vic-Iodothiocyanates and Iodoisothiocyanates. Part 8.[1] Addition of Iodine–Thiocyanogen to Alkenes under Ionic and Radical Conditions

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Addition of iodine–thiocyanogen to alkenes in the dark proceeds by a regioselective ionic reaction to give mainly vic-iodoisothiocyanates, and under irradiation with u.v. light by a radical reaction to give mainly vic-iodothiocyanates. However, in the case of 1-methylene-4-t-butylcyclohexane even under irradiation by u.v. light, ionic addition of the reagent competes successfully with, and almost to the exclusion of, the radical pathway.

In Part 3 [2] we showed that treatment of (E)-hex-3-ene (1) with iodine–potassium thiocyanate resulted in a marked difference in the ratio of the major products, viz. iodothiocyanate (3): iodoisothiocyanate (4) (68 : 18), from that obtained using iodine–thiocyanogen (12 : 69). Although the predominant initial ionic species in each case was assumed to be an iodonium ion, we suggested that in the former case the nucleophile was the thiocyanate anion while in the latter it was either iodine(I) thiocyanate or thiocyanogen itself. In an attempt to examine these suggestions in more detail we have studied the reactions of iodine–thiocyanogen with some terminal and other alkenes under conditions which favour either ionic or radical pathways.

Reactions of 4-methylpent-1-ene (8) with iodine–thiocyanogen were examined under a variety of conditions (Table 1). In order to ensure that the equilibrium, $I_2 + (SCN)_2 \rightleftharpoons 2 ISCN$, was fully established iodine and thiocyanogen were stirred together in benzene for 15 min prior to addition of the alkene. There is conflicting evidence [4-6] concerning the position of this equilibrium. Raby et al.[5] claim that iodine(I) thiocyanate formation is complete while other workers [4] could find little evidence for this, their studies suggesting partial formation of a species with an isothiocyanate moiety. Recently, iodine and thiocyanogen have been shown to remain completely dissociated in the gas phase,[6] in contrast to ClSCN and BrSCN which parallel their behaviour in solution [4] in being completely and partially formed, respectively, on mixing the halogen and thiocyanogen. In the present work, the u.v. spectrum of a solution of iodine and thiocyanogen in chloroform corresponded ($\lambda_{max.}$ 295 and 515 nm) with that expected from a mixture of equal concentrations of the reactants, and was unchanged after 50 min. No evidence for iodine(I) thiocyanate formation was observed. Furthermore, the use of u.v. light to irradiate the reaction mixtures induced a radical pathway which was especially favoured (see later) on changing the wavelength from 254 to 300 nm (near $\lambda_{max.}$ for thiocyanogen) indicating that homolysis of thiocyanogen was occurring. The recovery of compounds containing both iodine and thiocyanate (or isothiocyanate) moieties from the reactions summarised in Table 1 is consistent with addition of the elements of ' ISCN ', but in view of the above evidence iodine(I) thiocyanate itself is unlikely to be an important reactive species.

The regioisomeric vic-iodothiocyanates (9) and (10) were separated by multiple elution p.l.c. and were identified from their spectral properties. For example, 2-iodo-4-methyl-1-thiocyanatopentane (9) showed thiocyanato-absorption (2 160 cm^{-1}) in the i.r. spectrum and peaks at m/z 269 (M$^{+\cdot}$), 211 (M$^{+\cdot}$ − SCN·), and 142 (M$^{+\cdot}$ − I·) in the mass spectrum. The single frequency off-resonance decoupled (SFORD) ^{13}C n.m.r. spectrum showed no high field triplet and therefore a primary iodide [7] was not present; a triplet (J_R 21 Hz) at δ_C
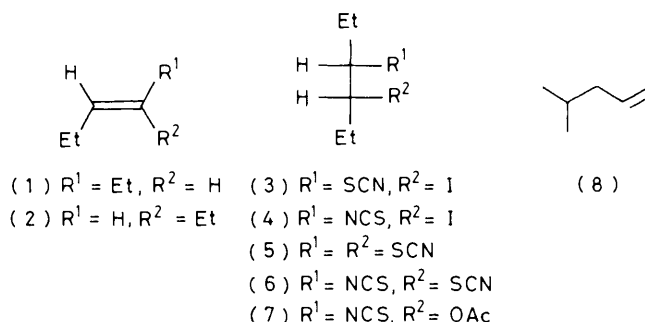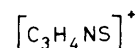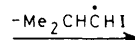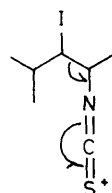

