

PSEUDOHALOGEN CHEMISTRY—VI¹

HOMOLYTIC THIOCYANATION OF MONO- AND DI-SUBSTITUTED ALKENES USING THIOCYANOGEN AND ULTRAVIOLET LIGHT

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Abstract—Under the influence of UV light, thiocyanogen reacts rapidly with mono- and di-substituted alkenes in benzene under nitrogen at 20–30°C to give, depending on the structure of the alkene, α,β -dithiocyanates, allylic isothiocyanates or mixtures of the two in high yields. Additions to acyclic alkenes are *trans*-stereoselective, while those to alkenes of the cyclohexene family are *trans*-stereospecific. A radical-chain mechanism, involving competing addition and substitution reactions initiated by the thiocyanato radical, is proposed.

In Part IV² it was shown that, under heterolytic conditions, thiocyanogen, (SCN)₂, behaves as a weak electrophile towards alkenes, adding slowly to form α,β -dithiocyanates and the corresponding α -isothiocyanato- β -thiocyanates. The additions to aliphatic alkenes are *trans*-stereospecific while the additions to α -arylalkenes are *trans*-stereoselective. A heterolytic mechanism involving a two-step, kinetically controlled addition, with a cyano-sulphonium ion intermediate in the case of aliphatic alkenes and an open thiocyanato-carbonium ion in the case of α -arylalkenes, was proposed. Söderbäck³ and Kaufmann⁴ noted that the reaction was stimulated by sunlight, and described the products as α,β -dithiocyanates, usually without structural proof. In view of the synthetic⁵ and analytical⁶ applications of the reaction of thiocyanogen with unsaturated compounds, we have investigated this photochemical variation using a range of acyclic and cyclic alkenes.⁷ We find it to be more complex than hitherto described, and to differ from the heterolytic reaction in rate, stereochemistry, product formation and scope. Here we describe the reactions of mono- and di-substituted alkenes.

RESULTS AND DISCUSSION

UV irradiation of equimolar amounts of thiocyanogen and the mono- and di-substituted alkenes and cycloalkenes 1–24 in benzene under nitrogen at 20–30°C led to the reaction times, products 25–56, and yields recorded in Table 1.

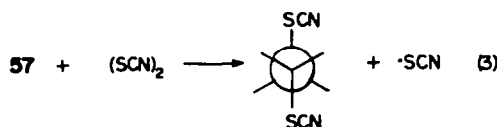
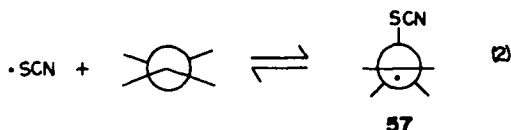
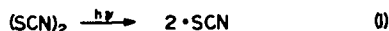
Comparison of these data with the corresponding data for heterolytic reactions² shows that for the photochemical reaction, (a) the reaction times are considerably shorter, (b) the yields are larger, (c) the products are different and more sensitive to alkene structure, and (d) the stereochemistry of the reaction is different. Thus, of the mono- and 1,1-di-substituted alkenes examined, alkenes 1–12 gave α,β -dithiocyanates exclusively (products 25–36), but 3-methylbut-1-ene 13 yielded small amounts of the isomeric allylic isothiocyanates 38 and 39 in addition to the α,β -dithiocyanate 37. The 1,2-disubstituted alkenes 14–20 gave mixtures of diastereoisomeric α,β -dithiocyanates (with *meso*- and *erythro*-isomers predominating) and/or allylic isothiocyanates which were virtually identical for each *cis/trans* pair of alkenes (products 40–48). The cycloalkenes 21–24

gave mixtures of *trans*- α,β -dithiocyanates and allylic isothiocyanates (products 49–56).

These reactions were strongly inhibited by oxygen, 2,6-di-*t*-butyl-4-methylphenol, or galvinoxyl. Thus, the reaction time for dec-1-ene 5 increased from 20 to 200 min, with a decrease in the yield of the dithiocyanate 29 from 84 to 60%, on carrying out the reaction under aerial atmosphere, while addition of 0.5–1.0% 2,6-di-*t*-butyl-4-methylphenol or galvinoxyl arrested the reaction completely for 10–50 min.

No reaction was observed with acrylonitrile or 1,1-dichloroethene. Alkenes of the type *cis*-RCH=CHR (R = Cl, CO₂H, CO₂Et) and *trans*-RCH=CHR (R = Cl, CO₂H, CO₂Et, CN, SCN, *t*-Bu) were recovered as the corresponding equilibrium mixture of *cis*- and *trans*-isomers. No telomer was observed in any of the reactions.

