-54-9; **11**, 61528-55-0; **12**, 51460-50-5; **13**, 61528-56-1; **14**, 61528-57-2; **15**, 61528-58-3; **16**, 61528-59-4; **17**, 61528-60-7; **18**, 61528-61-8; **19**, 61528-62-9; *O,O'*-diethylhydrogen dithiophosphate, 298-06-6; 3-thenoyl azide, 59445-89-5; propylamine, 107-10-8; propyl alcohol, 71-23-8; potassium *tert*-butoxide, 865-47-4; *tert*-butyl mercaptan, 75-66-1.

Supplementary Material Available. Chemical analyses and NMR data for the compounds listed in Table I (3 pages). Ordering information is given on any current masthead page.

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Thiocyanations. 2. Solvent Effects on the Product Distribution of the Thiocyanogen–Olefin Reaction

Robert J. Maxwell,* Leonard S. Silbert, and John R. Russell

Eastern Regional Research Center,[1,2] *Philadelphia, Pennsylvania 19118*

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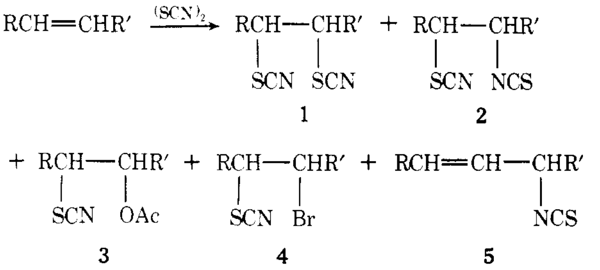
The heterolytic addition of thiocyanogen to *cis*- and *trans*-3-hexene has been carried out in a variety of solvent systems. Unlike ionic bromine addition to aliphatic olefins, this pseudohalogen reaction can yield either adduct 1 or 2 as the principal product dependent on the type of solvent employed. Dithiocyanates (1) are preferentially formed in polar and dipolar aprotic media, whereas isothiocyanatothiocyanates (2) become the principal products in nonpolar solvents. It was also observed that the product outcome was significantly altered when iron powder or ferric thiocyanate was added to the reaction medium. The effects of solvents and iron on the product composition are explicable through the Pearson HSAB concept. The free-radical thiocyanation reaction was also examined and the results are briefly discussed.

Thiocyanogen addition to alkyl olefins is a well-known procedure[3] for the preparation of α,β-dithiocyanates **1** as well as a classical analytical method for determination of the unsaturation in fats and oils. The reaction, traditionally carried out in acetic acid, had been known to yield only the adducts **1**[4] until the recent isolation of the isomeric α-isothiocyanato-β-thiocyanate **2** and ancillary coproducts **3–5** (eq 1).[5]



$$\mathrm{RCH{=}CHR'} \xrightarrow{\mathrm{(SCN)_2}} \underset{\mathbf{1}}{\underset{\mathrm{SCN}\quad\mathrm{SCN}}{\mathrm{RCH{-}CHR'}}} + \underset{\mathbf{2}}{\underset{\mathrm{SCN}\quad\mathrm{NCS}}{\mathrm{RCH{-}CHR'}}} + \underset{\mathbf{3}}{\underset{\mathrm{SCN}\quad\mathrm{OAc}}{\mathrm{RCH{-}CHR'}}} + \underset{\mathbf{4}}{\underset{\mathrm{SCN}\quad\mathrm{Br}}{\mathrm{RCH{-}CHR'}}} + \underset{\mathbf{5}}{\underset{\mathrm{NCS}}{\mathrm{RCH{=}CH{-}CHR'}}} \qquad (1)$$

trans olefin → erythro (meso) (**1a**–**4a**)
cis olefin → threo (*dl*) (**1b**–**4b**)

Quantitation of product distribution has only been reported for reactions carried out in acetic acid solution.[5] Although adduct **2** has also been identified as a coproduct in benzene and carbon tetrachloride solution reactions, the extent of its formation relative to adduct **1** had not been ascertained.[6] Since adducts **1** and **2** have recently found use as synthetic intermediates,[7] a need existed for an improved method of selective conversion of olefins to either **1** or **2**.

The present investigation was initiated to determine the influence of various reaction parameters on the composition of the product mixture, since only limited information was available in the literature.[3b,6] A specific aim of this work was to determine the influence of solvent variation on the product distribution. A quantitative examination of the addition reaction was also carried out under irradiative conditions to compare the products formed by ionic and free-radical pathways. It was anticipated that an understanding of the solvents' role in determining the products formed from thiocyanogen additions would aid in clarification of the mechanism of addition of this ambident pseudohalogen to olefins.

