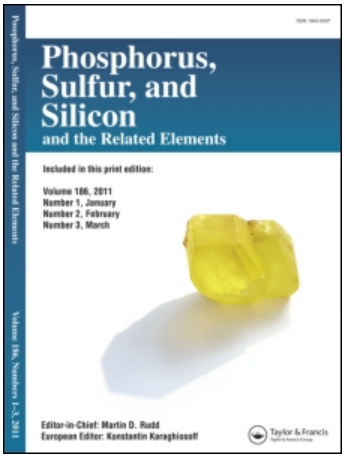

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PSEUDOHALOGEN CHEMISTRY. PART IV. HETEROLYTIC ADDITION OF THIOCYANOGEN TO ALKENES

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PSEUDOHALOGEN CHEMISTRY. PART IV.[1] HETEROLYTIC ADDITION OF THIOCYANOGEN TO ALKENES

by

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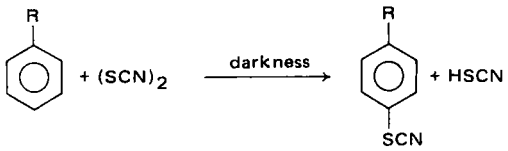
ABSTRACT

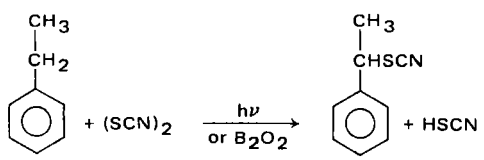
Thiocyanogen reacts slowly with alkenes, in the presence of a radical inhibitor in benzene or acetic acid in the dark at 25°, to yield α,β-dithiocyanates, α-isothiocyanates-β-thiocyanates and, in acetic acid, α-acetoxy-β-thiocyanates in varying proportions. The additions to alkyl alkenes are trans-stereospecific, and, in the case of the α-isothiocyanato-β-thiocyanates, non-regiospecific. The additions to aryl alkenes are trans-stereoselective and regiospecific, yielding the Markownikov-orientated α-isothiocyanato-β-thiocyanates. A heterolytic mechanism involving a two-step, kinetically controlled addition, with the formation of a cyano-sulfonium ion intermediate, *e.g.*, **35**, in the case of alkyl alkenes and an open carbonium ion, *e.g.*, **36**, in the case of aryl alkenes, is suggested. The diothiocyanate: isothiocyanato-thiocyanate ratios are discussed in terms of kinetic and steric control of reaction.

Thiocyanogen,[2] which has the structure N≡C–S–S–C≡N,[3] is the outstanding example of a pseudohalogen.[4] Like the halogens, it effects substitution of organic compounds under heterolytic and homolytic conditions. Under heterolytic conditions thiocyanogen behaves as a weak electrophile, giving nuclear thiocyanates with aromatic amines and phenols (Scheme I; R = NH_2, OH).[2]



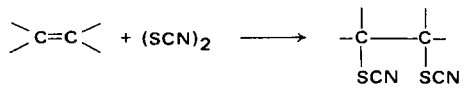
SCHEME I

Under homolytic conditions, thiocyanogen reacts with aralkyl hydrocarbons to give α-thiocyanates by a radical-chain reaction involving thiocyanato radicals as the hydrogen-abstraction agents (Scheme II).[5]



SCHEME II

Thiocyanogen further resembles the halogens in reacting with alkenes, cycloalkenes, dienes, and unsaturated alcohols, aldehydes, ketones, acids, esters,[2,6] and carbohydrates[7] giving addition products, which, on a very limited amount of chemical[8] and spectral[8b] evidence, are generally accepted to have the dithiocyanato structure shown in Scheme III.



SCHEME III

In early investigations, this reaction was examined solely from a preparative[2] or an analytical[9] point of view. More recently, the rate of addition to various alkenes has been investigated,[6] and addition to cyclooctane[8b,c] and to unsaturated acids[10] has been interpreted on chemical grounds as being trans-stereospecific. However, since none of these reactions was carried out under strictly controlled conditions, firm conclusions cannot be drawn about the mechanism(s), although the observation[8a] that some reactions proceed in the dark while others occur only under the influence of ultra-violet light suggests that more than one mechanism is involved. We have now investigated the reaction of thiocyanogen with alkenes under both heterolytic and homolytic conditions. Here we describe the reac-

tion of thiocyanogen with a variety of alkenes under conditions previously shown to be favourable to heterolytic fission of the related thiocyanogen chloride, ClSCN, *i.e.*, anhydrous solvents, darkness, room temperature, and added radical inhibitor.[11]

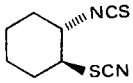
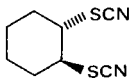
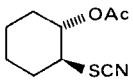
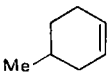
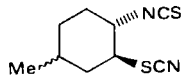
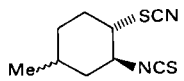
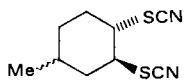
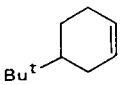
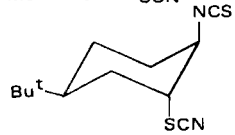
Results

Under these conditions, reactions in benzene were generally slow, varying from several hours to several days in length. In the latter case, polymerization of the reagent[2] was considerable, and yields were consequently low. Reactions in acetic acid were faster, produced less polymeric thiocyanogen, and gave higher yields. The data are presented in the Table.