These results are readily accounted for by two competing homolytic reactions, each of which is initiated by photochemical dissociation of thiocyanogen into thiocyanato radicals⁸ (eqn 1).



Formation of the observed α,β -dithiocyanates is consistent with the kinetically controlled radical-chain addition process shown in eqns (2) and (3). In the addition step (eqn 2), attack by the electrophilic⁹ and ambident² thiocyanato radical ($\dot{\text{S}}\text{C}\equiv\text{N}=\text{S}=\text{C}=\text{N}$) occurs exclusively via the sulphur atom, thus leading to the formation of the thiocyanatoalkyl radical 57 rather than the isomeric isothiocyanatoalkyl radical. This is consistent with the sulphur atom in the thiocyanato radical carrying the major share of the unpaired electron

Table I. Photothiocyanation of alkenes in benzene under nitrogen at 20-30°


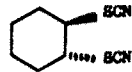



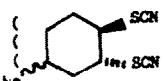
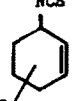
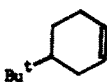
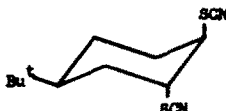
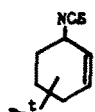
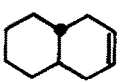
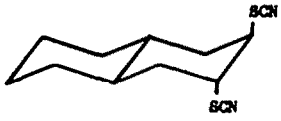
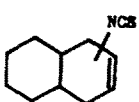
Alkene	Time (min)	Product(s)	Yield (%)
$\text{CH}_2=\text{CH}_2$	(1) 40	$\text{CH}_2(\text{SCN})\text{CH}_2\text{SCN}$	(25) 98
$\text{MeCH}=\text{CH}_2$	(2) 9	$\text{MeCH}(\text{SCN})\text{CH}_2\text{SCN}$	(26) 71
$\text{Bu}^{\text{B}}\text{CH}=\text{CH}_2$	(3) 20	$\text{Bu}^{\text{B}}\text{CH}(\text{SCN})\text{CH}_2\text{SCN}$	(27) 67
$\text{Bu}^{\text{t}}\text{CH}=\text{CH}_2$	(4) 11	$\text{Bu}^{\text{t}}\text{CH}(\text{SCN})\text{CH}_2\text{SCN}$	(28) 68
$\text{Me}(\text{CH}_2)_7\text{CH}=\text{CH}_2$	(5) 20	$\text{Me}(\text{CH}_2)_7\text{CH}(\text{SCN})\text{CH}_2\text{SCN}$	(29) 84
$\text{Me}(\text{CH}_2)_{17}\text{CH}=\text{CH}_2$	(6) 25	$\text{Me}(\text{CH}_2)_{17}\text{CH}(\text{SCN})\text{CH}_2\text{SCN}$	(30) 70
$\text{ClCH}=\text{CH}_2$	(7) 17	$\text{ClCH}(\text{SCN})\text{CH}_2\text{SCN}$	(31) 91
$\text{BrCH}=\text{CH}_2$	(8) 10	$\text{BrCH}(\text{SCN})\text{CH}_2\text{SCN}$	(32) 91
$\text{PhCH}=\text{CH}_2$	(9) 20	$\text{PhCH}(\text{SCN})\text{CH}_2\text{SCN}$	(33) 99
$\text{Me}_2\text{C}=\text{CH}_2$	(10) 4	$\text{Me}_2\text{C}(\text{SCN})\text{CH}_2\text{SCN}$	(34) 82
$\text{Et}_2\text{C}=\text{CH}_2$	(11) 14	$\text{Et}_2\text{C}(\text{SCN})\text{CH}_2\text{SCN}$	(35) 85
$\text{PhMeC}=\text{CH}_2$	(12) 10	$\text{PhMeC}(\text{SCN})\text{CH}_2\text{SCN}$	(36) 98
$\text{Pr}^{\text{i}}\text{CH}=\text{CH}_2$	(13) 45	($\text{Pr}^{\text{i}}\text{CH}(\text{SCN})\text{CH}_2\text{SCN}$)	(37) 63
		($\text{Me}_2\text{C}(\text{NCS})\text{CH}=\text{CH}_2$)	(38) 13
		($\text{Me}_2\text{C}=\text{CHCH}_2\text{NCS}$)	(39) 8
		(<i>threo</i> - $\text{PhCH}(\text{SCN})\text{CH}(\text{SCN})\text{Me}$)	(40) 14
<i>trans</i> - $\text{PhCH}=\text{CHMe}$	(14) 30	(<i>erythro</i> - $\text{PhCH}(\text{SCN})\text{CH}(\text{SCN})\text{Me}$)	(41) 80
		($\text{MeCH}(\text{SCN})\text{CH}(\text{SCN})\text{Me}$)	(42) 37
<i>cis</i> - $\text{MeCH}=\text{CHMe}$	(15) 29	(<i>meso</i> - $\text{MeCH}(\text{SCN})\text{CH}(\text{SCN})\text{Me}$)	(43) 57
		($\frac{42}{43}$)	39
<i>trans</i> - $\text{MeCH}=\text{CHMe}$	(16) 14	($\frac{42}{43}$)	60
		($\text{EtCH}(\text{SCN})\text{CH}(\text{SCN})\text{Et}$)	(44))
<i>cis</i> - $\text{EtCH}=\text{CHEt}$	(17) 12	(<i>meso</i> - $\text{EtCH}(\text{SCN})\text{CH}(\text{SCN})\text{Et}$)	(45))
		(<i>trans</i> - $\text{MeCH}(\text{NCS})\text{CH}=\text{CHEt}$)	(46) 48
		($\frac{44}{45}$)) (a)
<i>trans</i> - $\text{EtCH}=\text{CHEt}$	(18) 10	($\frac{45}{46}$))
		($\frac{46}{47}$)	21 (a)
		($\frac{46}{47}$)	48
<i>cis</i> - $\text{Pr}^{\text{i}}\text{CH}=\text{CHPr}^{\text{i}}$	(19) 60	(<i>trans</i> - $\text{Me}_2\text{C}(\text{NCS})\text{CH}=\text{CHPr}^{\text{i}}$)	(47) 28
		($\text{Me}_2\text{C}=\text{CHCH}(\text{NCS})\text{Pr}^{\text{i}}$)	(48) 72
<i>trans</i> - $\text{Pr}^{\text{i}}\text{CH}=\text{CHPr}^{\text{i}}$	(20) 45	($\frac{47}{48}$)	26
		($\frac{48}{49}$)	68
	(21) 12	()	(49) 26
		()	(50) 46
		()	