Results

The present study was implemented with *cis*- and-*trans*-3-hexene as convenient model olefins[8] for which the products were easily analyzed by GLC. Earlier studies in this laboratory[5] have indicated that the product outcome is not influenced by the chain length and hence it was anticipated that the results obtained on 3-hexene could be projected to longer chain internal olefins. The general thiocyanation procedure[5] consisted of the generation from lead thiocyanate of thiocyanogen in a specific solvent, filtration of insoluble salts, and delivery of the reagent to volumetric flasks containing the olefin. Any changes introduced in the procedure depended on the nature of the variables under study.

The parameters considered for reactions in each solvent included lead salt effects,[3,4] free-radical inhibitors, the ratio of thiocyanogen to olefin, and the influence of iron catalysts.[6] Because of thiocyanogen's photosensitivity leading to free-radical processes, the present series of thiocyanations were maintained in the absence of light except for the specifically photoinitiated conditions. Free-radical inhibition under dark conditions was suggested from preliminary studies of the reaction. Two variations in the molar ratio of olefin to the thiocyanogen reagent were studied to determine the effect of relative concentration on product distribution and overall yield.

The data showing the effects of the parameters for each solvent are assembled in Tables I and II. With the exception of acetic acid, the solvents listed in the tables are arranged in order of decreasing dielectric constant ϵ.

The results indicate that the stability of thiocyanogen as a reagent, unlike bromine and other halogens, is solvent dependent. The reagent is sensitive to the alcohol[3b] stabilizer in commercial chloroform, and this accounts for erratic results obtained in this system. The lower conversions for the thiocyanogen additions in acetonitrile suggest that the reagent is relatively unstable in dipolar aprotic media in comparison to acetic acid and the three nonpolar solvents employed.

Product distributions generally differed between reactions in filtered and unfiltered solutions. In the presence of insoluble lead salts retained after reagent generation there was a lack of stereospecificity and formation of significant amounts of bromothiocyanate adducts **4**. Experiments in which the recovered lead salts were readded to the filtered solutions prior to olefin addition yielded product mixtures analogous in composition to those obtained with filtered solutions of thiocyanogen (Experimental Section).

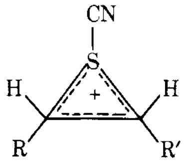
A related unexplained phenomenon concerns thiocyanogen additions in which the reagent was generated in benzene from lead thiocyanate that had been stored under refrigeration for several months (Table I). The thiocyanogen formed from the "aged" lead thiocyanate gave a product distribution in this solvent showing little variation among the complete set of parameters studied. This was in contrast to the corresponding set of experiments in which the reagent was derived from freshly prepared lead thiocyanate. The contrasting results found in this group of experiments established the necessity of using only freshly prepared lead thiocyanate in order to achieve reproducible data.

The addition of iron powder to the acetic acid experiments did not influence the product outcome, but marked changes occurred in the nonpolar media. In these solvents, the dithiocyanate adduct (**1**) became the principal product almost to the exclusion of adduct **2**. A refinement of this procedure using $Fe(SCN)_3$ instead of powdered iron further increased the conversion to **1** as well as the overall yield of the reaction.

Only limited studies of the photoinitiated addition of thiocyanogen to olefins were carried out, principally to contrast the results obtained in polar and nonpolar media. As in the addition of iron to the acetic acid medium, photoinitiation in this solvent did not affect the final product outcome. In benzene, however, the allylic isothiocyanate **5** was the principal product. This adduct, together with the isomeric dithiocyanates **1** (erthyro and threo), were the only previously reported[9] products of the free-radical addition. In addition to these two compounds, we have found that the isomeric isothiocyanato thiocyanates **2** (erythro and threo) are also formed under irradiative conditions.

