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PSEUDOHALOGEN CHEMISTRY—IV[1]

HETEROLYTIC ADDITION OF THIOCYANOGEN TO ALKENES

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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-isothiocyanato-β-thiocyanates and, in acetic acid, α-acetoxy-β-thiocyanates in various proportions. The additions to aliphatic alkenes are *trans*-stereospecific, and, in the case of the α-isothiocyanato-β-thiocyanates, non-regiospecific. The additions to α-arylalkenes 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-sulphonium ion intermediate, e.g. **35**, in the case of aliphatic alkenes and an open carbonium ion, e.g. **37**, in the case of α-arylalkenes, is suggested. The dithiocyanate: isothiocyanato-thiocyanate ratios are discussed in terms of kinetic and steric control of reaction.

Thiocyanogen, $(SCN)_2$, is the archetypal pseudohalogen.[2] Like the halogens, it effects substitution of organic compounds under both heterolytic and homolytic conditions.[3] Under heterolytic conditions, it behaves as a weak electrophile, giving nuclear thiocyanates with, e.g. aromatic amines and phenols; under homolytic conditions, it reacts with aralkyl hydrocarbons giving side-chain thiocyanates by a radical-chain reaction involving thiocyanato radicals.[4]

Thiocyanogen further resembles the halogens in reacting with alkenes in the dark or on exposure to sunlight, giving products which, for nearly 50 years, have been reported to be the corresponding α,β-dithiocyanates.[3] The reaction has also been developed into a quantitative analytical method for the determination of the degree of unsaturation in fats and oils.[5] Since no systematic study of experimental conditions, product isolation, structure determination, and the mechanism(s) of the reaction had been published, we undertook an investigation of this reaction under controlled heterolytic and homolytic conditions, and found it to be more complex than hitherto reported.[6] Here we describe the reaction of thiocyanogen with some alkenes under conditions previously shown to be favourable for heterolytic reaction of the related thiocyanogen chloride, ClSCN, with alkenes, i.e. anhydrous solvents, darkness, 25°, and added radical inhibitor.[1,7]

RESULTS

Under these conditions, reactions in benzene were generally slow, varying from several hours to several days in length. In the latter case, polymerisation of the reagent was considerable,[3] and yields were consequently low. Reactions in acetic acid were faster, produced less polymeric thiocyanogen, and gave higher yields. The data are presented in Table 1.

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 regioisomers and stereoisomers were not completely resolved, as indicated by further TLC and by IR and ^{1}H NMR spectroscopy. Structural assignments were made as before[1,7] by IR and ^{1}H NMR spectroscopy, using the characteristic 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 (Experimental). The data are presented in Table 1.

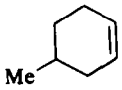
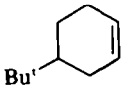
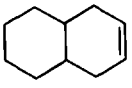
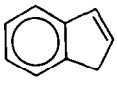
Control experiments showed that the products were stable under the conditions used in the reactions. No reaction occurred with alkenes of the types $RCH{=}CH_2$ (R = Cl, CO_2H, CO_2Me, CN) and *cis*- and *trans*-RCH=CHR (R = Cl, CO_2H, CO_2Me, Ph), or with 1,1-dichloroethylene, trichloroethylene and tetrachloroethylene during 7 days. No isomerisation 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 prevented by similarly situated electron-withdrawing groups; (b) the products of the reaction are α,β-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 Table 1); (c) these are primary products; (d) the addition is *trans*- stereospecific for aliphatic alkenes (see products **5–8** and **12–23** in Table 1) but *trans*- stereoselective for α-arylalkenes (see products **26–33** in Table 1); (e) the addition is regiospecific for α-arylalkenes, yielding Markownikov-orientated isothiocyanato- thiocyanates exclusively (see products **25**, **28**, **29**, **31** and **33** in the Table) but non-regiospecific for aliphatic alkenes (see products **10**, **11**, **16**, **17**, **19** and **20** in Table 1).

