Thiocyanations: I. Elucidation of Olefin Thiocyanations: Product Distribution, Mechanism and a Rationale of Thiocyanogen Value

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ABSTRACT

Thiocyanogen adds to monoolefins (*cis*-9-octadecene, *trans*-9-octadecene and methyl oleate) in acetic acid solution to yield α,β-dithiocyanate, α-thiocyanato-β-isothiocyanate, α-thiocyanato-β-acetate and α-bromo-β-thiocyanate adducts. A trace amount of a substitution product indicated to be an allylic isothiocyanate was detected in the reaction products from the *trans*-9-octadecene and methyl oleate reactions. Formation of the mixed adducts does not affect the stoichiometry of thiocyanogen addition to monoolefins but is responsible for the nonquantitative formation of dithiocyanate adducts obtained in preparative work. A mechanism accounting for the products and stereochemistry is proposed. A clearer understanding of the reactions underlying determinations of the thiocyanogen value of polyolefins is provided on the basis of the available current evidences.

INTRODUCTION

The thiocyanogen value, which is generally used in conjunction with the iodine value, is a classical method for the estimation of unsaturation in fats and oils (1). In the years since Kaufmann's discovery of olefin thiocyanations and development of the thiocyanogen value (2-4), many workers have contributed to improvements in the method (5-12) but not to a clarification of the underlying reactions.

The utility of the thiocyanogen value is based on the apparent specificity of thiocyanogen and the stoichiometric difference shown by thiocyanogen and interhalogen (BrCl or BrI) additions to olefins. In this context, thiocyanogen adds nearly quantitatively to the double bond of oleic acid (or ester), to one of the two double bonds of linoleic acid and to two of the three double bonds of linolenic acid, whereas halogens add quantitatively and equivalently to the available double bonds in each compound. The analytical method is also empirical because of the dependency on concentration and excess of thiocyanogen, the time allowed for absorption and the temperature (10,12,13).

vic-Dithiocyanate adducts have been the only products reported for the thiocyanations (equation 1) (14-16). The empiricism of the thiocyanogen

$$R-CH=CH-R' + (SCN)_2 \rightarrow R-\underset{SCN}{CH}-\!\!-\underset{SCN}{CH}-R' \qquad [1]$$

value, the known ambident characteristics of thiocyanogen (17), and for monoolefins the disparity expressed between the quantitative absorption of thiocyanogen determined analytically and yields of dithiocyanate adducts (∿80%) obtained preparatively (15) have long indicated the need for a detailed reexamination of the products. A resolution of the fundamental problem has practical interest since the dithiocyanates may serve as intermediates in the preparation of thiiranes (14) or of 2-imino-1,3-dithiolanes (18), which have potential lubricant (19) and pesticidal (20) properties, respectively.

On the basis of these considerations, we undertook a detailed product separation of the adducts prepared from *cis*- and *trans*-9-octadecene and methyl oleate using the mild separation techniques of countercurrent distribution and silicic acid chromatography. At the time our study was complete, a related separations investigation was reported in a brief communication on the thiocyanation of aliphatic and aromatic olefins (21). The latter investigators did not include many details of the reaction and, more importantly, failed to provide substantiating evidence in support of the stereochemical structures assigned to the products.

EXPERIMENTAL PROCEDURES

Apparatus

A 200 cell Post Automatic instrument was used for countercurrent distribution (CCD). Glassware was dried at 120 C for a minimum of 1 hr before use in the thiocyanogen reactions. NMR spectra were recorded on a Jeolco C-60H high resolution NMR spectrometer.

Materials

Anhydrous acetic acid was obtained by refluxing glacial acetic acid with acetic anhydride (25:1 ratio) for 3 hr. Skellysolve B ("hexane-pentane" fraction, bp 69 C) was purified by distillation. Methyl oleate of 99% minimum purity was acquired from Applied Science Lab., Inc. *cis*- and *trans*-9-Octadecenes were prepared by published methods (22,23).

Lead thiocyanate was prepared by reaction of solutions of lead nitrate (3000 ml of 1 M) and ammonium thiocyanate (816 ml of 10 M) for 30 min. The mixture was cooled to 5 C, filtered, water-washed and sucked dry under a rubber dam. The product was recrystallized from boiling water, dried, finely ground and further dried over P_2O_5 in vacuo for several days prior to use (24).