Discussion

The solvents listed in Tables I and II showed marked differences in their effect on the course of thiocyanations. Acetic acid, in which the additions were stereospecific and completely insensitive to variations in the reaction parameters, was effective for the preparation of adduct **1** as the predominant isomer. In this medium the product distribution and overall yield were invariable even under protoinitiated conditions. On the basis of a two-step kinetically controlled ionic reaction mechanism previously proposed for thiocyanations in acetic acid,[4,5] adduct specificity would be expected. In the initial step of the proposed pathway addition of the ^{+}SCN ion leads to the formation of a *S*-cyanosulfonium cation **6** as the intermediate species. This is attacked by the ambident thiocyanate anion or the solvent itself. The stereospecific formation of products **1–4** (eq 1) suggests that the intermediate **6** is the only cationic species formed in this medium. The predominance of α,β-dithiocyanates **1** and the invariance of yield and product distribution in this medium may be attributed to the ability of acetic acid to coordinate with the thiocyanate anion in a solvent cage principally through hydrogen bonding at its nitrogen terminus as in the equilibrium depicted below. Collapse of the caged pair will occur with preferential carbon–sulfur bond formation leading to adduct **1**. Formation of adduct **2** indicates some participation by the alternate hydrogen-bonded sulfur pair through reaction of the nitrogen terminus with **6**. Adducts of the type **3** arise through solvation of the intermediate **6** in polar media, and subsequent formation of the acetate product, a reaction that may be anticipated on the basis of the high solvent to reagent ratio. Although consistently high conversions of olefins to α,β-dithiocyanates were obtained in acetic acid, difficulties experienced in product separations have limited the usefulness of this solvent for preparation of these compounds.



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$$[\mathrm{CH_3C(=O)}\text{—}\mathrm{OH}\cdots\mathrm{S}\text{—}\mathrm{C}{\equiv}\mathrm{N}]^- \rightleftharpoons [\mathrm{CH_3C(=O)}\text{—}\mathrm{OH}\cdots\mathrm{N}{\equiv}\mathrm{C}\text{—}\mathrm{S}]^-$$

A rationale for the results of the thiocyanations carried out in CH_3CN, CH_2Cl_2, $CHCl_3$, and benzene became apparent when specific controls were placed on the parameters of this reaction. For example, the data in Tables I and II obtained for experiments using unfiltered and filtered thiocyanogen solutions containing no free-radical inhibitor display a wide distribution of nonstereoselective isomeric products arising from concurrent ionic and free-radical pathways. However, when 15 mol % inhibitor is added to the filtered thiocyanogen solution, products of inverted stereochemistry are much reduced in $CHCl_3$ and benzene and all but eliminated in CH_2Cl_2 and CH_3CN. Since no further change in product composition occurred above the addition of 15 mol % inhibitor in $CHCl_3$ and benzene, we consider that the products of inverted stereochemistry found in these experiments must arise via an *ionic* pathway. Therefore, the discussion of solvent–intermediate interactions is confined to those data obtained with filtered solutions of thiocyanogen using 15 mol % inhibitor (Tables I and II).

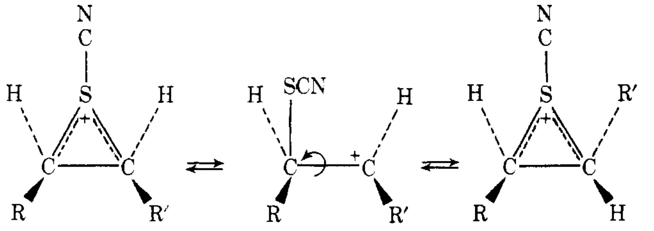
The stereoselective nature of the addition observed in

Table I. Thiocyanation of *trans*-3-Hexene. Parameter Effects on Product Composition and Yields