Table 1. (Contd)

Alkene	Time (min)	Product(s)	Yield (%)
 (22)	7	 (51)	24
		 (b) (52)	41
 (23)	10	 (53)	31
		 (b) (54)	57
 (24)	30	 (55)	40
		 (b) (56)	45

(a) Combined yield of 44 and 45; individual yields could not be determined from the ^1H NMR spectrum (see Experimental). (b) Mixture of isomers; structures not determined.

density,¹⁰ and being more polarisable than the nitrogen atom; similarly exclusive C–S bonding occurs in the homolytic additions of other ambident sulphur radicals.¹¹ The observed *cis-trans* isomerisations of unreactive alkenes indicate that this addition is readily reversible, probably due to the stability of the thiocyanato radical;† similar behaviour has been noted in homolytic additions of other sulphur-centred radicals.¹¹

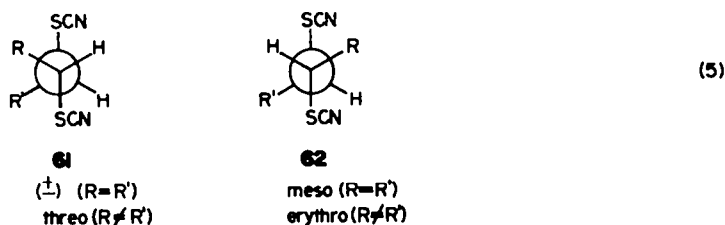
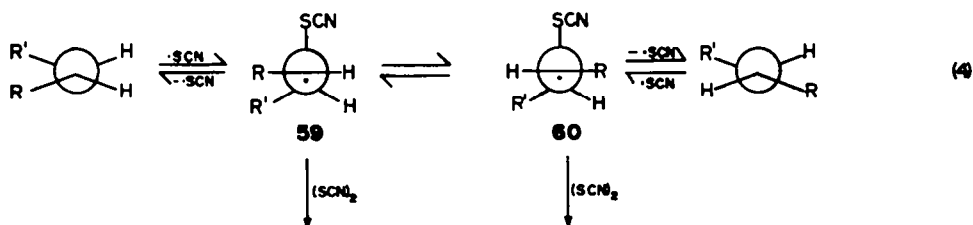
The transfer step (eqn 3) involves $\text{S}_\text{H}2$ displacement on one of the electron-deficient sulphur atoms of thiocyanato by the donor¹² thiocyanatoalkyl radical **57**, thus leading exclusively to the α,β -dithiocyanato product **58**. Attack by the thiocyanato radical (eqn 2) and by the bulky thiocyanogen molecule (eqn 3) occurs in each case by the sterically favourable axial route, thus leading to the thermodynamically unfavourable *trans*-diaxial products **53** and **55** from the conformationally rigid **23** and **24** respectively, and, by ring inversion, to the more stable *trans*-diequatorial products **49** and **51** from the conformationally mobile **21** and **22** respectively. In acy-