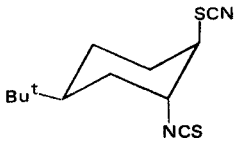
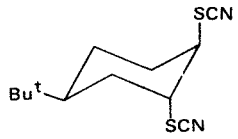
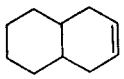
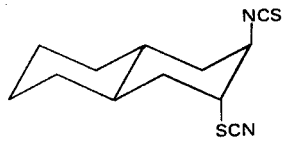
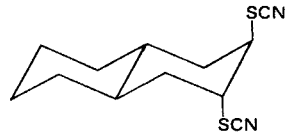
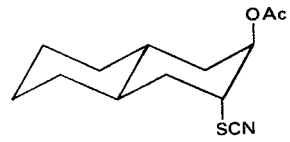
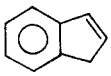
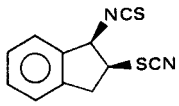
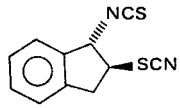
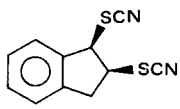
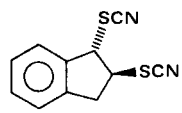
Examination of each reaction product by tlc showed the presence of two or more components in unequal amounts. Constitutionally different products of the reactions were readily separated by column chromatography on silica gel, but positional and stereo-isomers were not completely resolved, as indicated by further tlc and by ir and ^{1}H-nmr spectroscopy. Structural assignments were made as before[1,12] by ir and ^{1}H-nmr

TABLE

Products from Addition of Thiocyanogen to Alkenes

Alkene	Solvent	Reaction time (hr)	Products		Yield (%)
$Me_2C{=}CMe_2$	C_6H_6	1	$Me_2C(NCS)C(SCN)Me_2$	**1**	60
			$Me_2C(SCN)C(SCN)Me_2$	**2**	30
$Me_2C{=}CHMe$	C_6H_6	5	$Me_2C(NCS)CH(SCN)Me$	**3**	25
			$Me_2C(SCN)CH(SCN)Me$	**4**	45
cis-$Pr^iCH{=}CHPr^i$	C_6H_6	168	*threo*-$Pr^iCH(NCS)CH(SCN)Pr^i$	**5**	30
			(±)-$Pr^iCH(SCN)CH(SCN)Pr^i$	**6**	15
trans-$Pr^iCH{=}CHPr^i$	C_6H_6	168	*erythro*-$Pr^iCH(NCS)CH(SCN)Pr^i$	**7**	18
			meso-$Pr^iCH(SCN)CH(SCN)Pr^i$	**8**	12
$BuCH{=}CH_2$	C_6H_6	168	$BuCH(NCS)CH_2SCN$	**9**	27
			$BuCH(SCN)CH_2NCS$	**10**	
			$BuCH(SCN)CH_2SCN$	**11**	42
	C_6H_6	96		**12**	9
				**13**	18
	AcOH	1.5	**12**		14
			13		33
				**14**	15
	C_6H_6	144		**15**	6
				**16**	6
				**17**	26
	C_6H_6	168		**18**	6

TABLE—*continued*

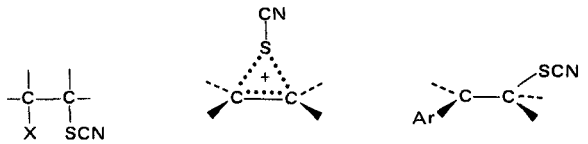
Alkene	Solvent	Reaction time (hr)	Products		Yield (%)
				**19**	6
				**20**	30
	C_6H_6	168		**21**	5
				**22**	10
	AcOH	5	**21**		18
			22		40
				**23**	21
PhCH=CH_2	C_6H_6	24	PhCH(NCS)CH_2SCN	**24**	22
			PhCH(SCN)CH_2SCN	**25**	44
trans-PhCH=CHMe	C_6H_6	168	*threo*-PhCH(NCS)CH(SCN)Me	**26**	2
			erythro-PhCH(NCS)CH(SCN)Me	**27**	10
			threo-PhCH(SCN)CH(SCN)Me	**28**	2
			erythro-PhCH(SCN)CH(SCN)Me	**29**	6
	C_6H_6	72		**30**	22
				**31**	14
				**32**	15
				**33**	45

spectroscopy, using the characteristic ir absorption bands of thiocyanates and isothiocyanates to determine the nature of the products, and the chemical shifts, splitting patterns, and line-widths of the proton signals of the CH(SCN), CH(NCS), and CH(OAc) groups to establish the configurations of the products and the orientation of addition; isomer ratios were determined from the integral traces of appropriate absorption bands in the ^{1}H-nmr spectra of the mixtures (see Experimental Section for details). The data are presented in the Table.

Control experiments showed that the products were stable under the conditions used in the reactions. No reaction occurred with alkenes of the types $RCH{=}CH_2$ (R = Cl, CO_2H, CO_2Me, CN) and *cis*- and *trans*-RCH=CHR (R = Cl, CO_2H, CO_2Me, Ph), or with 1,1-dichloroethylene, trichloroethylene and tetrachloroethylene during 7 days. No isomerization of the alkenes was observed.