Solvent[a]	R in $-\overset{\mathrm{NCS}}{\overset{\vert}{\mathrm{C}}}\mathrm{H}-\overset{\mathrm{R}^{b}}{\overset{\vert}{\mathrm{C}}}\mathrm{H}-$	Unfiltered	Filtered				
		No inhib[c]	No inhib[c]	15% inhib[c,d]	15% inhib[d] 2.4 mol $(SCN)_2$	15% inhib[c,d,e] 10% iron	No inhib[c] light
Acetic acid	$-Br_{(e)}$	0.7	0.6	0.7	0.7	1.3	
	$-OAc_{(e)}$	4.2	3.9	3.3	3.4	4.9	
	$-NCS_{(e)}$	11.5	12.3	11.4	11.0	11.6	
	$-SCN_{(e)}$	83.4	83.2	84.6	84.9	82.2	
	Yield[h]	97.8	89.1	99.0	96.5	99.0	
Acetonitrile	$-NCS_{(e)}$		30.7	31.3	31.1	9.4	
	$-NCS_{(t)}$						
	$-SCN_{(e)}$		69.3	68.7	68.9	84.2	
	$-SCN_{(t)}$					6.4	
	Yield[h]		31.4	37.0	61.7	45.0	
Methylene chloride	$-Br$	3.5					
	$-NCS_{(e)}$	33.3	49.8	52.2	54.0	8.3	
	$-NCS_{(t)}$	1.0	1.0	0.1			
	$-SCN_{(e)}$	58.6	47.0	46.9	44.9	89.3	
	$-SCN_{(t)}$	3.6	2.2	0.8	1.1	2.4	
	Yield[h]	89.6	73.4	67.6	82.6	86.7	
Chloroform[f]	$-Br$	10.3					
	$-NCS_{(e)}$	39.5	56.6	59.4	61.2	0.7	
	$-NCS_{(t)}$	2.1	3.3	0.7	0.5		
	$-SCN_{(e)}$	43.1	35.6	37.3	35.5	93.6	
	$-SCN_{(t)}$	5.4	4.5	2.6	2.8	5.5	
	Yield[h]	61.1	55.3	51.2	73.5	86.6	
Benzene[g]	$\mathrm{Et{-}CH{=}CH{-}\overset{NCS}{\overset{\vert}{C}}HCH_3}$[i]	4.9	5.1	2.6	4.5		60.8
	$-Br$	10.2	0.6	6.7	5.1		
	$-NCS_{(e)}$	20.2	26.7	34.4	31.7	2.5	4.4
	$-NCS_{(t)}$	9.6	16.5	5.9	8.1		2.3
	$-SCN_{(e)}$	36.4	30.8	40.9	37.5	92.3	19.9
	$-SCN_{(t)}$	18.7	20.4	9.5	13.1	5.2	12.6
	Yield[h]	31.7	58.9	57.9	75.5	75.1	68.2
Benzene	$\mathrm{Et{-}CH{=}CH{-}\overset{NCS}{\overset{\vert}{C}}HCH_3}$						
	$-Br$	10.2					60.1
	$-NCS_{(e)}$	25.8	55.0	62.0	65.8	3.4	3.8
	$-NCS_{(t)}$	12.5	8.1	1.0	1.9		2.7
	$-SCN_{(e)}$	32.2	30.8	35.3	30.9	92.9	19,3
	$-SCN_{(t)}$	19.3	6.1	1.4	1.4	3.7	14.1
	Yield[h]	55.3	50.9	48.1	58.2	82.8	68.4

[a] All solvents except acetic acid are in order of decreasing dielectric constant ϵ. [b] Structures of products are formulated in eq 1. [c] Reactions in these columns carried out in the ratio 1.2 mol $(SCN)_2$/1.0 mol olefin. [d] 2,6-Di-*tert*-butyl-4-methylphenol. [e] Reactions carried out in acetic acid and benzene used powdered iron, and those run in acetonitrile, methylene chloride, and chloroform used $Fe(SCN)_3$ as catalyst. [f] Ethanol stabilizer removed prior to use. The presence of alcohol in chloroform polymerizes $(SCN)_2$, changes product distribution, and reduces the overall conversions by half. [g] These data reflect the results obtained with "aged" $Pb(SCN)_2$. [h] Total isolated yield of thiocyanated products. [i] Product is primarily *trans*-$CH_3CH_2CH{=}CHCH(NCS)CH_3$ (ref 9).

benzene and chloroform solutions may be due to the exceedingly slow rate of the reaction in these solvents.[10] Slow addition rates may, to a limited extent, allow for ring opening of the intermediate cation **6** prior to collapse of the solvent–anion coordinated pair as shown in eq 2.[11] Since the extent of formation of the minor stereoisomeric products is less for *cis*-3-hexene (Table II) compared to *trans*-3-hexene (Table I) because of the faster reaction rates of cis olefins,[10] it is logical that the longer lifetime of the cyclic intermediate **6** is responsible for the formation of these compounds.



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(2)

It is evident from the data in Tables I and II that the overall ratio of the major reaction products **2**/**1** is dependent on the dielectric constant ϵ of the solvent medium employed. The results of the present study, compiled in Table III, clearly establish a trend of increasing production of adduct **2** relative to adduct **1** with decreasing ϵ. In some studies[12,13] of equilibrium interconversions of thiocyanates–isothiocyanates, a linear correlation has been determined for this relationship; however, since thiocyanogen addition is kinetically controlled[6,10] a *linear plot* of the data in the present study would not be expected. Although the results of the present experiments may be correlated with both the rate of reaction[10] and the dielectric constant of the medium, these relationships do not completely explain the product outcome. For this reason it is necessary to understand the nature of the solution effects on the intermediate ambident thiocyanate anion.