Column Chromatography

Silicic acid (100 mesh) was used for silicic acid column chromatography (SACC) and silicic acid dry column chromatography (SADCC) (25). Difficulties were encountered in the normal use of SACC for separation of α,β-dithiocyanate adducts from isomeric α-thiocyanato-β-isothiocyanate adducts described in the subsequent procedures, because of partial decomposition of the isothiocyanate derivatives by prolonged contact on silicic acid columns. SADCC (25) involving short eluant-to-solid phase contact time served satisfactorily for the separations. For the latter procedure, a column is packed with dry silicic acid while vibrated by an air vibrator or tapped with a rubbter-tipped hammer. The neat mixture was added to the column and developed with chloroform or other designated solvent by capillary action that was terminated when the solvent reached the bottom of the column. The column was marked into zones, and each zone was separately scraped out and extracted with methylene chloride.

Reaction of *trans*-9-Octadecene

Addition of $(SCN)_2$ to trans-9-octadecene: Bromine

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TABLE I

Weight and Per Cent of Product Fractions from Counter Current Distribution

Product	9-Octadecene			Methyl oleate, %
	Peak fractions	cis, %	trans, %	
Olefin	A	2.3	2.7	2.3
Allylic derivative	A'		1.3	
α-Bromo-β-thiocyanate	B	4.2	2.0	7.5
α-Thiocyanato-β-isothiocyanate	C_1	13.3	8.4	11.6
α-Thiocyanato-β-acetate	C_2	8.8	8.1	10.7
α,β-Dithiocyanate	D	64.9	72.3	65.0
Residue fraction	E	2.9	1.6	2.3
Recovery		96.4	96.4	99.4
Initial charge		35.0 g	17.1 g	40.5 g

(8.23 g, 0.0515 mol) was added dropwise to a vigorously stirred suspension of finely ground lead thiocyanate (20.0 g, 0.0618 mol) and anhydrous acetic acid (150 ml/0.01 mol Br_2). After stirring for 3.5 hr, the suspension turned white indicating completion of thiocyanogen formation. *trans*-9-Octadecene (12.7 g, 0.0504 mol) was added and the suspension left overnight (16 hr) to ensure complete reaction. Stirring was automatically stopped by a timer after the first 8 hr. All additions to the light- and moisture-sensitive reaction were carried out in a flask wrapped in aluminum foil placed in a suitable plastic dry bag and maintained under a positive pressure of nitrogen. The following day the supernatant liquid as well as acetic acid washings of the precipitate were filtered through a Buchner funnel. The pale yellow filtrate was shaken with water to destroy excess thiocyanogen and the aqueous layer extracted with ethyl ether. The extract was washed with water, dried over anhydrous magnesium sulfate and concentrated to a thick, amber colored liquid. Traces of acetic acid were removed in vacuo from the stirred liquid over a dish of solid potassium hydroxide. The crude adduct slowly solidified on standing. Elemental analysis of the crude product indicated the presence of bromine as well as the expected C, H, S and N.

CCD of trans-9-octadecene-thiocyanogen adduct mixture: The apparatus was primed with mutually saturated Skellysolve B and acetonitrile in a 15-40 ml ratio, respectively. The thiocyanogen adduct of *trans*-9-octadecene (17.1 g) was added in equal amounts to the first three cells. Transfers (880) were collected in a fraction collector. The initial 200 transfers, which contained none of the sample, were discarded. A weight distribution curve of the evaporated transfers 201-880 appears in Figure 1 and the weights in Table I.

Analysis of the CCD Peaks

Peak A was unreacted oleinf in accordance with its IR spectrum. *Peak A'* was isolated and purified by SADCC using 5% methylene chloride in Skellysolve B. According to IR and elemental analyses, the compound is *trans*-9-octadecene or a positional isomer thereof, containing one isothiocyanate group presumably at the allylic position.

Analysis—calculated for $C_{19}H_{35}SN$: C, 73.71; H, 11.40; S, 10.36; N, 4.52. Found—C, 73.30; H, 11.42; insufficient sample available for S and N analysis.

IR showed very strong bands at 2100 and 968 cm^{-1} for the respective -NCS and *trans*-unsaturation groups.

Peak B was purified by silicic acid column chromatography (SACC) using 0.5% ethyl ether in Skellysolve B and identified by IR and elemental analyses as a bromothiocyanate adduct to *trans*-9-octadecene (*erythro*-9-bromo-10-thiocyanato-octadecane). The -SCN group was confirmed by a sharp peak at 2170 cm^{-1}.