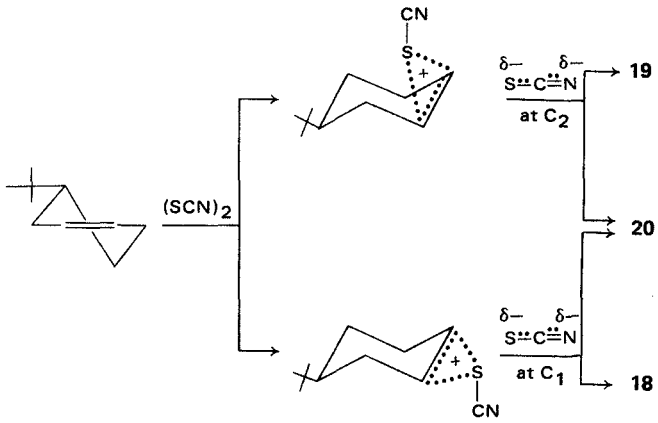
Discussion

These data show that, under the conditions used, the reaction of thiocyanogen with alkenes exhibits the following characteristics: (a) reaction is facilitated by electron-donating groups on the C=C bond and is presented by similarly situated electron-withdrawing groups; (b) the products of the reaction are $\alpha\beta$-dithiocyanates (**34**, X = SCN), α-isothiocyanato-β-thiocyanates (**34**, X = NCS), and, in acetic acid solvent, α-acetoxy-β-thiocyanates (**34**, X = OAc) (see products **1–33** in the Table); (c) these are primary products; (d) the addition is *trans*-stereospecific for aliphatic alkenes (see products **5–8** and **12–23** in the Table) but *trans*-stereoselective for aryl alkenes (see products **26–33** in the Table); (e) the addition is regiospecific for aryl alkenes, yielding the Markownikov-orientated isothiocyanatothiocyanates exclusively, (see products **24**, **26**, **27**, **30**, and **31** in the Table) but non-regiospecific for aliphatic alkenes (see products **9**, **10**, **15**, **16**, **18**, and **19** in the Table.



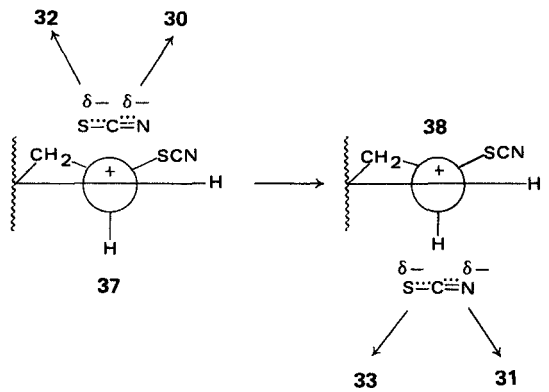
34 **35** **36**

These results are readily accounted for by two carbonium ion mechanisms analogous to those proposed for the corresponding reactions of thiocyanogen chloride with alkenes.[1,12] For aliphatic alkenes, a two-step, kinetically controlled heterolytic addition involving (a) initial electrophilic attack on the alkene by the electron-deficient sulfur atom of the thiocyanogen molecule with the formation of a cyano-sulfonium ion, *e.g.*, **35**,[12a] and (b) subsequent *trans*-diaxial opening of the sulfonium ring at either of the ring atoms by the ambident thiocyanato anion, $\bar{S}{-}C{\equiv}N \leftrightarrow S{=}C{=}\bar{N}$ or by solvent molecules in acetic acid, accounts for the observed *trans*-stereospecificity and non-regiospecificity of these and other[8b,c,10] reactions. This is illustrated with 4-t-butylcyclohexene in Scheme IV.



SCHEME IV

For the aryl alkenes, a similar mechanism, but with the formation of the more stable of the two possible open thiocyanato-carbonium ions, *e.g.*, **36**, (due to the stabilizing effect of the adjacent +M group),[12b] accounts for the observed non-stereospecificity and regiospecificity of these and other[7] reactions. The observed preference for *trans*-addition is again ascribed to steric control of reaction by the bulky thiocyanato group of the carbonium ion. Thus, for indene, the initially formed ion-pair **37** and its isomer **38**, formed by thiocyanato-anion migration, and the various reaction pathways are shown in Scheme V. The sterically favored pathways, outlined in the lower half of the Scheme, lead to the observed *trans*-adducts.



SCHEME V

The dithiocyanate : isothiocyanato-thiocyanate ratio also appears to be sterically controlled. Thus, sterically unhindered alkenes give the dithiocyanate preferentially, whereas sterically hindered alkenes, *e.g.*, $Me_2C{=}CMe_2$, $Pr^iCH{=}CHPr^i$ and PhCH=CHMe, give the isothiocyanato-thiocyanate preferentially (see Table). This is consistent with kinetically controlled attack by the sulfur atom of the thiocyanato anion (the sulfur atom carries 70% of the negative charge)[13] on sterically unhindered carbonium ion intermediates and with sterically controlled attack by the nitrogen atom of the thiocyanato anion (the van der Waals radii of the sulfur and nitrogen atoms are 1.85 Å and 1.40 Å, respectively)[14] on sterically hindered intermediates. A similar explanation, but with steric control being exerted by the thiocyanato group of the open carbonium ion (see Scheme V) accounts for the marked differences in the dithiocyanate isothiocyanato-thiocyanate ratio observed for the *cis*- and *trans*-products of indene.

2-Methylbut-2-ene resembles the α-aryl alkenes rather than the aliphatic alkenes in giving the Markownikov-orientated isothiocyanato-thiocyanate **3** exclusively. This suggests that it reacts via an open carbonium ion rather than a cyano-sulphonium ion, due to the second methyl group conferring stability comparable to that of a single aryl group (*cf.*, the exclusive Markownikov-orientated addition of thiocyanogen chloride to 2-ethylbut-1-ene[1] and of iodine isocyanate to 2-methylpropene[15]).