The phenomena of ambident behavior of this anion has

Table II. Thiocyanation of *cis*-3-Hexene. Parameter Effects on Product Composition and Yields

Solvent[a]	R in $\overset{\mathrm{NCS}\quad\mathrm{R}^b}{\text{–CH–CH–}}$	Unfiltered	Filtered				
		No inhib[c]	No inhib[c]	15% inhib[c,d]	15% inhib[d] 2.4 mol $(SCN)_2$	15% inhib[c,d,e] 10% iron	No inhib[c] light
Acetic acid	$-Br_{(t)}$	2.9	0.9	0.5	0.7		0.8
	$-OAc_{(t)}$	10.7	9.7	10.2	9.6	11.7	9.4
	$-NCS_{(t)}$	8.0	12.5	12.2	12.6	7.3	12.0
	$-SCN_{(t)}$	78.4	76.9	77.1	77.1	81.0	77.8
	Yield[g]	97.1	92.0	97.0	98.3	97.0	90.1
Acetonitrile	$-NCS_{(e)}$						
	$-NCS_{(t)}$		31.0	30.9	31.6	10.7	
	$-SCN_{(e)}$					11.6	
	$-SCN_{(t)}$		69.0	69.1	38.4	77.7	
	Yield[g]		43.1	46.0	61.7	39.8	
Methylene chloride	$-Br$	12.9					
	$-NCS_{(e)}$	2.4	2.6				
	$-NCS_{(t)}$	31.5	45.7	48.7	52.4	14.6	
	$-SCN_{(e)}$	3.9	2.5				
	$-SCN_{(t)}$	49.3	49.2	51.3	47.6	85.2	
	Yield[g]	90.4	73.2	84.5	86.8	85.0	
Chloroform[f]	$-Br$	7.3					
	$-NCS_{(e)}$	3.1		0.2	0.6		
	$-NCS_{(t)}$	39.6		54.5	56.8	1.4	
	$-SCN_{(e)}$	4.8		0.7	0.7	0.8	
	$-SCN_{(t)}$	45.2		44.6	41.9	97.8	
	Yield[g]	79.4		76.3	97.6	84.5	
Benzene	$\mathrm{Et{-}CH{=}CH{-}\overset{NCS}{C}HCH_3}$[h]						44.9
	$-Br$	8.6					1.9
	$-NCS_{(e)}$	12.0	13.5	0.2	1.2		7.4
	$-NCS_{(t)}$	26.8	46.5	56.7	60.9	1.8	7.2
	$-SCN_{(e)}$	19.9	8.5	0.6	1.1	0.9	21.7
	$-SCN_{(t)}$	32.7	31.5	42.5	37.0	97.3	16.9
	Yield[g]	61.7	52.8	71.6	83.6	91.7	67.5

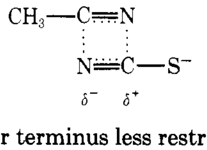
[a] All solvents except acetic acid are in order of decreasing dielectric constant ϵ. [b] Structures of products are formulated in eq 1. [c] Reactions in these columns carried out in the ratio 1.2 mol $(SCN)_2$/1.0 mol olefin. [d] 2,6-Di-*tert*-butyl-4-methylphenol. [e] Reactions carried out in acetic acid and benzene used powdered iron and those run in acetonitrile, methylene chloride, and chloroform used $Fe(SCN)_3$ as catalyst. [f] Solvent purified to remove ethanol prior to use. [g] Total isolated yield of thiocyanated products. [h] Product is primarily *trans*-$CH_3CH_2CH{=}CHCH(NCS)CH_3$, among allylic isothiocyanate mixture (ref 9).

Table III. Change in Product Ratio with Increasing Dielectric Constant[a]

Solvent	ϵ	2/1[b]
Benzene	2.3	2.15
$CHCl_3$	4.8	1.47
CH_2Cl_2	8.9	1.14
CH_3CN	37.5	0.46

[a] The results represent the average obtained from the thiocyanation of *cis*- and *trans*-3-hexene. [b] **2**, *erythro*- and *threo*-3-isothiocyanato-4-thiocyanatohexane; **1**, *erythro*- and *threo*-3,4-dithiocyanatohexane.