Analysis—calculated for $C_{19}H_{36}SNBr$: C, 58.44; H, 9.29; S, 8.21; N, 3.59; Br, 20.47. Found—C, 58.68; H, 9.10; S, 8.07; N, 3.68; Br, 19.63.

The small amount of material remaining did not justify further purification for improving these analytical values.

Peak C was shown by thin layer chromatography (TLC) to be a mixture of two compounds of very similar polarities. IR analysis showed peaks for thiocyanate (2170 cm^{-1}), isothiocyanate (2100 cm^{-1}) and acetate (1750 cm^{-1}) groups. CCD recycling gave only partial separation of the compounds. Silicic acid dry column chromatography (SADCC) gave partial separation with chloroform as eluant. The less polar compound was further purified by SADCC using 1.5% ethyl ether-Skellysolve B and the more polar compound by SADCC with 5% ethyl ether-Skellysolve B. IR and elemental analyses indicated the less polar compound was a thiocyanate-isothiocyanate (C_1) adduct to *trans*-9-octadecene (*erythro*-9-thiocyanato-10-isothiocyanato-octadecane). A sharp peak at 2170 cm^{-1} adjacent to a broad peak at 2100 cm^{-1} represented thiocyanate and isothiocyanate groups, respectively.

Analysis—calculated for $C_{20}H_{36}S_2N_2$: C, 65.16; H, 9.84; S, 17.40; N, 7.60. Found—C, 64.96; H, 9.82; S, 17.07; N, 7.51.

The more polar compound was a thiocyanate-acetate adduct (C_2) to *trans*-9-octadecene. A sharp peak at 2170 cm^{-1} and a somewhat broader peak at 1750 cm^{-1} were due to thiocyanate and acetate absorptions, respectively.

Analysis—calculated for $C_{21}H_{37}O_2SN$: C, 68.24; H, 10.64; S, 8.67; N, 3.79. Found—C, 68.52; H, 10.81; S, 8.86; N, 3.92.

Peak D was eluted from a silicic acid column by 2% ethyl ether-Skellysolve B. The low melting solid was further purified by crystallization at -22 C in Skellysolve B at a 13 ml/g ratio. IR and elemental analyses proved the waxy solid to be a dithiocyanate adduct to *trans*-9-octadecene (*erythro*-9,10-dithiocyanato-octadecane). A very sharp deep peak at 2170 cm^{-1} confirmed the thiocyanate group. The dithiocyanate adduct recrystallized from hexane (mp 45.5-46.5 C).

Analysis—calculated for $C_{20}H_{36}S_2N_2$: C, 65.16; H, 9.84; S, 17.40; N, 7.60. Found—C, 65.01; H, 10.07; S, 17.22; N, 7.42.

Reaction of *cis*-9-Octadecene

Addition of $(SCN)_2$ to cis-9-octadecene: The addition of $(SCN)_2$ to *cis*-9-octadecene was performed in accordance with the following procedure.

CCD of cis-9-octadecene-thiocyanogen adduct mixture: The CCD separation of the reaction mixture from the *cis*-addition paralleled that of the *trans*- adduct mixture; the same peak designations will accordingly be used. The thiocyanogen adduct of *cis*-9-octadecene (35.0 g) was added in equal amounts to the first 10 cells. Transfers (977) were collected at the rate of one transfer per tube. Transfers up to 210 were discarded. A weight distribution curve of the evaporated transfers from 211 to 977 was derived similar to the distribution in Figure 1, and the weights appear in Table I.

Analysis of the CCD peaks: According to IR and elemental analyses, *peak A* was unreacted *cis*-9-octadecene.

Analysis–calculated for $C_{18}H_{36}$: C, 85.63; H, 14.37. Found–C, 85.27. H, 14.13.

CCD of the heart cut of *peak B* did not improve its purity. It was purified by SACC with Skellysolve B as eluant. IR and elemental analyses indicated it to be a bromothiocyanate adduct to *cis*-9-octadecene (*threo*-9-bromo-10-thiocyanato-octadecane). The -SCN functionality was confirmed by a sharp peak at 2170 cm^{-1}.

Analysis–calculated for $C_{19}H_{36}SNBr$: C, 58.44; H, 9.29; S, 8.21; N, 3.59; Br, 20.47. Found–C, 58.33; H, 9.49; S, 8.14; N, 3.46; Br, 20.28.