The relative rates of addition of thiocyanogen to the alkenes investigated, and in the solvents used, show a dependence on carbonium ion stability and solvating power of the solvent similar to that of the corresponding additions of thiocyanogen chloride.[1,12] Thiocyanogen, however, is considerably less reactive than thiocyanogen chloride in these addition reactions; this difference in reactivity, also noted in aromatic substitution reactions, is consistent with the greater electrophilic character of thiocyanogen chloride, which is polarized in the manner $\overset{\delta-}{Cl}{-}\overset{\delta+}{SCN}$[16].

Experimental Section

Alkenes

4-*t*-Butylcyclohexene and *trans*-Δ^2-octalin were prepared as described in earlier papers.[1,12a] The other alkenes used were commercial samples purified until their physical constants agree with those recorded in the literature.

General Procedure

Bromine (2 ml) was added to a suspension of lead thiocyanate (13.2 g., 10% excess) in the anhydrous solvent (175 ml). The suspension was stirred until the color of bromine had been replaced by the pale yellow color of thiocyanogen. When the lead salts had settled 150 ml of the solution (~0.2 M) was pipetted into a dry, opaque flask, and analysed by addition of aliquot parts (5 ml) to 10% methanolic potassium iodide (25 ml; ~200% excess), followed by iodometric titration with 0.1 *N*-thiosulphate.[2]

2,6-Di-*t*-butyl-*p*-cresol (0.1 g) was added as a radical inhibitor, and the peroxide-free alkene (1 mol) was added in the solvent (10 ml) to the reagent (1 mol) held in a thermostat bath at 25°. The disappearance of thiocyanogen was followed by iodometric titration of aliquot parts of the reaction solution. Reactions were allowed to proceed until all the reagent had been consumed. When acetic acid was used as solvent, the reaction solution was filtered to remove any polymeric thiocyanogen, and the product was isolated by dilution of the solution with ice-cold water (1 l) followed by extraction with an organic solvent, washing with water to remove acetic acid, drying ($MgSO_4$), and removal of solvent under reduced pressure. When benzene was used as solvent, the solution was filtered, and the solvent and unreacted alkene (if sufficiently volatile) were removed under reduced pressure. Allowance was made for material removed during titration in the calculation of yields.

The product was examined by tlc using 20 x 10 cm glass plates spread with silica gel (250 μm thick). After development with benzene, the plates were dried at 40° and the spots located with iodine vapor or with fluorescein spray. Quantitative separation of the components was achieved by chromatography of aliquot parts (4–7 g) on columns of silica gel (B.D.H. Laboratory Reagent, 60–120 mesh; 150 g), the purity of the eluted fractions (each 100 ml) being monitored by refractive index measurements and by ir spectroscopy. Typically, elution with benzene–light petroleum (bp 60–80°) (1 : 1) gave unreacted alkene in fractions 1 and 2, and the α-isothiocyanato-β-thiocyanate in fractions 5–15; elution with benzene gave the α,β-dithiocyanate in fractions 20–30; and elution with benzene/ether or benzene/chloroform (1 : 1) gave the α-acetoxy-β-thiocyanate in fraction 35–45.

It should be noted that most of these products were malodorous, vesicant, and dermatitic; consequently, in a few virulent cases, full details of physical constants are not available, and the analytical data are for products purified by chromatography only

2,3-Dimethylbut-2-ene

2,3-Dimethylbut-2-ene gave (a) 2-isothiocyanato-3-thiocyanato-2,3-dimethylbutane (**1**) as colorless prisms; mp 30–31° (from benzene–light petroleum); ν 2150 (SCN) and 2070 (NCS) cm^{-1}; τ ($CDCl_3$) 8.37 (6H, s, $C(CH_3)_2$(NCS), 8.41 (6H, s, $C(CH_3)_2$SCN).

Anal. Calc. for $C_8H_{12}N_2S_2$: C, 48.0; H, 6.0; N, 14.0. Found: C, 48.2; H, 6.0; N, 14.1.

(b) 2,3-Dimethyl-2,3-dithiocyanatobutane (**2**) as colorless prisms; mp 56–57° (from benzene-light petroleum); ν 2150 (SCN) cm^{-1}; τ ($CDCl_3$) 8.25 (δ, $C(CH_3)_2$SCN).

Anal. Found: C, 47.8; H, 6.1; N, 13.7.

2-Methylbut-2-ene

2-Methylbut-2-ene gave (a) 2-isothiocyanato-3-thiocyanato-2-methylbutane (**3**) as a pale yellow liquid; ν 2165 (SCN) and

2070 (NCS) cm^{-1}; τ ($CDCl_3$) 6.04 (1H, q, J 7Hz, C*H* SCN), 8.51 (3H, d, J 7Hz, CH_3C SCN), and 8.77 (6H, δ, $(CH_3)_2$CNCS).

Anal. Calc. for $C_7H_{10}N_2S_2$: C, 45.2; H, 5.4; N, 15.05. Found: C, 45.6; H, 5.6; N, 14.7.

(b) 2,3-Dithiocyanato-2-methylbutane (4) as a pale yellow liquid; ν 2170 (SCN) cm^{-1}; τ ($CDCl_3$) 6.37 (1H, q, J 7Hz, C*H*SCN), 8.25 (6H, δ, $(CH_3)_2$ CSCN), and 8.29 (3H, d, J 7Hz, CH_3CSCN).