been studied in displacement reactions,[12,13] in equilibrium interconversions of thiocyanate and isothiocyanate compounds,[12,14] and in the elucidation of bonding modes in many metal–thiocyanate and metal–isothiocyanate complexes.[15] Recourse to Pearson's HSAB concept[16] has provided the best means of explaining the bonding behavior of this anion.[17] Under this classification, the large sulfur atom is a "soft base" with charge dispersal over a large volume compared to the nitrogen atom, a "hard base" bearing a greater charge to size ratio. To determine the relative influence of solvent on the reactions of hard and soft bases with hard and soft acids, Klopman[18] developed a theoretical basis of the Pearson concept that included the solvent as a parameter. Klopman's equations predict that hard base–hard acid interactions are charge controlled and depend primarily on the ionic interactions of the reagents, whereas soft base–soft acid interactions are frontier controlled in reactions of nucleophiles having low electronegativity and are enhanced by high polarizability and low solvation energies of the reactants. In solvents of low dielectric constant, ions and ion pairs are more strongly associated than in polar solvents. The ambident thiocyanate anion is thus more effectively solvated at the soft sulfur atom by nonpolar solvents, presumably by charge transfer interactions, leading principally to a charge controlled nitrogen attack on the episulfonium cation. Strong ion pair association would account for slower reaction rates (only qualitatively determined) in nonpolar solvents. With increasing dielectric constant in the order PhH < $CHCl_3$ < CH_2Cl_2 ≪ CH_3CN, the rates increased in favor of sulfur attack (Table III). Increasing ϵ, therefore, changed the direction of reaction from charge controlled (nitrogen attack) to frontier controlled (sulfur attack) with diminution in the 2/1 adduct ratio. A dipolar aprotic solvent like acetonitrile may, however, also associate with thiocyanate anion by dipole alignment, pictorially represented below in one possible arrangement, that would leave



the polarizable sulfur terminus less restricted than nitrogen,[17] effectively contributing to the bonding mode of the thiocyanate anion.

Table IV. Thiocyanation of *trans*-3-Hexene in Benzene.[a] Effect of Catalyst on Product Distribution and Yield

R in product	Percent products		
$\overset{NCS}{-CH}-\overset{R}{CH}-$	No added metal	Iron powder[c]	Fe $(SCN)_3$
$-NCS_{(e)}$	62.3	3.4	0.2
$-NCS_{(t)}$	1.0		
$-SCN_{(e)}$	35.3	92.9	98.9
$-SCN_{(t)}$	1.4	3.7	0.9
Yield[b]	48.1	82.8	92.8

[a] Reactions conditions: 1.2 mol $(SCN)_2$/1.0 mol olefin + 15 mol % inhibitor. [b] Total isolated yield of thiocyanated products. [c] Incomplete studies indicate that grade of iron powder used affects product distribution and yield.

The use of iron catalysts was an intriguing alternative to acetic acid for directing the primary, if not exclusive, formation of dithiocyanates. The hypothesis of ferric thiocyanate as the active agent arising by reaction of iron and thiocyanogen in nuclear thiocyanations of aromatic rings[3a] was also confirmed for the present series of olefin thiocyanations. Remarkably, the ferric thiocyanate catalyzed thiocyanations of internal olefins in benzene solution gave almost exclusively the dithiocyanate adduct 1 compared to 35% yield in catalyst-free reactions (Table IV).

The metal catalyst provided an example of the utility of the HSAB concept as an aid in the clarification of the mechanism. Since ferric thiocyanate in solution is a metal coordination complex,[15e,f] the metal–ligand interaction is responsible for the stereochemical specificity. The HSAB concept predicts that Fe^{3+} is a hard acid[16,18] and should be expected to form hard anion–hard metal ligand bonds. The nitrogen terminus of thiocyanate is coordinatively bound to ferric ion with the sulfur terminus in free projection. It has been observed in other cases[15c,f] that the degree of hardness or softness of a metal atom is solvent dependent. Burmeister[15c] found that Pd^{2+} (a soft acid) in complexes showed only Pd–S bonding in "class a" solvents (dipolar, aprotic; high ϵ) whereas in "class b" solvents (benzene, $CHCl_3$; low ϵ) Pd–S, Pd–N, and bridged -NCS- bonding was observed. Presumably, the Pd^{2+} ion becomes *harder* with decreasing dielectric constant. Our results with ferric thiocyanate indicate a similar trend. In benzene,[15c] metal–ligand bonding is exclusively through nitrogen, whereas both Fe–NCS and Fe–SCN evidently appear as the solvent dielectric constant is increased (Tables I and II).Using Pearson's terminology, it would seem that Fe^{3+} cation becomes softer as the solvent medium is shifted from benzene to acetonitrile. Unfortunately, the instability of thiocyanogen in solvents of higher dielectric constant than acetonitrile limits the determination of the soft–soft interactions for this system.