Thin layer chromatographic analysis of *peak C* obtained from CCD indicated the peak contained two compounds of very similar polarities. An attempt to resolve the compounds by CCD was unsuccessful, but SADCC gave a good separation. The compounds were further purified by SADCC using 1.5% ethyl ether in Skellysolve B as eluant for the less polar compound and 5% ethyl ether in Skellysolve B as eluant for the more polar compound. IR and elemental analyses indicated the less polar compound was a thiocyanate-isothiocyanate adduct (C_1) to *cis*-9-octadecene (*threo*-9-thiocyanato-10-isothiocyanato - octadecane). A sharp peak at 2170 cm^{-1} adjacent to a broad peak at 2100 cm^{-1} represented thiocyanate and isothiocyanate groups, respectively.

Analysis–calculated for $C_{20}H_{36}S_2N_2$: C, 65.16; H, 9.84; S, 17.40; N, 7.60. Found–C, 65.36; H, 9.95; S, 17.71; N, 7.37.

The more polar compound was an acetate-thiocyanate adduct (C_2) of *cis*-9-octadecene (*threo*-9-acetato-10-thiocyanato octadecane). A sharp peak at 2170 cm^{-1} and a somewhat wider one at 1750 cm^{-1} were due to the respective thiocyanate and acetate absorptions.

Analysis–calculated for $C_{21}H_{39}O_2SN$: C, 68.24; H, 10.64; S, 8.67; N, 3.79. Found–C, 68.31; H, 10.55; S. 8.95; N, 3.77.

Attempts to purify *peak D* by two recyclings through the CCD apparatus were unsuccessful for improvement of its purity. SADCC with 10% ethyl ether in Skellysolve B as eluant resulted in isolation of a yellow liquid that solidified on standing. The product was dissolved in Skellysolve B at a 15 ml/g ratio and a white crystalline solid recovered on refrigeration at -31 C (mp 40.6-40.9 C). IR and elemental analyses proved peak D to be a dithiocyanate adduct of *cis*-9-octadecene (*threo*-9,10-dithiocyanato octadecane). A very sharp, deep peak at 2170 cm^{-1} confirmed the thiocyanate group.

Analysis–calculated for $C_{20}H_{36}S_2N_2$: C, 65.16; H, 9.84; S, 17.40; N, 7.60. Found–C, 65.16; H, 9.93; S, 17.37; N, 7.66.

Reaction of Methyl Oleate

Addition of $(SCN)_2$ to methyl oleate: The reaction of $(SCN)_2$ to methyl oleate was conducted by the same procedure. Elemental analysis of the crude product indicated the presence of bromine as well as the expected elements.

CCD of methyl oleate-thiocyanogen adduct mixture: The CCD fraction collections of the highly polar methyl oleate adducts differ slightly from the procedure of the previous two experiments. The method is described in more detail below, but for clarification it is emphasized that the least polar materials were transferred through the instrument leaving a distribution of the more polar adducts in the cells. The most polar materials were located in the first 50 cells (peak E), the largest fraction in the next 50 cells (peak D) and the third fraction in the subsequent 50 cells (peak C). (Note: Designation of these fractions as peaks conveniently relates the methyl oleate adducts to the octadecene adducts listed in Table I.) Twenty milliliters of lower phase

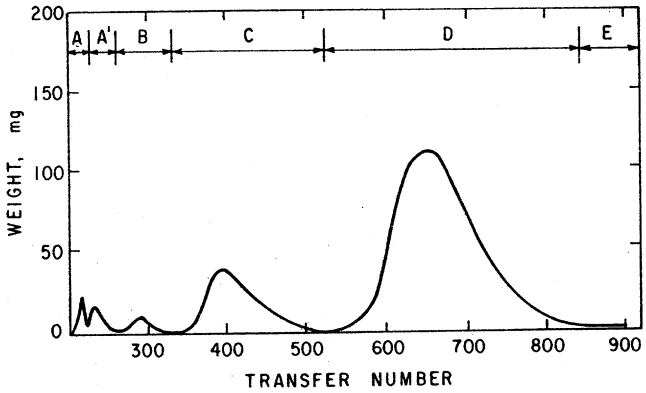


FIG. 1. Countercurrent distribution of thiocyanation products from *trans*-9-octadecene reaction (cosolvents: Skellysolve B and acetonitrile).

were removed from each of the first five cells. The methyl oleate adduct mixture (40.5 g) was diluted to 100 ml with this lower phase solvent and added equally to the first five cells. Transfers (totaling 1420) were collected at two transfers per collector tube. The first 190 transfers containing no material were discarded. The remaining 1230 transfers were selectively analyzed by IR and TLC and then combined into 20 groups ranging from 15 to 75 transfers per group.