Anal. Found: C, 45.8; H, 5.45; N, 15.1.

cis-2,5-Dimethylhex-3-ene

cis-2,5-Dimethylhex-3-ene gave (a) *threo*-2,5-dimethyl-3-isothiocyanato-4-thiocyanatohexane (5) as colorless prisms: mp 41–43° (from methanol); ν 2160 (SCN) and 2060 (NCS) cm^{-1}; τ ($CDCl_3$) 6.23 (1H, d of d, J 4.1 and 7.4 Hz, C*H* NCS), 6.83 (1H, d of d, J 4.1 and 7.0 Hz, C*H* SCN), 7.83 (2H, m, C*H* Me_2), 8.84 and 8.94 (12H, 2 overlapping d, $J \sim 8$ Hz, 2 non-identical $C(CH_3)_2$).

Anal. Calc. for $C_{10}H_{16}N_2S_2$: C, 52.6; H, 7.1; N, 12.25. Found: C, 52.4; H, 7.0; N, 12.5.

(b) (±)-2,5-Dimethyl-3,4-dithiocyanatohexane (6) as colorless prisms; mp 44–46° (from methanol), ν 2160 (SCN) cm^{-1}; τ ($CDCl_3$) 6.62 (2H, 6-line m, band-width 14 Hz, C*H* SCN), 7.85 (2H, m, C*H* Me_2),

Anal. Found: C, 52.7; H, 6.9; N, 12.0.

The *threo*-configuration of compound 5 follows from the size of the mutual splitting of the vicinal C*H* SCN and C*H* NCS proton signals (*cf.* the *erythro*- compound 7 below).[17] The (±)-configuration of compound 6 was established by comparison of the appearance of the C*H* SCN proton signal with that of the C*H* Br proton signal of (±)-2,5-dimethyl-3,4-dibromohexane, prepared as described below.

Under the standard heterolytic conditions used, *cis*-2,5-dimethylhex-3-ene reacted with an equimolar amount of bromine in chloroform giving (±)-2,5-dimethyl-3,4-dibromohexane as colorless prisms; mp 73.5–74.5° (from methanol); τ ($CDCl_3$) 6.12 (2H, 6-line m, bandwidth 13 Hz, C*H* Br), 7.87 (2H, m, C*H* Me_2), 8.90 and 8.96 (12H, 2 overlapping d, $J \sim 6.5$ Hz, 2 pairs of non-equivalent CH_3).

Anal. Calc. for $C_8H_{16}Br_2$: C, 35.3; H, 5.95; Br, 58.75. Found: 35.3; H, 6.1; Br, 58.9.

trans-2,5-Dimethylhex-3-ene

trans-2,5-Dimethylhex-3-ene gave (a) *erythro*-2,5-dimethyl-3-isothiocyanato-4-thiocyanatohexane (7) as colorless prisms; mp 154–156° (from methanol); ν 2160 (SCN) and 2070 (NCS) cm^{-1}; τ ($CDCl_3$) 6.15 (1H, d of d, J 9.5 and 3.5 Hz, C*H* NCS), 6.75 (1H, d of d, J 9.5 and 3.0 Hz, C*H* SCN), 7.55 (2H, m, C*H* Me_2), 8.60–9.10 (12H, 8-line m, 4 non-identical CH_3).

Anal. Calc. for $C_{10}H_{16}N_2S_2$: C, 52.6; H, 7.1; N, 12.25. Found: C, 52.3; H, 6.7; N, 12.0.

(b) *meso*-2,5-Dimethyl-3,4-dithiocyanatohexane (8) as colorless prisms; mp 153–156° (from methanol); ν 2160 (SCN) cm^{-1}; τ ($CDCl_3$) 6.60 (2H, 3-line m, band-width 3 Hz, C*H* SCN), 7.20 (2H, m, C*H* Me_2), 8.65–9.10 (12H, m, overlapping CH_3).

Anal. Found: C, 52.5; H, 6.9; N, 11.85.

The *erythro*-configuration of compound 7 follows from the size of the mutual splitting of the vicinal C*H* SCN and C*H* NCS proton signals (*cf.*, the *threo*-compound 5 above).[17] The *meso*-configuration of compound 8 was established by comparison of the appearance of the C*H* SCN proton signal with that of the C*H* Br proton signal of *meso*-2,5-dimethyl-3,4-dibromohexane, prepared as described below.

Under the standard heterolytic conditions used, *trans*-2,5-dimethylhex-3-ene reacted with an equimolar amount of bromine in chloroform giving *meso*-2,5-dimethyl-3,4-dibromohexane as colorless prisms, mp 52–53° (from methanol); τ ($CDCl_3$) 5.77 (2H, 3-line m, band-width 2 Hz, C*H* Br), 7.45 (2H, m, C*H* Me_2), 8.90 and 9.08 (12H, 2d, J 6.5 Hz, 2 pairs of non-equivalent CH_3).

Anal. Calc. for $C_8H_{16}Br_2$: C, 35.3; H, 5.95; Br, 58.75. Found: C, 34.75; H, 6.1; Br, 58.8.

Hex-1-ene

Hex-1-ene gave (a) a mixture of 2-isothiocyanato-1-thiocyanatohexane (9) and 1-isothiocyanato-2-thiocyanatohexane (10) as a yellow liquid; ν 2160 (SCN) and 2070 (NCS) cm^{-1}; τ (CCl_4) 5.50–6.96 (3H, m, overlapping C*H* SCN, C*H* NCS, CH_2SCN, CH_2NCS), 7.65–9.30 (9H, m, overlapping CH_2 and CH_3).