These results are readily accounted for by two carbonium ion mechanisms analogous to those proposed for the corresponding reactions of thiocyanogen chloride with alkenes.[1,7] For aliphatic alkenes, a two-step kinetically controlled heterolytic addition involving (a) initial electrophilic attack on the alkene by the electron-deficient sulphur atom of the thiocyanogen molecule with the formation of a cyano-sulphonium ion, e.g. **35**, and (b)

Table 1. Heterolytic addition of thiocyanogen to alkenes at 25°C

Alkene	Ratio[a]	Solvent	Time[b] (h)	Product	Yield (%)	k_S/k_N[c]
$Me_2C{=}CMe_2$	1:1	C_6H_6	1	**1**	30	0.50
				2	60	
$Me_2C{=}CHMe$	1:1	C_6H_6	5	**3**	45	1.80
				4	25	
cis-$Pr^iCH{=}CHPr^i$	1:3	C_6H_6	168	**5**	15	0.50
				7	30	
trans-$Pr^iCH{=}CHPr^i$	1:3	C_6H_6	168	**6**	12	0.66
				8	18	
$Bu^nCH{=}CH_2$	1:2	C_6H_6	168	**9**	42	1.55
				10	27[d]	
				11		
	5:1	C_6H_6	96	**12**	32	2.00
				13	16	
	5:1	AcOH	1	**12**	48	2.18
				13	22	
				14	24	
	2:1	C_6H_6	144	**15**	26	2.17
				16	6	
				17	6	
	2:1	C_6H_6	168	**18**	30	2.50
				19	6	
				20	6	
	1:1	C_6H_6	168	**21**	10	2.00
				22	5	
	1:1	AcOH	5	**21**	40	2.22
				22	18	
				23	21	
$PhCH{=}CH_2$	5:1	C_6H_6	29	**24**	44	2.00
				25	22	
trans-$PhCH{=}CHMe$	1:1	C_6H_6	168	**26**	2	1.00
				28	2	
				27	6	0.60
				29	10	
	4:1	C_6H_6	72	**30**	15	0.68
				31	22	
				32	45	3.22
				33	14	

[a]Alkene:thiocyanogen. [b]Time required for disappearance of thiocyanogen, or 1 week if shorter. [c]Relative nucleophilicity of S and N ends of the thiocyanato anion as derived from the dithiocyanate:isothiocyanato-thiocyanate product ratio; see text. [d]Combined yield of **10** and **11**; individual yields could not be determined from the ^1H NMR spectrum; see Experimental.

subsequent *trans*-diaxial opening of the sulphonium ring at either of the ring carbon atoms by the ambident thiocyanato anion, which has the hybrid structure and charge distribution shown in **36**,[8] or by solvent molecules in acetic acid, accounts for the observed *trans*- stereospecificity and non-regiospecificity of these and other reactions.†[9] This is illustrated with 4-t-butylcyclohexene in Scheme 1.

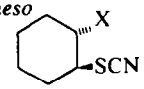
For the α-arylalkenes, a similar mechanism, but with the formation of the more stable of the two possible open thiocyanato-carbonium ions, e.g. **37**, due to the stabilising effect of the adjacent +M group, accounts for the observed non-stereospecificity and regiospecificity of these and other reactions.†[10] The observed preference for *trans*-addition is again ascribed to steric control of reaction by the bulky thiocyanato group of the carbonium ion.[1,7] Thus, for indene, the initially formed ion-pair **38** and its isomer **39**, formed by thiocyanato-anion migration, and the various reaction pathways are shown in Scheme 2.

†The other reactions were carried out in darkness or diffuse light, but in the *absence* of a radical inhibitor. Since our work[11] has shown that competing, or even dominant, homolytic reactions can occur under these conditions, the addition of a radical inhibitor is essential to guarantee the exclusive operation of the heterolytic mechanism.