A further test of the HSAB concept as it relates to these studies would involve the effect of other metal salts on the course of thiocyanation addition reactions. It would seem unlikely that ferric ion among metal ions is unique in directing the course of this addition. Metal–ligand interactions in nonpolar solvents may further explain the results of thiocyanations in the presence of unfiltered lead salts by which a higher proportion of dithiocyanate adduct was obtained than in lead salt-free solutions. Like ferric thiocyanate, lead may be influencing the direction of attack through interaction with the nitrogen end of the thiocyanate anion. However, the limited solubility of lead thiocyanate in these solvent studies precludes a verifiable extension of the concept.

Finally, brief mention must be made of the results obtained with thiocyanogen addition under homolytic conditions (Tables I and II). Reports in the literature are in slight disagreement with our results presented in this study. Guy and Thompson[9] had irradiated thiocyanogen in the presence of *cis*- and *trans*-3-hexene in benzene solution. They obtained two products: identical mixtures of erythro and threo dithiocyanates I (30%) and the allylic isothiocyanate (**5**, 70%). We, on the other hand, have additionally found that under similar conditions the erythro and threo isothiocyanatothiocyanates (**2**) are formed in amounts ranging from 7 to 15%. The presence of these compounds is not unexpected, since the reaction involves the thiocyanate radical, which, like the thiocyanate anion, should display ambident behavior. It can

$$\cdot S{-}C{\equiv}N \leftrightarrow S{=}C{=}N\cdot$$

be seen from the results in Tables I and II that the erythro and threo adducts 1 and 2 from both olefins are formed in nearly equal amounts. These findings would support the view[9] that the intermediate in this reaction is formed by reversible addition of the thiocyanate radical to the olefin. Since *erythro*-**2** and *threo*-**2** are in equal amounts in these reactions, a requirement for free-radical addition, their formation cannot be attributed to a concurrent ionic pathway.

Experimental Section

Equipment. Product mixtures were analyzed on a Model 810 F & M gas chromatograph (8 ft × 3/16 in. SS column containing 15% HI-EFF DEGS on 50/60 Mesh Anakrom[19] ABS). The IR spectra were obtained with a Perkin-Elmer Model 457 grating infrared spectrophotometer and NMR spectra were recorded on a Jeolco Model 60H spectrometer.

Solvents and Materials. Benzene and acetonitrile (both Mallinckrodt nanograde) and methylene chloride (Fisher ACS grade) were used as obtained. The acetic acid (Baker Reagent grade) contained an added 1% acetic anhydride. Commercial chloroform (Baker Reagent grade) contained 0.75% ethanol as preservative. For reactions requiring alcohol-free chloroform, the alcohol was removed by successive treatments of stirring with concentrated sulfuric acid for several hours, repetitive water washings, drying over potassium carbonate, and distillation prior to use.

cis- and *trans*-3-hexenes were obtained from Chemical Samples Co. The isomeric purity of the olefins was established by bromination of each olefin to its corresponding α,β-dibromide and GLC analysis of the crude product mixtures. Lead thiocyanate was prepared by the method of Lambou and Dollear.[20]

General Reaction Procedures. The techniques and experimental conditions used for reactions in each solvent were similar. Thiocyanogen solution for the unfiltered reactions was prepared separately in each experiment whereas this reagent was prepared in single batches for use in the series of filtered experiments. Equipment was thoroughly dried prior to use. All reactions were run at room temperature under a nitrogen atmosphere.

Reactions with Unfiltered Thiocyanogen. Thiocyanogen was prepared in the specific solvent under investigation by batchwise addition of bromine (1.92 g, 0.012 mol) to a stirred solution of lead thiocyanate (7.95 g, 0.024 mol) in 70 mL of solvent. The mixture was stirred in the dark for 1.5 h prior to addition of the olefin (0.84 g, 0.01 mol) dissolved in 10 mL of solvent. Stirring was continued for 24 h, then the mixture was quenched with sodium thiosulfate solution. The internal standard, methyl stearate (0.25 g in 10 mL of benzene), was added and the organic layer was filtered and reduced in volume. The crude reaction mixture was analyzed by glc without further workup.

Reactions with Filtered Thiocyanogen. Bromine (13.5 g, 0.084 mol) was added to a stirred solution of lead thiocyanate (54.5 g, 0.168 mol) in solvent (490 mL) in the manner described above. The thiocyanogen solution was filtered through a sintered glass funnel and the calculated volumes delivered to the series of reaction vessels with a glass syringe fitted with a Teflon needle. In the present study, the admixture of thiocyanogen (70 mL containing 0.012 mol) and olefin (0.01 mol per 10 mL of solvent) provided the 1.2 mole ratio and twice the volume of thiocyanogen solution gave the 2.4 mole ratio for reactions. Inhibition of the homolytic reaction was examined with 2,6-di-*tert*-butyl-4-methylphenol as the inhibitor at concentrations of 5 mol % (0.132 g, 0.6 mmol) and 15 mol % (0.396 g, 1.8 mmol) for the 1.2 mole ratio of thiocyanogen to olefin. Other concentrations were accordingly calculated. Metal catalysis was determined with powdered iron (0.1 g, 1.8 mmol) or ferric thiocyanate.