Anal. Calc. for $C_8H_{12}N_2S_2$: C, 48.0; H, 6.0; N, 14.0. Found: C, 48.5; H, 6.4; N, 13.4.

(b) 1,2-Dithiocyanatohexane (11) as a pale yellow liquid; bp 136–139°/23 mm Hg; ν 2160 (SCN); τ (CCl_4) 6.50–6.80 (3H, m, overlapping C*H* SCN and CH_2SCN), 7.65–9.35 (9H, m, overlapping CH_2 and CH_3).

Anal. Found: C, 47.9; H, 5.95: N, 14.0.

The presence of the two isothiocyanato-thiocyanates 9 and 10 was indicated by the complexity of the signal between τ 5.50 and τ 6.96; tlc indicated that the two components were present in the approximate ratio of 2 : 1.

The reaction also gave a small amount of an unsaturated isothiocyanate; ν 2080 (NCS) and 1645 (C=C) cm^{-1}; this was not investigated further due to its dermatitic nature.

Cyclohexene

Cyclohexene gave (a) *trans*-1-isothiocyanato-2-thiocyanatocyclohexane (12) as a colorless liquid; bp 130°/0.5 mm Hg; n_D^{22} 1.5800; ν 2165 (SCN) and 2070 (NCS) cm^{-1}; τ ($CDCl_3$) 6.25 (1H, t of d, J 9.5 and 4 Hz, C*H* NCS), 6.90(1H, t of d, J 9.5 and 4 Hz, C*H* SCN), and 7.35–8.90 (8H, m, CH_2).

Anal. Calc. for $C_8H_{10}N_2S_2$: C, 48.5; H, 5.1; N, 14.15; S, 32.3. Found: C, 48.75; H, 5.35; N, 13.8; S, 31.9).

(b) *trans*-1,3-Dithiocyanatocyclohexane (**13**) as colorless prisms; mp 57–58° (from benzene-light petroleum) (lit.,[18] mp 58–58.5°); ν 2160 (SCN) cm^{-1}; τ ($CDCl_3$) 6.80 (2H, m, band-width 23 Hz, C*H* SCN) and 7.15–9.00 (8H, m, CH_2).

(*Anal.* Found: S, 32.3).

In acetic acid solvent, cyclohexane gave, in addition to the above products, *trans*-1-acetoxy-2-thiocyanatocyclohexane (**14**) as a colorless liquid; bp 102–103°/0.2 mm Hg; n_D^{20} 1.4971; identical in physical properties with the compound prepared by the addition of thiocyanogen chloride to cyclohexene in acetic acid.[12a]

The configuration and conformation of compounds **12** and **13** follow from the splitting patterns and large band-widths of the C*H* SCN and C*H* NCS proton signals, which are those expected for compounds existing predominantly in the di-equatorial conformation.[19]

4-Methylcyclohexene

4-Methylcyclohexene gave (a) a mixture of *trans*-1-isothiocyanato-2-thiocyanato-4-methylcyclohexane (**15**) and *trans*-2-isothiocyanato-1-thiocyanato-4-methylcyclohexane (**16**) as a pale yellow liquid; bp 135–137°/0.4 mm Hg; ν 2160 (SCN) and 2070 (NCS) cm^{-1}; τ ($CDCl_3$) 6.05 (2H, m, band-width 24 Hz [31 Hz at 100 Hz], overlapping nonequivalent (C*H*NCS), 6.50 (2H, m, bandwidth 24 Hz [35 Hz at 100 MHz], overlapping non-equivalent C*H*SCN), and 7.68–9.60 [20H, m, remaining CH_3, CH_2 and C*H*).

Anal. Calc. for $C_9H_{12}N_2S_2$; C, 50.9; H, 5.7; N, 13.2. Found: C, 50.5; H, 5.5; N, 13.0.

(b) *trans*-1,2-Dithiocyanato-4-methylcyclohexane (**17**) as colorless prisms; mp 69–70° (from benzene-light petroleum); ν 2160 (SCN) cm^{-1}; τ ($CDCl_3$) 6.40 (2H, m, band-width 28 Hz [35 Hz at 100 MHz], overlapping non-equivalent C*H*SCN), and 7.50–9.10 (10H, m, remaining CH_3, CH_2 and C*H*).

Anal. Found: C, 50.6; H, 5.7; N, 13.2

The configuration and predominantly di-equatorial conformation of compounds **15** and **17** follow from the splitting patterns and large band-widths of the C*H*SCN and the C*H*NCS proton signals. The presence of the two positional isomers **15** and **16**, indicated by tlc, was confirmed by the increase in the peak width of the overlapping C*H*SCN and the overlapping C*H*NCS proton signals on increasing the field strength.[19] The isomer ratios were deduced from the symmetrical appearance of each of these signals.

4-t-Butylcyclohexene

4-*t*-Butylcyclohexene gave (a) a mixture of 1*ax*-isothiocyanato-2*ax*-thiocyanato-4*eq*-*t*-butylcyclohexane (**18**) and 2*ax*-isothiocyanato-1*ax*-thiocyanato-4*eq*-*t*-butylcyclohexane (**19**) as a pale yellow liquid; ν 2160 (SCN) and 2070 (NCS) cm^{-1}; τ ($CDCl_3$) 5.80 (1H, distorted q, *J* 3 Hz, C*H*NCS), 6.0 (2H, m, band-width 9 Hz [14 Hz at 100 MHz], overlapping C*H*NCS and C*H*SCN), 6.2 (1H, distorted q, *J* 3 Hz, C*H*SCN), and 7.65–9.50 (16H, m, remaining CH_3, CH_2 and C*H*).