clic systems, the thiocyanatoalkyl radical derived from each member of a *cis/trans* pair of alkenes (**59** and **60** respectively) undergoes conformational equilibration (eqn 4) faster than it reacts in the transfer step (eqn 5), thus leading to identical ratios of products **61** and **62**. Preferential transfer via the more stable adduct radical **60** leads to the observed preponderance of *meso*- and *erythro*-dithiocyanates **62** (eqn 5). Similar stereochemical behaviour has been noted in homolytic additions of other sulphur-centred radicals.¹³

Both the addition and displacement steps (eqns 2 and 3) are rapid, as shown by the short reaction times and high yields in Table 1, and the absence of telomers. This is attributed to the favourable acceptor-radical/donor-substrate and donor-radical/acceptor-substrate relationships^{11,12} in the addition and displacement steps respectively. These relationships are not so favourable in the corresponding reactions of the structurally related dialkyl disulphides, which react sluggishly and give large amounts of telomers at the expense of 1:1-adducts.¹⁴

The lack of reactivity of, e.g. acrylonitrile, 1,1-dichloroethene, and alkenes of the type $\text{RCH}=\text{CHR}'$ ($\text{R} = \text{R}' = \text{Cl}, \text{CO}_2\text{Et}, \text{t-Bu}$) is attributed to a reduction of the donor characteristics of the thiocyanatoalkyl radical, e.g. **59** or **60**, by the electron-withdrawing and/or steric effects of the substituents R and R', and the consequent

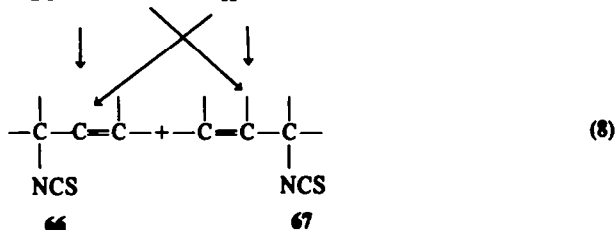
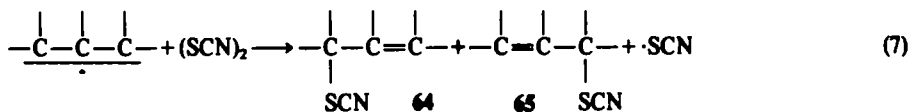
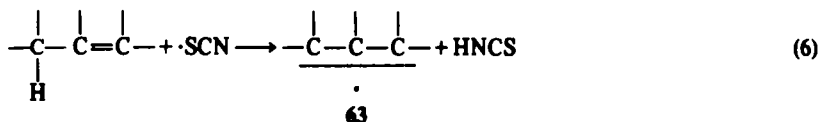
† A similar mechanism, with successive additions of thiocyanato radicals but elimination of iodine atoms, accounts for Söderbäck's interesting observation that the photothiocyanoation of *trans*-1,2-di-iodoethene leads to the equilibrium mixture of *cis* and *trans*-1,2-dithiocyanatoethene.³



arrest of the displacement reaction on the bulky thiocyanogen molecule. The lower reactivity of thiocyanogen than that of thiocyanogen chloride¹ in these homolytic addition reactions is consistent with the steric barrier to displacement at the sulphur atoms of the reagents increasing in the order $\text{ClSCN} < \text{NCSSCN}$.

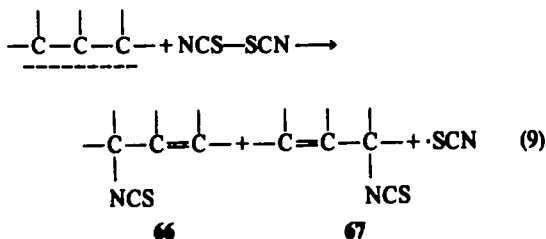
the bulky secondary and tertiary allylic radicals attack the more readily accessible terminal nitrogen atoms rather than the central sulphur atoms of the thiocyanogen molecule (eqn 9).