Analysis of CCD data: IR, TLC and elemental analyses further indicated the first 10 groups (peak A) contained the least polar compounds that consisted of unreacted oleate and a very small amount of *trans*-unsaturated ester containing an acetate, isothiocyanate or bromide function in the chain beyond the double bond position. The last 10 groups (peak B) contained a bromothiocyanate adduct to methyl oleate (*threo*-9-[10]-bromo-10(9)-thiocyanato-methyl octadecanoate). This product was purified by SADCC using 20-25% ethyl ether in Skellysolve B as eluant and identified by IR and elemental analyses. The -SCN group was confirmed by a sharp peak at 2170 cm^{-1}.

Analysis–calculated for $C_{20}H_{36}O_2SNBr$: C, 55.29; H, 8.35; S, 7.38; N, 3.22; Br, 18.39. Found–C, 55.29; H, 8.49; S, 7.47; N, 3.27; Br, 18.32.

The contents of every fifth cell were evaporated and analyzed by IR and TLC to determine the extent of separation among the remaining solutes. The contents of the other cells were evaporated and a weight distribution curve analogous to that for olefin shown in Figure 1 was obtained. The weight distribution of all isolated compounds appears in Table I.

Peak C was shown by TLC to be a mixture of two compounds of very similar polarities. CCD failed to separate the mixture. The less polar compound was separated by SADCC with 30% Skellysolve B in methylene chloride. IR and elemental analyses indicated this compound to be the thiocyanate-isothiocyanate adduct (C_1) to methyl oleate (*threo*-9([10]-thiocyanato-10[9]-isothiocyanato methyl stearate). The presence of -SCN and -NCS groups was confirmed by their respective peaks at 2170 and 2100 cm^{-1}.

Analysis–calculated for $C_{21}H_{35}O_2S_2N_2$: C, 61.12; H, 8.79; S, 15.54; N, 6.79. Found–C, 60.95; H, 9.09; S, 15.59; N, 6.75.

The more polar compound was also separated by SADCC using 30% Skellysolve B in methylene chloride and purified by SADCC using 10% Skellysolve B in methylene chloride. IR and elemental analyses indicated this to be the thiocyanate-acetate adduct (C_2) to methyl oleate (*threo*-9[10]-acetato-10[9]-thiocyanato methyl stearate). The -SCN and CH_3COO-groups were confirmed by their respective peaks at 2170 and 1750 cm^{-1}.

Analysis–calculated for $C_{22}H_{39}O_4SN$: C, 63.88; H,

TABLE II

Selected NMR Data for Thiocyanated Adducts of *cis*- and *trans*-9-Octadecene and Methyl Oleate

Compound	Proton chemical shifts[a]			
	SCN, X; H_α, H_β		SCN, O, C–CH_3	–C–O–CH_3
Threo series from *cis*-9,10-octadecene	H_α	H_β	Acetoxyl methyl	Ester methyl
α,β-Dithiocyanate	3.60 *m*	3.60 *m*	—	—
α-Thiocyanato-β-isothiocyanate	3.24 *m*	4.02 *m*	—	—
α-Thiocyanato-β-acetate	3.20 *m*	5.17 *m*	2.17 *s*	
α-Thiocyanato-β-bromide	3.50 *m*	4.40 *m*	—	—
Erythro series from *trans*-9,10-octadecene				
α,β-Dithiocyanate	3.43 *m*	3.43 *m*	—	—
α-Thiocyanato-β-isothiocyanate	3.27 *m*	4.06 *m*	—	—
α-Thiocyanato-β-acetate	3.57 *m*	5.12 *m*	2.14 *s*	—
α-Thiocyanato-β-bromide	3.48 *m*	4.30 *m*	—	—
Threo series from methyl oleate[b]				
α,β-Dithiocyanate	3.60 *m*	3.60 *m*	—	3.73 *s*
α-Thiocyanato-β-isothiocyanate	3.25 *m*	4.00 *m*	—	3.69 *s*
α-Thiocyanato-β-acetate	3.20 *m*	5.19 *m*	2.11 *s*	3.64 *s*
α-Thiocyanato-β-bromide	3.48 *m*	4.25 *m*	—	3.61 *s*

[a] In ppm from internal TMS in $CDCl_3$.
[b] Equimolar mixture of 9(10),10(9)-disubstituted esters.