$Me_2CXC(SCN)Me_2$
1: X = SCN
2: X = NCS

$Me_2CXCH(SCN)Me$
3: X = SCN
4: X = NCS

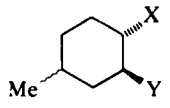
$Pr^iCH(SCN)CH(SCN)Pr^i$
5: (±)
6: *meso*

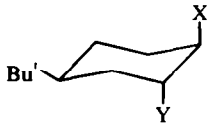


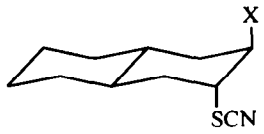
$Pr^iCH(NCS)CH(SCN)Pr^i$
7: *threo*
8: *erythro*

Bu^nCHXCH_2Y
9: X = Y = SCN
10: X = NCS, Y = SCN
11: X = SCN, Y = NCS

12: X = SCN
13: X = NCS
14: X = OAc







15: X = Y = SCN
16: X = NCS, Y = SCN
17: X = SCN, Y = NCS

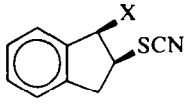
18: X = Y = SCN
19: X = NCS, Y = SCN
20: X = SCN, Y = NCS

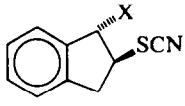
21: X = SCN
22: X = NCS
23: X = OAc

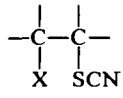
$PhCHXCH_2SCN$
24: X = SCN
25: X = NCS

$PhCH(SCN)CH(SCN)Me$
26: *threo*
27: *erythro*

$PhCH(NCS)CH(SCN)Me$
28: *threo*
29: *erythro*



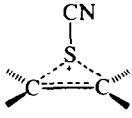




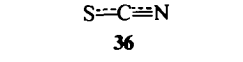
30: X = SCN
31: X = NCS

32: X = SCN
33: X = NCS

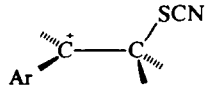
34



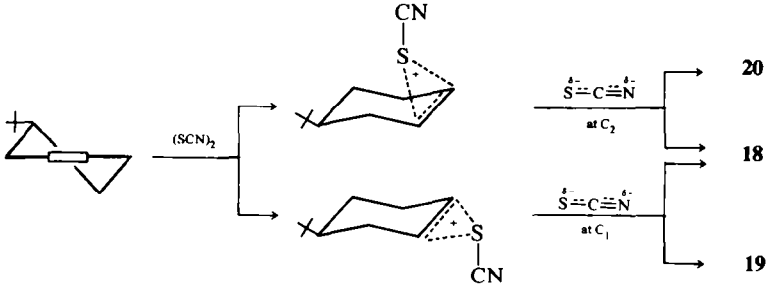
35



36



37

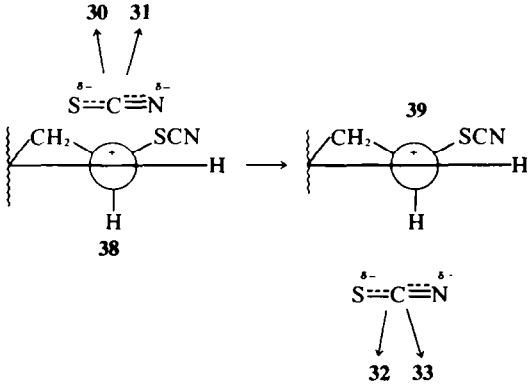


Scheme 1.

The sterically favoured pathways, outlined in the lower half of the Scheme, lead to the preferred *trans*-adducts.

2-Methylbut-2-ene resembles the α-arylalkenes rather than the aliphatic alkenes in giving the Markownikov-orientated isothiocyanato-thiocyanate **4** 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]

The relative nucleophilicity, k_S/k_N,[12] of the S and N ends of the thiocyanato anion **36**, as measured by the kinetically controlled dithiocyanate:isothiocyanato-thiocyanate product ratio, varies from 0.50 to 3.22 (see Table 1), and appears to be controlled by electronic and steric factors. Thus, sterically unhindered alkenes give the



Scheme 2.

dithiocyanate preferentially, whereas sterically hindered alkenes, e.g. $Me_2C{=}CMe_2$, *cis*- and *trans*- $Pr^iCH{=}CHPr^i$, and PhCH=CHMe, give the isothiocyanate preferentially (Table 1). This is consistent with charge-controlled attack by the S atom of **36** on sterically unhindered carbonium ion intermediates, and with sterically controlled attack by the N atom of **36** on sterically hindered intermediates.† A similar explanation, but with steric control being exerted by the thiocyanato group of the open carbonium ion (Scheme 2), accounts for the marked differences in the dithiocyanate:isothiocyanato-thiocyanate ratio observed for the *cis*- and *trans*- products of indene (Table 1). In other reactions of the thiocyanato anion with carbonium ions,[14] values of 1–9 have been reported for k_S/k_N, but have usually been interpreted in terms of the Principle of Hard and Soft Acids and Bases.[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.[1,7] Thiocyanogen, however, is considerably less reactive than thiocyanogen chloride in these addition reactions; this difference in reactivity, also noted in aromatic substitution reactions,[3] is consistent with the greater electrophilic character of thiocyanogen chloride, which is polarised in the manner $\overset{\delta-}{Cl}\text{–}\overset{\delta+}{SCN}$.[16]