A similar change in the position of radical attack on trifluoromethanesulphenyl chloride (CF_3SCI) from the



Formation of the allylic isothiocyanates may be rationalised in terms of the thermodynamically-controlled radical-chain substitution process shown in eqns (6-8). Abstraction of an allylic hydrogen atom by the thiocyanato radical produces the radical 63 which yields the labile⁵ allylic thiocyanates 64 and 65 in the kinetically-controlled $\text{S}_{\text{H}}2$ chain-transfer step (eqn 7); subsequent thermodynamically-controlled allylic rearrangement (eqn 8), through one or more of the several mechanisms available,⁵ yields a mixture of isothiocyanates 66 and 67. The intermediate allylic thiocyanates 64 and 65, unlike those described in the corresponding reactions of thiocyanogen with secondary and tertiary aralkyl hydrocarbons,⁸ were not detected; this is consistent with the greater ease of isomerisation of allylic thiocyanates than aralkyl thiocyanates through the sigmatropic rearrangement mechanism.⁵

Alternatively, the formation of 66 and 67 may be due to a sterically-controlled chain transfer reaction in which



sulphur atom to the chlorine atom through a series of primary, secondary, and tertiary radicals has also been attributed to steric effects.¹⁵

The data in Table 1 show that for sterically unhindered alkenes, e.g. the terminal alkenes 1-12, this substitution reaction is very much slower than the competing addition reaction, and is only significant when a tertiary allylic radical is involved (see alkene 13). However, as steric resistance to addition increases, and the stability of the

allylic radical increases, the substitution reaction becomes important or even exclusive. This is well illustrated in the series *trans*-RCH=CHR (R = Me, Et, *i*-Pr) for which the addition/substitution ratios are 99/0, 21/48 and 0/94 respectively (Table 1).

This photolytic behaviour of thiocyanogen emphasizes further its marked pseudohalogen character,⁵ and may well be responsible, at least in part, for the lack of reproducibility of rate data⁵ and "thiocyanogen numbers"¹⁶ of alkenes when determined in diffuse light, since these conditions would allow both heterolytic and homolytic reactions to take place simultaneously (cf. the reactions of thiocyanogen chloride with hydrocarbons).¹⁶

EXPERIMENTAL

Alkenes

These were purified as described in Part IV.²

General procedure

Thiocyanogen solutions in benzene (~0.2 M) were prepared and analysed as described in Part IV.² A steady stream of dry N₂ was bubbled through the thiocyanogen solution (150 ml), which was contained in a 3-necked Pyrex flask fitted with a water condenser and a CaCl₂ drying tube, for 10 min before and during the reaction. The solution was irradiated using a 125 W, high-pressure Osram lamp placed 10 cm from the flask wall. An equimolar amount of the peroxide-free alkene was introduced into the solution at ambient temperatures (~20°) and the disappearance of thiocyanogen followed by iodometric titration. Reaction temperatures did not exceed 30°. Products were isolated, examined by TLC, and separated by column chromatography on silica gel as described in Part IV.² Typically, elution with benzene-light petroleum (b.p. 60–80°) (1:3) gave allylic isothiocyanates; elution with benzene-light petroleum (1:1) gave α -isothiocyanato- β -thiocyanates; and elution with benzene or benzene-ether (9:1) gave α,β -dithiocyanates. Different products of the reactions were readily separated, but structural isomers and stereo-isomers were not completely resolved; in such cases the isomer ratios could usually be determined from the integral traces of appropriate absorption bands in the ¹H NMR spectra of the mixtures (see below). Reaction times and yields are given in Table 1.

Product characterisation

Products were identified by (a) comparison of their physical and spectral properties with those of authentic samples prepared previously by the heterolytic method,² or (b) by IR and ¹H NMR spectroscopy as described in earlier papers. IR spectra were recorded with a Perkin-Elmer 237 and 337 spectrometers, and were taken for films of liquid products and for Nujol mulls of solid products. Unless otherwise stated, ¹H NMR spectra were recorded at 60 MHz in CDCl₃ with Perkin-Elmer R12 and Varian A60A spectrometers, using SiMe₄ as internal standard. In the NMR data given below, s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

It should be noted that most of these products are 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.

Ethene 1 gave 1,2-dithiocyanatoethane 25 as colourless prisms; m.p. 89–90° (from light petroleum/benzene) (lit.⁹ 90°); ν 2160 (SCN) cm⁻¹; τ 6.62 (s, CH₂SCN). (Found: C, 33.15; H, 2.95; N, 19.0. Calc. for C₂H₄N₂S₂: C, 33.3; H, 2.8; N, 19.45%).

Propene 2 gave 1,2-dithiocyanatopropane 26 as a colourless liquid; b.p. 172–174°/22 mm Hg; ν 2170 (SCN) cm⁻¹; τ 6.25–7.02 (3H, m, CH₃SCN and CH₂SCN), 8.34 (3H, d, J 6 Hz, CH₃). (Found: C, 38.0; H, 3.8; N, 18.05. Calc. for C₃H₆N₂S₂: C, 38.0; H, 3.8; N, 17.75%).