The homolytic reaction between thiocyanogen and olefin (1.2 mole ratio) was carried out under nitrogen for 24 h by irradiation with a 300-W incandescent bulb.

Control Experiments. The following experiments were carried out on the products **1a** and **2a** from *trans*-3-hexene to demonstrate the resistance of the products to isomerization under the experimental conditions employed. A sample of 3,4-dithiocyanatohexane **1a** was added to unfiltered thiocyanogen in benzene solution and stirred in the dark for 24 h. The crude reaction mixture showed only **1a** by GLC analysis. Repetition of the experiment with the corresponding **2a** similarly demonstrated that **2a** was not isomerized.

The effect of added salts on the product composition of the thiocyanation of *trans*-3-hexene was determined in the following manner. A benzene solution of thiocyanogen was prepared, filtered, and delivered into four flasks each containing a mixture of 0.01 mol of *trans*-3-hexene in 10 mL of benzene. Lead thiocyanate (2.0 g) was freshly prepared and added to flask a, freshly prepared lead bromide (2.0 g) was added to flask b, a mixture of 2.0 g of lead thiocyanate and 2.0 g of lead bromide was added to the contents of flask c, and 2.0 g of the crude salts obtained from the filtration of thiocyanogen solution was added to flask d. The above four mixtures were stirred in the dark under nitrogen for 24 h. Analysis of the contents of flasks a, b, c, and d by GLC showed nearly identical chromatographic traces for all four mixtures, essentially unchanged from a trace obtained from the filtered thiocyanation additions carried out in benzene.

Registry No.—*trans*-3-Hexene, 13269-52-8; *cis*-3-hexene, 7642-09-3; $(SCN)_2$, 505-14-6.

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Thiocyanations. 3.[1] Preparation of 2-Imino-1,3-dithiolane Salts by Cyclization of *vic*-Dithiocyanates

Robert J. Maxwell* and Leonard S. Silbert*

Eastern Regional Research Center,[2] Philadelphia, Pennsylvania 19118

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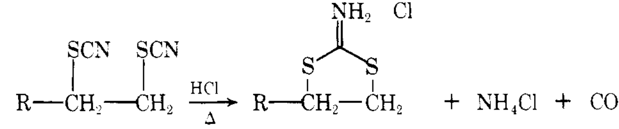
A series of 2-imino-1,3-dithiolane salts has been formed stereospecifically through the cyclization of *vic*-dithiocyanate derivatives of alkenes and unsaturated fatty acids. This cyclization has been accomplished using methanesulfonic acid as both coreactant and solvent. Methods of isolation of the product salts are briefly described.

Derivatives of 2-imino-1,3-dithiolane salts[3,4] demonstrate synthetic utility as intermediates in the preparation of pesticidally active compounds.[5–7] Although the heterocyclic structure was initially derived by cyclization of *vic*-dithiocyanates of ethane and propane by Miolati in 1891,[8] the method has received little attention since that time. Iminodithiolane derivative were subsequently prepared by reaction of *vic*-dithiols and cyanogen chloride[4–7] and by acid-catalyzed cyclization of allylic[6a,9] or β-hydroxyalkyl[10] esters of dithiocarbamic acid.

The alkyl substituted iminodithiolanes that had been prepared previously[4–10] were short-chain species of fewer than seven carbon atoms. Our efforts to obtain new long-chain aliphatic substituted compounds by incorporation of the heterocyclic structure into unsaturated fatty acids were precluded by difficulties encountered in the preparation of *vic*-dithiols[11] and by the indirect syntheses required for dithiocarbamate derivatives. As a result of our recent studies on the elucidation of olefin thiocyanations,[12] the *vic*-dithiocyanates that were readily obtainable presented the opportunity to study their chemistry as an essentially unexplored route to the titled compounds.

The 2-imino-1,3-dithiolane hydrochlorides (**2**) were first prepared by Miolati[8] from *vic*-dithiocyanates (**1**) in refluxing hydrochloric acid (eq 1). This technique required prolonged heating and resulted in diminished yields. Miolati[8] improved the yield of **2** by a method using the tin and hydrochloric acid



1 **2** (1)

$R = H; CH_3$