EXPERIMENTAL

General procedure. Bromine (2 ml) was added to a suspension of lead thiocyanate (13.2 g, 10% excess) in the anhyd solvent (175 ml). The suspension was stirred until the colour of Br_2 had been replaced by the pale yellow colour of thiocyanogen. When the lead salts had settled, 150 ml of the soln (~0.2M) was pipetted into a dry, opaque flask, and analysed by addition of aliquot parts (5 ml) to 10% methanolic KI (25 ml; 200% excess), followed by iodometric titration with 0.1N thiosulphate.[2] 2,6-Di-t-butyl-*p*-cresol (0.1 g) was added as a radical inhibitor, and the peroxide-free alkene was added in the solvent (10 ml) to the reagent held at 25°. The disappearance of thiocyanogen was followed by iodometric titration. When AcOH was used as solvent, the reaction soln was filtered to remove any polymeric thiocyanogen, and the product was isolated by dilution of the soln with ice-cold water (1l) followed by extraction with ether, washing with water, drying ($MgSO_4$), and removal of solvent under reduced pressure. When benzene was used as solvent, the soln was filtered, and the solvent was removed under reduced pressure. The product was examined by TLC using 20 × 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 vapour 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 (b.p. 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 fractions 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) compound **2** as colourless prisms; m.p. 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, $C(CH_3)_2SCN$) (Found: C, 48.2; H, 6.0; N, 14.1. Calc. for $C_8H_{12}N_2S_2$: C, 48.0; H, 6.0; N, 14.0%), and (b) compound **1** as colourless prisms; m.p. 56–57° (from benzene–light petroleum); ν 2150 (SCN) cm^{-1}; τ ($CDCl_3$) 8.25 (δ, $C(CH_3)_2SCN$) (Found: C, 47.8; H, 6.1; N, 13.7).

2-*Methylbut*-2-*ene.* 2-Methylbut-2-ene gave (a) **4** as a pale yellow liquid; ν 2165 (SCN) and 2070 (NCS) cm^{-1}; τ ($CDCl_3$) 6.04 (1H, q, *J* 7 Hz, CHSCN), 8.51 (3H, d, *J* 7 Hz, CH_3CSCN), and 8.77 (6H, s, $(CH_3)_2CNCS$) (Found: C, 45.6; H, 5.6; N, 14.7. Calc. for $C_7H_{10}N_2S_2$: C, 45.2; H, 5.4; N, 15.05), and (b) **3** as a pale yellow liquid; ν 2170 (SCN) cm^{-1}; τ ($CDCl_3$) 6.37 (1H, q, *J* 7 Hz, CHSCN), 8.25 (6H, s, $(CH_3)_2CSCN$), and 8.29 (3H, d, *J* 7 Hz, CH_3CSCN) (Found: C, 45.8; H, 5.45; N, 15.1).

cis-2,5-*Dimethylhex*-3-*ene.* *cis*-2,5-Dimethylhex-3-ene gave (a) **7** as colourless prisms: m.p. 41–43° (from MeOH); ν 2160 (SCN) and 2060 (NCS) cm^{-1}; τ ($CDCl_3$) 6.23 (1H, d of d, *J* 4.1 and 7.4 Hz, CH NCS), 6.83 (1H, d of d, *J* 4.1 and 7.0 Hz, CH SCN), 7.83 (2H, m, $CH Me_2$), 8.84 and 8.94 (12H, 2 overlapping d, *J* ~ 8 Hz, 2 non-identical $C(CH_3)_2$) (Found: C, 52.4; H, 7.0; N, 12.5; Calc. for $C_{10}H_{16}N_2S_2$: C, 52.6; H, 7.1; N, 12.25%), and (b) **5** as colourless prisms; m.p. 44–46° (from MeOH), ν 2160 (SCN) cm^{-1}; τ ($CDCl_3$) 6.62 (2H, 6-line m, band-width 14 Hz, CH SCN), 7.85 (2H, m, CH Me_2), 8.82 (12H, d, *J* 7 Hz, $C(CH_3)_2$) (Found: C, 52.7; H, 6.9; N, 12.0).