Hex-1-ene 3 gave 1,2-dithiocyanatohexane 27 identical with an authentic sample.²

3,3-Dimethylbut-1-ene 4 gave 3,3-dimethyl-1,2-dithiocyanatobutane 28 as colourless prisms; m.p. 96–97° (from light petroleum/benzene); ν 2140 (SCN) cm⁻¹; τ 6.17–6.97 (3H, m, CH₃SCN and CH₂SCN), 8.85 (9H, s, C(CH₃)₂). (Found: C, 48.05; H, 6.0; N, 13.9. Calc. for C₈H₁₂N₂S₂: C, 48.0; H, 6.0; N, 14.0%).

Dec-1-ene 5 gave 1,2-dithiocyanatodecane 29 as a pale yellow liquid; n_D^{20} 1.5088; ν 2170 (SCN) cm⁻¹; τ 6.20–7.00 (3H, m, CH₃SCN and CH₂SCN). (Found: C, 56.4; H, 7.8; N, 11.0. Calc. for C₁₂H₂₀N₂S₂: C, 56.3; H, 7.7; N, 10.9%).

Eicos-1-ene 6 gave 1,2-dithiocyanato-eicosane 30 as colourless prisms; m.p. 59–60° (from MeOH); ν 2160 (SCN) cm⁻¹; τ 6.50–6.80 (3H, m, CH₃SCN and CH₂SCN). (Found: C, 66.5; H, 10.0; N, 6.8. Calc. for C₂₂H₄₀N₂S₂: C, 66.65; H, 10.1; N, 7.05%).

Vinyl chloride 7 gave 1-chloro-1,2-dithiocyanatoethane 31 as colourless prisms (from MeOH); m.p. 45–46° (lit.¹⁷ 46–46.5°); IR and NMR spectra identical with those recorded in the literature.¹⁷ (Found: C, 26.9; H, 1.75; N, 15.65. Calc. for C₄H₃ClN₂S₂: C, 26.9; H, 1.7; N, 15.7%).

Vinyl bromide 8 gave 1-bromo-1,2-dithiocyanatoethane 32 as colourless prisms (from MeOH); m.p. 43–44° (lit.¹⁷ 43.5–44°); IR and NMR spectra identical with those recorded in the literature.¹⁷ (Found: C, 21.2; H, 1.1; N, 12.7. Calc. for C₄H₃BrN₂S₂: C, 21.5; H, 1.35; N, 12.55%).

Styrene 9 gave 1-phenyl-1,2-dithiocyanatoethane 33 identical with an authentic sample.²

2-Methylpropene 10 gave 2-methyl-1,2-dithiocyanatopropane 34 as a colourless liquid; b.p. 162°/11 mm Hg; ν 2165 (SCN) cm⁻¹; τ 6.60 (2H, s, CH₂SCN), 8.32 (6H, s, C(CH₃)₂). (Found: C, 41.9; H, 4.8; N, 16.35. Calc. for C₄H₈N₂S₂: C, 41.9; H, 4.65; N, 16.35%).

2-Ethylbut-1-ene 11 gave 2-ethyl-1,2-dithiocyanatobutane 35 as a pale yellow liquid; b.p. 148–150°/12 mm Hg; ν 2170 (SCN) cm⁻¹; τ 6.53 (2H, s, CH₂SCN), 8.12 (4H, q, J 7 Hz, CH₂), 8.94 (6H, t, J 7 Hz, CH₃). (Found: C, 48.6; H, 6.3; N, 14.1. Calc. for C₆H₁₂N₂S₂: C, 48.0; H, 6.0; N, 14.0%).

2-Phenylpropene 12 gave 2-phenyl-1,2-dithiocyanatopropane 36 as colourless prisms; m.p. 43–44° (from MeOH); ν 2155 (SCN) cm⁻¹; τ (CCl₄) 2.62 (5H, s, C₆H₅), 6.00 (1H, d, J 12 Hz, CH₃SCN), 6.38 (1H, d, J 12 Hz, CH₃SCN), 7.86 (3H, s, CH₃). (Found: C, 56.65; H, 4.35; N, 11.8. Calc. for C₁₁H₁₀N₂S₂: C, 56.45; H, 4.3; N, 11.95%).