9.20; S, 7.75. Found—C, 63.95; H, 9.39; N, 3.32; S, 7.61.

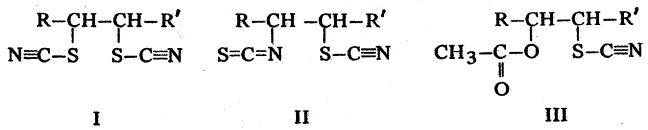
Peak D was purified by SADCC with 25% ethyl ether in Skellysolve B after a purification attempt by CCD failed. IR and elemental analyses confirmed the compound as the dithiocyanate adduct to methyl oleate (*threo*-9,10-dithiocyanato methyl octadecanoate). A sharp peak at 2170 cm^{-1} in the IR spectrum of D was due to -SCN.

Analysis—calculated for $C_{21}H_{36}O_2S_2N_2$: C, 61.12; H, 8.79; S, 15.54; N, 6.79. Found—C, 61.26; H, 9.18; S, 15.40; N, 6.74.

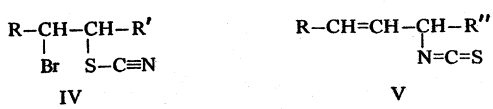
RESULTS AND DISCUSSION

Identification of Products

Thiocyanogen adds to olefins in acetic acid solution to yield a mixture of α,β-dithiocyanate (I), α-thiocyanato-β-isothiocyanate (II), α-thiocyanato-β-acetate (III) and α-bromo-β-thiocyanate (IV) adducts. A trace amount of a fifth product appearing to be an allylic isothiocyanate (V) was isolated from the *trans*-9-octadecene reaction mixture and was detected in the methyl oleate reaction mixture. A small quantity of thiocyanogen polymer was also isolated.



I II III

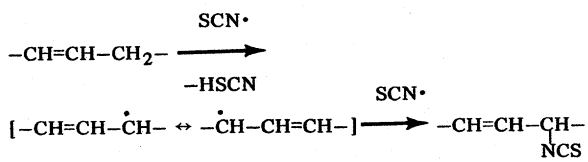


IV V

Guy et al. (21) in their independent study isolated similar adducts typified by structures I, II and III, but did not detect the α-bromo-β-thiocyanate adduct (IV) nor the allylic isothiocyanate derivative (V).

The relative amounts of products isolated in a complete material balance for each of the thiocyanated olefins are recorded in Table I. The α,β-dithiocyanate adduct is obtained as the major product and the α-thiocyanato-β-isothiocyanate adduct as the next significant product in a ratio of ca. 6:1. The α-thiocyanato-β-acetate adduct (∿9%) and α-bromo-βthiocyanate adduct (2-7%) together comprised 10-15% of the mixture's composition. These products were obtained from thiocyanations conducted in the presence of excess lead thiocyanate and of the lead bromide produced in the formation of thiocyanogen.

A fifth product isolated from the *trans*-9-octadecene reaction on further purification gave only a few milligrams of pure compound V. The small sample size limited elemental analysis to carbon and hydrogen determinations. The analyses together with the IR absorption for a *trans* double bond and isothiocyanate functionality suggested the presence of an allylic isothiocyanate, presumably a mixture of the positional isomers of 8-isothiocyanato-*trans*-9-octadecene. Similar IR absorptions on a less polar CCD fraction isolated from the methyl oleate reaction mixture were observed, but isolation of the allylic isothiocyanate was precluded by the small sample size. The minor quantities of allylic-substituted compounds apparently originate by the free radical mechanism (equation 2) proposed by Bacon et al. (26). They had isolated allylic isothiocyanates as



[2]

the predominant products from photoinitiated reactions of thiocyanogen on cyclohexene and 1-methylcyclohexene. They also demonstrated the resistance of acyclic olefins to photoinitiated α-thiocyanations by the near exclusive isolation of 1,2-dithiocyanatooctane from octene-1.