The *threo*-configuration of compound **7** follows from the size of the mutual splitting of the vicinal CH SCN and CH NCS proton signals (cf *erythro*-**8** below).[17] The (±)-configuration of **5** was established by comparison of the appearance of the CH SCN proton signal with that of the CHBr 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 Br_2 in chloroform giving (±)-2,5-dimethyl-3,4-dibromohexane as colourless prisms; m.p. 73.5–74.5° (from MeOH); τ ($CDCl_3$) 6.12 (2H, 6-line m, band-width 13 Hz, CH Br), 7.87 (2H, m, CH Me_2), 8.90 and 8.96 (12H, 2 overlapping d, *J* ~ 6.5 Hz, 2 pairs of non-equivalent CH_3) (Found: C, 35.3; H, 6.1; Br, 58.9. Calc. for $C_8H_{16}Br_2$: C, 35.3; H, 5.95; Br, 58.75%).

trans-2,5-*Dimethylhex*-3-*ene.* *trans*-2,5-Dimethylhex-3-ene gave (a) **8** as colourless prisms; m.p. 154–156° (from MeOH); ν 2160 (SCN) and 2070 (NCS) cm^{-1}; τ ($CDCl_3$) 6.15 (1H, d of d, *J* 9.5 and 3.5 Hz, CH NCS), 6.75 (1H, d of d, *J* 9.5 and 3.0 Hz, CH SCN), 7.55 (2H, m, $CHMe_2$), 8.60–9.10 (12H, 8-line m, 4-non-identical CH_3) (Found: C, 52.3; H, 6.7; N, 12.0. Calc. for $C_{10}H_{16}N_2S_2$: C, 52.6; H, 7.1; N, 12.25%), and (b) **6** as colourless prisms; m.p. 153–156° (from MeOH); ν 2160 (SCN) cm^{-1}; τ ($CDCl_3$) 6.60 (2H, 3-line m, band-width 3 Hz, CH SCN), 7.20 (2H, m, CH Me_2), 8.65–9.10 (12H, m, overlapping CH_3) (Found: C, 52.5; H, 6.9; N, 11.85).

The *erythro*-configuration of **8** follows from the size of the mutual splitting of the vicinal CH SCN and CH NCS proton signals (cf. *threo*-**7** above).[17] The *meso*-configuration of **6** was established by comparison of the appearance of the CH SCN proton signal with that of the CH 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 Br_2 in chloroform giving *meso*-2,5-dimethyl-3,4-dibromohexane as colourless prisms, m.p. 52–53° (from MeOH); τ ($CDCl_3$) 5.77 (2H, 3-line m, band-width 2 Hz, CH Br), 7.45 (2H, m, CH Me_2), 8.90 and 9.08 (12H, 2d, *J* 6.5 Hz, 2 pairs of non-equivalent CH_3) (Found: C, 34.75; H, 6.1; Br, 58.8. Calc. for $C_8H_{16}Br_2$: C, 35.3; H, 5.95; Br, 58.75%).

Hex-1-*ene.* Hex-1-ene gave (a) a mixture of **10** and **11** as a yellow liquid; ν 2160 (SCN) and 2070 (NCS) cm^{-1}; τ (CCl_4) 5.50–6.96 (3H, m, overlapping CH SCN, CH NCS, CH_2SCN, CH_2NCS), 7.65–9.30 (9H, m, overlapping CH_2 and CH_3) (Found: C, 48.5; H, 6.4; N, 13.4. Calc. for $C_8H_{12}N_2S_2$: C, 48.0; H, 6.0; N, 14.0%), and (b) **9** as a pale yellow liquid; b.p. 136–139°/23 mm Hg; ν 2160 (SCN); τ (CCl_4) 6.50–6.80 (3H, m, overlapping CH SCN and CH_2SCN), 7.65–9.35 (9H, m, overlapping CH_2 and CH_3) (Found: C, 47.9; H, 5.95; N, 14.0). The presence of **10** and **11** was

†The van der Waals' radii of the sulphur and nitrogen atoms are 1.85Å and 1.40Å respectively.[13]

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.