3-Methylbut-1-ene 13 gave (a) 3-methyl-1,2-dithiocyanatobutane 37 as a pale yellow liquid which solidified under high vacuum; m.p. 27–29°; ν 2170 (SCN) cm⁻¹; τ 6.50–6.95 (3H, m, CH₃SCN and CH₂SCN), 7.50–8.00 (1H, m, Me²CH), 8.85 (3H, d, J 6.5 Hz, CH₃), 8.94 (3H, d, J 6.5 Hz, CH₃). (Found: C, 45.2; H, 5.6; N, 14.7. Calc. for C₇H₁₀N₂S₂: C, 45.15; H, 5.4; N, 15.05%); (b) a mixture of 3-isothiocyanato-3-methylbut-1-ene 38 [ν 2070 (NCS), 1660 (C=C), 890 and 965 (C–H of RCH=CH₂) cm⁻¹; τ 4.20–5.08 (m, CH=CH₂), 8.50 (s, CH₃) and 1-isothiocyanato-3-methylbut-2-ene 39 [ν 2070 (NCS), 1660 (C=C), 790 (C–H of RCH=CR₂) cm⁻¹; τ 4.20–5.08 (m, C=CH and CH₂NCS), 8.20 (s, CH₃), 8.26 (s, CH₃)] as a pale yellow volatile and vesicant liquid. (Found: C, 56.4; H, 7.0. Calc. for C₇H₁₀N₂S: C, 56.65; H, 7.1%). The yields of 38 and 39 were determined from the integral traces of their CH₃ signals in the crude product.

trans-1-Phenylpropene 14 gave a mixture of *threo*-1-phenyl-1,2-dithiocyanatopropane 40 and *erythro*-1-phenyl-1,2-dithiocyanatopropane 41 as colourless prisms identical in spectral properties (apart from band intensities) with the mixture prepared by the heterolytic method.² The isomer ratio was determined from the integral traces of the PhCH₃SCN proton signals.

cis-But-2-ene 15 gave a mixture of (\pm)-2,3-dithiocyanatobutane 42 [ν 2165 (SCN) cm⁻¹; τ (neat) 6.20–6.75 (2H, m, CH₃SCN), 8.53 (6H, d, J 8 Hz, CH₃)] and *meso*-2,3-dithiocyanatobutane 43 [ν 2165 (SCN) cm⁻¹; τ (neat) 6.20–6.75 (2H, m, CH₃SCN), 8.48 (6H, d, J 8 Hz, CH₃)] as a pale yellow liquid. (Found: C, 41.7; H, 4.5; N, 16.3. Calc. for C₆H₁₀N₂S₂: C, 41.85; H, 4.65; N, 16.3%). By analogy with the assignments made for (\pm)- and *meso*-2,3-dibromobutane,¹⁸ the lower-field doublet was assigned to the *meso*-isomer, and the higher field doublet to the (\pm)-isomer. The isomer ratio was determined from the integral traces of these doublets.

trans-But-2-ene 16 gave a mixture of 42 and 43 identical with that derived from *cis*-but-2-ene (see above) as shown by completely superimposable IR and NMR spectra.

cis-Hex-3-ene 17 gave (a) a mixture of (*±*)- and *meso*-3,4-dithiocyanatohexane (44 and 45 respectively) as a pale yellow liquid; ν 2160 (SCN) cm^{-1} ; τ 6.38–6.93 (2H, m, CHSCN), 7.60–8.30 (4H, m, CH₂), 8.83 (6H, t, \int 7.5 Hz, CH₃). (Found: C, 48.15; H, 5.75; N, 14.2. Calc. for C₆H₁₂N₂S₂: C, 48.0; H, 6.0; N, 14.0%); and (b) *trans*-2-isothiocyanatohex-3-ene 46 as a pale yellow liquid; ν 2070 (NCS), 1670 (C=C), 970 (vinyl C-H); τ 4.18 (1H, d of t, \int 15 and 5 Hz, =CHCH₂), 4.59 (1H, d of d, \int 15 and 5 Hz, =CHCH(NCS)), 5.55–6.30 (1H, m, CHNCS), 7.68–8.42 (2H, m, CH₂Me), 8.58 (3H, d, \int 7 Hz, CH₃CH(NCS)), 9.00 (3H, t, \int 7 Hz, CH₃CH₂). (Found: C, 59.5; H, 7.75; N, 9.85. Calc. for C₇H₁₁NS: C, 59.55; H, 7.85; N, 9.9%). Due to overlapping signals, the isomer ratio of the mixture of 44 and 45 could not be determined.

trans-Hex-3-ene 18 gave a mixture of 44, 45 and 46 identical with that obtained from *cis*-hex-3-ene (see above) as shown by completely superimposable IR and NMR spectra.