Anal. Calc. for $C_{12}H_{18}N_2S_2$: C, 56.7; H, 7.15; N, 11.0; S, 25.15. Found: C, 56.9; H, 7.4; N, 10.7; S, 24.8.

(b) 1*ax*,2*ax*-Dithiocyanato-4*eq*-*t*-butylcyclohexane (**20**) as a pale yellow liquid; bp 138°/0.05 mm Hg; n_D^{20} 1.5388; ν 2160 (SCN) cm^{-1}; τ ($CDCl_3$) 5.90 (2H, m, band-width 17 Hz, overlapping nonequivalent C*H*SCN [at 100 MHz this is resolved into two eight-line signals at τ 5.82 and 5.95, each 1H and a band-width 10 Hz]), and 7.25–9.40 (16H, m, remaining CH_3, CH_2 and C*H*).

Anal. Found: C, 56.4; H, 7.2; N, 11.25; S, 25.6.

The diaxial configuration of compounds **18–20** follow from the splitting patterns and small band-widths of the non-equivalent C*H*SCN and the non-equivalent C*H*NCS proton signals.[19] The ratio of the two positional isomers **18** and **19** was determined from the integral trace of these signals.

trans-Δ^2-Octalin

trans-Δ^2-Octalin gave (a) 2*ax*-isothiocyanato-3*ax*-thiocyanato-*trans*-decalin (**21**) as a colorless liquid which decomposed on attempted distillation under reduced pressure, ν 2160 (SCN) and 2070 (NCS) cm^{-1}; τ ($CDCl_3$) 5.83 (1H, distorted q, *J* 3 Hz, C*H*NCS), 6.10 (1H, distorted q, *J* 3 Hz, C*H*SCN), and 7.80–9.35 (14H, m, remaining CH_2 and C*H*).

Anal. Calc. for $C_{12}H_{16}N_2S_2$: C, 57.15; H, 6.4; N, 11.1; S, 25.35. Found: C, 57.5; H, 6.9; N, 10.6.

(b) 2*ax*,3*ax*-Dithiocyanato-*trans*-decalin (**22**) as colorless prisms; mp 102–104° (from methanol); ν 2150 (SCN) cm^{-1}; τ ($CDCl_3$) 5.90 (2H, distorted q, *J* 2.5 Hz, C*H*SCN) and 7.80–9.20 (14H, m, remaining CH_2 and C*H*).

Anal. Found: C, 56.9; H, 6.3; N, 11.2; S, 25.55.

In acetic acid solvent, *trans*-Δ^2-octalin gave, in addition to the above products, 2*ax*-acetoxy-3*ax*-thiocyanato-*trans*-decalin (**23**) as colorless needles; mp 107–108° (from methanol); identical in physical and spectral properties with the compound prepared by the addition of thiocyanogen chloride to *trans*-Δ^2-octalin in acetic acid.[12a] The diaxial configuration of compounds **21** and **22** follows from the splitting patterns and small band-widths of the C*H*SCN and C*H*NCS proton signals.[19]

Styrene

Styrene gave (a) 1-isothiocyanato-2-thiocyanato-1-phenylethane (**24**) as a pale yellow liquid; bp 150–152°/0.4 mm Hg; ν 2155 (SCN) and 2070 (NCS) cm^{-1}; τ ($CDCl_3$) 2.60 (5H, s, ring *H*), 4.89 (1H, m, C*H*NCS), and 6.72 (2H, m, CH_2SCN).

Anal. Calc. for $C_{10}H_8N_2S_2$: C, 54.55; H, 4.0; N, 12.4. Found: C, 54.3; H, 4.0; N, 12.4.

(b) 1,2-Dithiocyanato-1-phenylethane (**25**) as colorless needles; mp 101–102° (from methanol) (lit.,[18] mp 102.5–103°); ν 2160 and 2165 (SCN) cm^{-1}; ($CDCl_3$) 2.60 (5H, s, ring *H*), 5.32 (1H, m, C*H*SCN), and 6.30 (2H, m, CH_2SCN).

Anal. Found: C, 54.4; H, 3.8.

trans-1-Phenylpropene

trans-1-Phenylpropene gave (a) a mixture of *threo*- and *erythro*-1-isothiocyanato-2-thiocyanato-1-phenylpropane [(**26**) and (**27**) respectively] as a viscous yellow oil; ν 2160 (SCN) and 2070 (NCS) cm^{-1}; τ (CCl_4) 2.59 (s, aromatic *H*), 4.86 (d, *J* 5.0 Hz, *threo*-PhC*H*NCS), 5.12 (d, *J* 7.5 Hz, *erythro*-PhC*H*NCS), 6.00–6.80 (m, *threo*- and *erythro*-MeC*H*SCN), 8.49 (d, *J* 6.5 Hz, CH_3), 8.53 (d, *J* 6.5 Hz, CH_3).

Anal. Calc. for $C_{11}H_{10}N_2S_2$: C, 56.4; H, 4.3; N, 11.95. Found: C, 56.8; H, 4.8; N, 11.5.