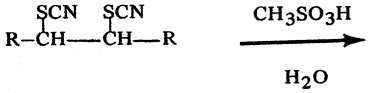
Stereochemistry and Mechanism

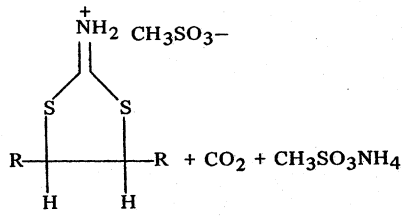
The stereochemical assignments of vic-dithiocyanates were initially designated by McGhie et al. (15) on the premise of a stereoselective addition of thiocyanogen analogous to halogen addition, e.g., the expectation of the *threo*-adduct from *cis*-olefin and *erythro*-adduct from *trans*-olefin. Although their analogy to halogen addition seems reasonable, stereoselective addition of halogen to olefins is not strictly obeyed as in the examples of bromine

addition to aromatic olefins (27). It is now evident that the stereochemistry of electrophilic addition depends upon the nature of the reagent, the structure of the olefin and the reaction conditions (28). Hence confidence in assignments designated for the thiocyanogen adducts clearly depends upon reliable determinations by more definitive structural methods.

The chemical shifts of the methine protons in the stereoisomeric pairs of adducts are listed in Table II. The signal of the thiocyanate methine proton (H_α) is observed at 3.2-3.6 ppm and the vicinal substituent methine proton (H_β) at 4.0-5.2 ppm, H_α and H_β being equivalent for dithiocyanate protons. Shift differences in H_α and H_β between corresponding *threo* and *erythro* adducts either are confined to a narrow range or appear indistinguishable within the limits of error. The stereochemical assignments of each pure isomeric dithiocyanate cannot be resolved directly, since the high degree of symmetry precludes evaluation of the respective vicinal coupling constants $J_{H_\alpha H_\beta}$. Guy et al. (21) have designated stereochemical structures for adducts prepared from several aliphatic olefins (*cis*- and *trans*-diisopropylethylenes, *trans*-Δ^2-octalin and cyclohexene) but not for unbranched acyclic internal olefins. Their assignments, however, must be considered tentative by their omissions of NMR data and discussion of the mode of analysis employed, which would be based on rotamer populations and average vicinal coupling constants.

In the course of this work we undertook and reported an independent, detailed NMR examination of the dithiocyanate structures from their cyclic *cis*- and *trans*-2-imino-1,3-dithiolane derivatives (R.J. Maxwell, P.E. Pfeffer, and L.S. Silbert, submitted for publication to J. Org. Chem.). Cyclization of the *erythro* and *threo* dithiocyanates was achieved with retention of the stereochemistry, since ring closure does not involve bond breaking at the asymmetric centers (equation 3).



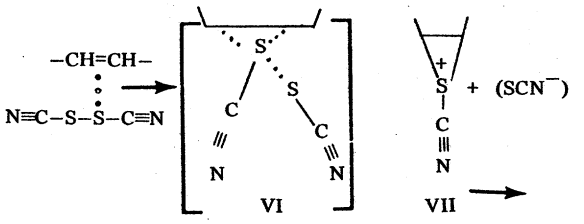


[3]

NMR configurational analysis of the *cis* and *trans* products thereby confirmed the stereochemistry of the corresponding *erythro* and *threo* dithiocyanate precursors.

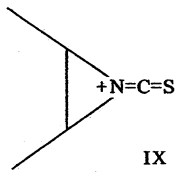
Our corresponding cyclization of α-thiocyanato-β-isothiocyanate adducts to the analogous *cis* and *trans* cyclic derivatives is currently under examination (G.G. Moore, R.J. Maxwell and L.S. Silbert, unpublished data.) and must be studied in more detail since the chemistry of the former mixed adducts has not previously been examined. The coupling constants for the unsymmetrical adducts were derived by a direct analysis of the adducts, although these determinations necessitate the incorporation of assumptions concerning the average rotamer populations. The stereochemical structures of the isomeric adducts were thus concluded to parallel those of dithiocyanates.

The NMR examination therefore supports McGhie's (15) conclusions of a *trans* addition of thiocyanogen to aliphatic olefins. The results are consistent with an intermediate that controls the stereochemistry of an electrophilic addition, such as the episulfonium ion VII (equation 4).



[4]

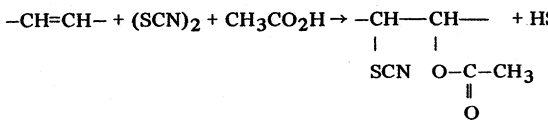
A representation of an episulfonium ion transition state, formerly proposed for the interaction of sulfur with π-electrons (29), gains strong support from the existence of stable episulfonium salts (30). The interaction of thiocyanogen with olefin may possibly proceed through a transition state VI to generate the reactive intermediate VII. Rearward attack of the intermediate VII by thiocyanogen, acid solvent and ions accounts for the observed products. The ambident characteristics of the thiocyanate moiety ($\overline{S}$–C≡N ↔ S=C=$\overline{N}$) (17) lead to formation of the isomeric vic-thiocyanato-isothiocyanate adduct. The absence of a diisothiocyanate adduct excludes from consideration an aziridinium ion transition state or intermediate IX as a competitive species.