cis-3,5-Dimethylhex-3-ene 19 gave a mixture of *trans*-2-isothiocyanato-2,5-dimethylhex-3-ene 47 [ν 2070 (NCS), 1670 (C=C), 970 (vinyl C-H)]; τ (CCL₄) 4.35 (1H, d of d, \int 15 and 5 Hz, =CHCH), 4.75 (1H, d, \int 15 Hz, =CHC(NCS)), 7.60–8.10 (1H, m, CHMe₂), 8.55 (6H, s, (CH₃)₂C(NCS)) 9.05 (6H, d, \int 7 Hz, (CH₃)₂CH) and 4-isothiocyanato-2,5-dimethylhex-2-ene 48 [ν 2070 (NCS), 1670 (C=C)]; τ (CCL₄) 4.85 (1H, d, \int 9 Hz, C=CH), 5.98 (1H, d of d, \int 9 and 6 Hz, CHNCS), 7.60–8.10 (1H, m, CHMe₂), 8.25 (3H, s, C=CC₂), 8.34 (3H, s, C=CC₂), 9.00 (6H, d, \int 7 Hz, (CH₃)₂CH) as a pale yellow liquid; b.p. 98–100°/14 mm Hg. (Found: C, 63.75; H, 8.9; N, 8.75. Calc. for C₉H₁₅NS: C, 63.9; H, 8.9; N, 8.3%). The isomer ratio was determined from the integral traces of the vinyl and methyl proton signals.

trans-2,5-Dimethylhex-3-ene 20 gave a mixture of 47 and 48 identical with that obtained from *cis*-2,5-dimethylhex-3-ene (see above) as shown by completely superimposable IR and NMR spectra.

Cyclohexene 21 gave (a) *trans*-1,2-dithiocyanatocyclohexane 49 identical with an authentic sample,² and (b) 3-isothiocyanatocyclohexene 50 as a pale yellow liquid; b.p. 116–119°/12 mm Hg; ν 2080 (NCS), 1670 (C=C), 3050 and 960 (vinyl C-H) cm^{-1} . (Found: C, 60.6; H, 6.4; N, 9.8. Calc. for C₇H₉NS: C, 60.4; H, 6.5; N, 10.1%). Compound 50 was identical in physical and spectral properties with an authentic sample prepared from 3-bromocyclohexene and potassium thiocyanate.¹⁹

4-Methylcyclohexene 22 gave (a) 4-methyl-*trans*-1,2-dithiocyanatocyclohexane 51 identical with an authentic sample,² and (b) a mixture of unsaturated isothiocyanates 52 as a pale yellow liquid; b.p. 60–62°/0.15 mm Hg; ν 2080 (NCS), 1660 (C=C), 3040 and 960 (vinyl C-H) cm^{-1} . (Found: C, 62.6; H, 7.3; N, 9.0. Calc. for C₈H₁₁NS: C, 62.8; H, 7.2; N, 9.1%). The mixture 52 contained two isomers in unequal amounts (TCL) and gave positive tests for allylic isothiocyanates²⁰ with alcoholic silver nitrate and ferric chloride solutions but was not investigated further due to its dermatitic nature.

4-t-Butylcyclohexene 23 gave (a) 4eq-t-butyl-*trans*-1,2-dithiocyanatocyclohexane 53 identical with an authentic sample,² and (b) a mixture of unsaturated isothiocyanates 54 as a pale yellow liquid; b.p. 65–66°/0.03 mm Hg; ν 2080 (NCS), 1670 (C=C), 3050 and 950 (vinyl C-H) cm^{-1} . (Found: N, 7.05; S, 16.0. Calc. for C₁₁H₁₇NS: N, 7.15; S, 16.4%). The mixture 54 contained two isomers in unequal amounts (TCL) and gave

positive tests for allylic isothiocyanates,²⁰ but was not investigated further due to its dermatitic nature.

trans- Δ^2 -Octalin 24 gave (a) 2ax,3ax-dithiocyanato-*trans*-decalin 55 identical with an authentic sample,² and (b) a mixture of unsaturated isothiocyanates 56 as a pale yellow liquid; b.p. 82–84°/0.05 mm Hg; n_D^{20} 1.5575–1.5701; ν 2080 (NCS), 1660 and 1680 (C=C), 3040 (vinyl C-H); τ 3.8–4.6 (2H, 2 overlapping m, =C-H), 5.6–6.1 (1H, 2 overlapping m, CHNCS), 7.5–9.5 (12H, m, CH and CH₂). (Found: C, 67.95; H, 7.7; N, 7.2; S, 16.85. Calc. for C₁₁H₁₃NS: C, 68.35; H, 7.8; N, 7.25; S, 16.55%). The mixture 56 contained two isomers in unequal amounts (TLC), and gave positive tests for allylic isothiocyanates,²⁰ but was not investigated further due to its dermatitic nature.

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