Cyclohexane. Cyclohexene gave (a) **13** as a colourless liquid; b.p. 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, CH NCS), 6.90 (1H, t of d, *J* 9.5 and 4 Hz, CH SCN), and 7.35–8.90 (8H, m, CH_2) (Found: C, 48.75; H, 5.35; N, 13.8; S, 31.9. Calc. for $C_8H_{10}N_2S_2$: C, 48.5; H, 5.1; N, 14.15; S, 32.3%), and (b) **12** as colourless prisms; m.p. 57–58° (from benzene–light petroleum) (lit.,[18] m.p. 58–58.5°); ν 2160 (SCN) cm^{-1}; τ ($CDCl_3$) 6.80 (2H, m, band-width 23 Hz, CH SCN) and 7.15–9.00 (8H, m, CH_2) (Found: S, 32.3). In AcOH solvent, cyclohexene gave, in addition to the above products, **14** as a colourless liquid; b.p. 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 AcOH.[7]

The configuration and conformation of compouds **12** and **13** follow from the splitting patterns and large band-widths of the CH SCN and CH 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 **16** and **17** as a pale yellow liquid; b.p. 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 non-equivalent CHNCS), 6.50 (2H, m, bandwidth 24 Hz [35 Hz at 100 MHz], overlapping non-equivalent CHSCN), and 7.68–9.60 (20H, m, remaining CH_3, CH_2 and CH) (Found: C, 50.5; H, 5.5; N, 13.0. Calc. for $C_9H_{12}N_2S_2$: C, 50.9; H, 5.7; N, 13.2%), and (b) **15** as colourless prisms; m.p. 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 CHSCN), and 7.50–9.10 (10H, m, remaining CH_3, CH_2 and CH) (Found: C, 50.6; H, 5.7; N, 13.2).

The configuration and predominantly di-equatorial conformation of compounds **15–17** follow from the splitting patterns and large band-widths of the CHSCN and the CHNCS proton signals. The presence of the two positional isomers **16** and **17**, indicated by TLC, was confirmed by the increase in the peak width of the overlapping CHSCN and the overlapping CHNCS 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 **19** and **20** as a pale yellow liquid; ν 2160 (SCN) and 2070 (NCS) cm^{-1}; τ ($CDCl_3$) 5.80 (1H, distorted q, *J* 3 Hz, CHNCS), 6.0 (2H, m, band-width 9 Hz [14 Hz at 100 MHz], overlapping CHNCS and CHSCN), 6.2 (1H, distorted q, *J* 3 Hz, CHSCN), and 7.65–9.50 (16H, m, remaining CH_3, CH_2 and CH) (Found: C, 56.9; H, 7.4; N, 10.7; S, 24.8. Calc. for $C_{12}H_{18}N_2S_2$: C, 56.7; H, 7.15; N, 11.0; S, 25.15%), and (b) **18** as a pale yellow liquid; b.p. 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 non-equivalent CHSCN [at 100 MHz this is resolved into two eight-line signals at τ 5.82 and 5.95, each 1H and band-width 10 Hz]), and 7.25–9.40 (16H, m, remaining CH_3, CH_2 and CH) (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 CHSCN and the non-equivalent CHNCS proton signals.[19] The ratio of the two positional isomers **19** and **20** was determined from the integral trace of these signals.