(b) A mixture of *threo*- and *erythro*-1,2-dithiocyanato-1-phenylpropane [(**28**) and (**29**) respectively] as a colorless solid; ν 2160 (SCN) cm^{-1}; τ ($CDCl_3$) 2.60 (s, aromatic *H*), 5.42 (d, *J* 8 Hz, *threo*-PhC*H*SCN), 5.54 (d, *J* 9.5 Hz, *erythro*-PhC*H*SCN), 5.90–6.50 (m, *threo*- and *erythro*-MeC*H*SCN), 8.15 (d, *J* 6.5 Hz, CH_3), 8.49 (d, *J* 6.5 Hz, CH_3).

Anal. Found: C, 56.45; H, 4.45; N, 11.95.

The configurations of compounds **26–29** were assigned on the basis of the relative sizes of the splittings of the PhNCS and PhC*H*SCN proton signals.[17] The isomer ratios for the mixtures were determined from the integral traces of these signals.

Indene

Indene gave (a) mixture of *cis*- and *trans*-1-isothiocyanato-2-thiocyanatoindane [(**30**) and (**31**) respectively] as a yellow oil; ν 2160 (SCN) and 2070 (NCS) cm^{-1}; τ ($CDCl_3$) 2.40–2.90 (m, aromatic *H*), 4.60 (d, *J* 6.5 Hz, *cis*-C*H*NCS), 4.76 (d, *J* 4 Hz, *trans*-C*H*NCS), 5.70–7.20 (m, overlapping *cis*- and *trans*-C*H*SCN and CH_2).

Anal. Calc. for $C_{11}H_8N_2S_2$; C, 56.9; H, 3.45; N, 12.05; S, 27.55. Found: C, 57.4; H, 3.55; N, 11.5.

(b) A mixture of *cis*- and *trans*-1,2-dithiocyanatoindane [(**32**) and (**33**) respectively] as a yellow oil; ν 2160 (SCN) cm^{-1}; τ ($CDCl_3$) 2.40–2.85 (m, aromatic *H*), 4.90 (d, *J* 7 Hz, *cis*-C_1HSCN), 5.10 (d, *J* 4 Hz, *trans*-C_1HSCN), 5.30–7.15 (m, overlapping *cis*- and *trans*-C_2HSCN and CH_2).

Anal. Found: C, 56.9; H, 3.7; N, 11.7.

On standing, the dithiocyanato mixture partially solidified; crystallization from methanol gave *trans*-1,2-dithiocyanatoindane (**33**) as colorless prisms; mp 57–58°; ν 2160 (SCN) cm^{-1}; τ ($CDCl_3$) 2.40–2.70 (4H, m, aromatic *H*), 5.10 (1H, d, *J* 4 Hz, *trans*-C_1HSCN), 5.80 (1H, d of t, *J* 4 and 7 Hz, *trans*-C_2HSCN), 6.21 (1H, d of d, *J* 7 and 17.5 Hz, H of CH_2 *cis* to C_2HSCN), 6.85 (1H, d of d, *J* 4 and 17.5 Hz, H of CH_2 *trans* to C_2HSCN).

Anal. Found: C, 56.5; H, 3.45; N, 12.2; S, 27.85.

The configurations of compounds **30–33** were determined from the characteristic splitting patterns of the C*H*SCN, C*H*NCS and CH_2 proton signals,[20] and the isomer ratios for the mixtures were determined from the integral traces of the low-field C_1HSCN and C_1HNCS proton signals.

Control Experiments

The following experiments carried out on the products derived from styrene and cyclohexene (see above) are typical.

1-Isothiocyanato-2-thiocyanato-1-phenylethane (**24**) (0.50 g) and 2,6-di-*t*-butyl-*p*-cresol (0.02 g) were dissolved in 0.2 *M* thiocyanogen solution in benzene (50 ml) and left at room temperature in darkness for 7 days. The solution was then treated in the usual way and gave starting material (0.48 g) as shown by the identity of ir spectra and tlc behavior. 1,2-Dithiocyanato-1-phenylethane (**25**) (0.50 g) was similarly treated, and gave starting material (0.48 g) as shown by the identity of ir spectra and tlc behavior.

Trans-1-isothiocyanato-2-thiocyanatocyclohexane (**12**) (0.50 g), potassium thiocyanate (0.25 g) and 2,6-di-*t*-butyl-*p*-cresol (0.02 g) were dissolved in 0.2 *M* thiocyanogen solution in acetic acid (50 ml), and left at room temperature in darkness for 1.5 h. The solution was then treated in the usual way, and gave starting material (0.48 g) as shown by the identity of ir spectra and tlc behaviour. *Trans*-1,2-Dithiocyanato-cyclohexane (**13**) and *trans*-1-acetoxy-2-thiocyanato-cyclohexane (**14**) were similarly treated in separate experiments; each gave starting material (0.48 g) exclusively, as shown by the identity of ir spectra and tlc behaviour.

Unreactive Alkenes

Non-volatile alkenes were recovered quantitatively from the reaction mixtures and identified by their ir spectra. Vinyl chloride, acrylonitrile, and *cis*- and *trans*-dichloro-ethylene were not recovered due to their loss by volatilization during the isolation procedure.

Spectra

Ir spectra were recorded with a Perkin-Elmer 237 spectrometer, and were taken for films of liquid products and for Nujol mulls of solid products. ^{1}H-nmr spectra were recorded with Varian A60A and HA100 spectrometers, using tetramethylsilane as internal standard. In the nmr data given above, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; bandwidths are separations of outer lines[19].

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