IX

Critique on Thiocyanogen Value

In the officially prescribed procedure for the thiocyanogen value (1), the reagent is prepared in acetic acid-carbon tetrachloride solution and filtered free of insoluble lead salts. An analytical determination of the product distribution formed by this procedure with 3-hexene as the model olefin was readily obtained by gas liquid phase chromatography. The product mixture was comprised of 3,4-dithiocyanato (81.2%), 3-thiocyanato-4-isothiocyanato (15.4%), 3-thiocyanato-4-acetato (3.3%) and 3-bromo-4-thiocyanato (∿0.1%) hexanes, which together corresponded quantitatively and equivalently to the thiocyanogen absorbed. The stoichiometric balance between vic-thiocyanato-acetate adduct and thiocyanogen is maintained in accordance with equation 5. The removal of lead salts prior to thiocyanogen's addition to olefin accounts for the



[5]

insignificant formation of the bromothiocyanate adduct, compared to significant quantities (Table I) formed in the presence of lead bromide.

Corresponding determinations with polyolefins are rendered difficult by the increasing complexity of the mixture of polar products that may arise. A preliminary and incomplete CCD separation of thiocyanated methyl linoleate permitted partial separation of products in which addition occurred at one of the two double bonds, of products thiocyanated at both double bonds, and a small amount of impure compound believed (but not proven) to have a cyclic structure in the chain. Further examination of the complex mixture was terminated, in view of the need to extend the study to appropriate model diolefins from which the products would be more amenable to separation and identification. Nevertheless a rationale of the thiocyanogen value of linoleic and linolenic acids may be proposed from the available evidence on hand.

As an electrophilic reaction, olefin thiocyanation should be subject to the same factors influencing epoxidations; namely, the dependency of rate on the number and nature of substituents attached to or in the vicinity of the double bond (31). Several thiocyanation studies show this concordance on rates, e.g., internal double bond > terminal double bond, the latter requiring photoactivation (32); *cis* > *trans* (16,33); steric effects that decrease rates (16); and inertness of double bonds bearing electronegative substituents (21). The effects of the carboxyl group on rates of electrophilic additions to double bonds situated at different positions in the chain, which have been established for epoxidations, should be applicable to thiocyanations. Epoxidation studies show that the rate diminishes as the double bond position approaches the vicinity of the carboxyl group (34); that double bonds furthest removed from the carboxyl are most nearly preferentially epoxidized (35,36) but not differentiated beyond $\Delta^{9,10}$ (37); and that in linolenic acid one of the three double bonds (presumed to be $\Delta^{12,13}$) is least reactive because of steric effects of epoxy groups incorporated at two double bond sites (35).

On the basis of these evidences, thiocyanogen addition is evidently strongly affected by structural factors. Following the thiocyanation of one double bond in linoleic and linolenic acids, further thiocyanogen addition to the remaining double bonds declines dramatically (10,38). Evidently subsequent additions of thiocyanogen to double bonds that are adjacent to vicinal sulfur-containing substituents must be severely restricted by steric effects. In linolenic acid initial addition to the outside double bonds ($\Delta^{9,10}$ and $\Delta^{15,16}$) may prevent addition to the central $\Delta^{12,13}$, whereas statistical addition to the latter may limit additions to the flanking olefinic sites. Prolonged reaction times would tend to result in additional though incomplete thiocyanations. The polyolefinic acids would also be expected to undergo significantly more extensive allylic substitutions than oleic because of the reduced C-H bond energy of the skipped methylene protons, as indicated below for the relative reactivity and bond energies in oleic and linoleic acids (39). Hence the empiricism of the thiocyanogen value and the increasing complexity of products formed in preparative work

$$\underset{\substack{\uparrow \\ 1(\sim 80\ \text{Kcal/mol})}}{R-CH_2-CH=CH-R} \qquad \underset{\substack{\uparrow \\ 10\ (\sim 60\ \text{Kcal/mol})}}{R-CH=CH-CH_2CH=CH-R}$$

may be more clearly ascertained from these analyses and deliberations.

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