trans-Δ^2-*Octalin. trans*-Δ^2-Octalin gave (a) **22** as a colourless 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, CHNCS), 6.10 (1H, distorted q, *J* 3 Hz, CHSCN), and 7.80–9.35 (14H, m, remaining CH_2 and CH) (Found: C, 57.5; H, 6.9; N, 10.6. Calc. for $C_{12}H_{16}N_2S_2$: C, 57.15; H, 6.4; N, 11.1; S, 25.35%), and (b) **21** as colourless prisms; m.p. 102–104° (from MeOH); ν 2150 (SCN) cm^{-1}; τ ($CDCl_3$) 5.90 (2H, distorted q, *J* 2.5 Hz, CHSCN) and 7.80–9.20 (14H, m, remaining CH_2 and CH) (Found: C, 56.9; H, 6.3; N, 11.2; S, 25.55). In AcOH solvent, *trans*-Δ^2-octalin gave, in addition to the above products, **23** as colourless needles; m.p. 107–108° (from MeOH); identical in physical and spectral properties with the compound prepared by the addition of thiocyanogen chloride to *trans*-Δ^2-octalin in AcOH.[7]

The axial configuration of compounds **21** and **22** follows from the splitting patterns and small band-widths of the CHSCN and CHNCS proton signals.[19]

Styrene. Styrene gave (a) **25** as a pale yellow liquid; b.p. 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, CHNCS) and 6.72 (2H, m, CH_2SCN) (Found: C, 54.3; H, 4.0; N, 12.4. Calc. for $C_{10}H_8N_2S_2$: C, 54.55; H, 4.0; N, 12.4%), and (b) **24** as colourless needles; m.p. 101–102° (from MeOH) (lit.,[18] m.p. 102.5–103°); ν 2160 and 2165 (SCN) cm^{-1}; τ ($CDCl_3$) 2.60 (5H, s, ring H), 5.32 (1H, m, CHSCN) and 6.30 (2H, m, CH_2SCN) (Found: C, 54.4; H, 3.8).

trans-1-*Phenylpropene. trans*-1-Phenylpropene gave (a) a mixture of **28** and **29** 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*-PhCHNCS), 5.12 (d, *J* 7.5 Hz, *erythro*- PhCHNCS), 6.00–6.80 (m, *threo*- and *erythro*-MeCHSCN), 8.49 (d, *J* 6.5 Hz, CH_3), 8.53 (d, *J* 6.5 Hz, CH_3) (Found: C, 56.8; H, 4.8; N, 11.5. Calc. for $C_{11}H_{10}N_2S_2$: C, 56.4; H, 4.3; N, 11.95%), and (b) a mixture of **26** and **27** as a colourless solid; ν 2160 (SCN) cm^{-1}; τ ($CDCl_3$) 2.60 (s, aromatic H), 5.42 (d, *J* 8 Hz, *threo*-PhCHSCN), 5.54 (d, *J* 9.5 Hz, *erythro*-PhCHSCN), 5.90–6.50 (m, *threo*- and *erythro*-MeCHSCN), 8.15 (d, *J* 6.5 Hz, CH_3), 8.49 (d, *J* 6.5 Hz, CH_3) (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 PhCHSCN proton signals.[17] The isomer ratios for the mixtures were determined from the integral traces of these signals.

Indene. Indene gave (a) mixture of **31** and **33** 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*-CHNCS), 4.76 (d, *J* 4 Hz, *trans*-CHNCS), 5.70–7.20 (m, overlapping *cis*- and *trans*-CHSCN and CH_2) (Found: C, 57.4; H, 3.55; N, 11.5. Calc. for $C_{11}H_8N_2S_2$: C, 56.9; H, 3.45; N, 12.05; S, 27.55%), and (b) a mixture of **30** and **32** 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) (Found: C, 56.9; H, 3.7; N, 11.7). On standing, the dithiocyanato mixture partially solidified; crystallisation from MeOH gave **32** as colourless prisms; m.p. 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) (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 CHSCN, CHNCS 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. Compound **25** (0.50 g) and 2,6 di-t-butyl-*p*-cresol (0.02 g) were dissolved in 0.2 M thiocyanogen soln in benzene (50 ml) and left at room temp. in darkness for 7 days. The soln 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. Compound **24** (0.50 g) was similarly treated, and gave starting material (0.48 g) as shown by the identity of IR spectra and TLC behaviour.

Compound **13** (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 soln in AcOH (50 ml), and left at room temp. in darkness for 1.5 hr. The soln 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. Compounds **12** and **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*-dichloroethylene were not recovered due to their loss by volatilisation 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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