(1) R^1 = Et, R^2 = H
(2) R^1 = H, R^2 = Et
(3) R^1 = SCN, R^2 = I
(4) R^1 = NCS, R^2 = I
(5) R^1 = R^2 = SCN
(6) R^1 = NCS, R^2 = SCN
(7) R^1 = NCS, R^2 = OAc
(8)

Table 1. Reactions of 4-methylpent-1-ene with I_2–(SCN)$_2$

Reaction conditions [a,b]	Products and yields (%) [c]					
	(9) (10)	(11) (12)	(13) [d]	(14)	(22)	(15)
N$_2$, dark, 0.5 h	10 (1.6 : 1)	31 (2.5 : 1)	3	1		
N$_2$, dark, 18 h	17 (1.6 : 1)	49 (2 : 1)	7	1	1	
N$_2$, dark, 17 h [e]	15 (1.5 : 1)	41 (2 : 1)				
N$_2$(O$_2$-free), dark, 18 h	17 (3 : 1)	51 (2 : 1)	6			
N$_2$(O$_2$-free), dark, 19 h [f]	20	10 (2 : 1)				
O$_2$, dark, 18 h	13 (1.8 : 1)	40 (2 : 1)				
N$_2$(O$_2$-free), u.v., 18 h	80	8 (2 : 1)		3	1	6

[a] Molar ratio (8) : I$_2$: (SCN)$_2$ = 2 : 1.2 : 1.2. [b] In benzene at room temperature. [c] Yields after p.l.c.; ratio by ^{1}H n.m.r. analysis. [d] Mixture with (14) and (16). [e] 1 week-old Pb(SCN)$_2$ used. [f] Pb(SCN)$_2$ prepared with non-distilled H$_2$O. Like (SCN)$_2$ itself,[3] the reactivity of I$_2$–(SCN)$_2$ is affected by the quality of Pb(SCN)$_2$ used in its preparation.

43.7 was assigned to C-1 and a doublet (J_R 22 Hz) at δ_C 29.6 was assigned to C-2. Chemical shifts in the ^{1}H n.m.r. spectrum were consistent with expected values, the CHI proton resonating at δ_H 4.29 and the diastereoisotopic CH$_2$SCN protons and methyl protons resonating at δ_H 3.37 and 3.68, and at δ_H 0.96 and 1.06, respectively.

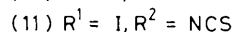The regioisomeric vic-iodoisothiocyanates (11) and (12) ($\nu_{max.}$ 2 060 cm^{-1}) were obtained as an inseparable (by p.l.c.) mixture in which the presence of the components was ascertained from the ^{13}C n.m.r. spectrum. Thus, a triplet (J_R 20 Hz) at δ_C 9.1 in the SFORD spectrum indicated that the major component (11) was a terminal iodide, the chemical shift being consistent with the heavy atom effect of iodine.[8] The carbon atom β to iodine is strongly deshielded, and therefore a doublet at δ_C 57.1 was assigned to C-2. The minor isomer (12)

(9) R^1 = SCN, R^2 = I
(10) R^1 = I, R^2 = SCN
(11) R^1 = I, R^2 = NCS
(12) R^1 = NCS, R^2 = I
(13) R^1 = SCN, R^2 = NCS
(14) R^1 = R^2 = SCN
(15) R^1 = R^2 = I
(16) R^1 = NCS, R^2 = SCN

(17) R^1 = R^2 = I
(18) R^1 = I, R^2 = SCN
(19) R^1 = I, R^2 = NCS
(20) R^1 = SCN, R^2 = NCS
(21) R^1 = R^2 = SCN

(22)

(23)

$$-Me_2CH\overset{\bullet}{C}HI \longrightarrow \left[C_3H_4NS\right]^+$$

m/z 86

Scheme 1.

(24) R^1 = SCN, R^2 = I
(25) R^1 = I, R^2 = SCN
(26) R^1 = I, R^2 = NCS
(27) R^1 = NCS, R^2 = I
(28) R^1 = R^2 = SCN
(29) R^1 = SCN, R^2 = NCS
(30) R^1 = NCS, R^2 = SCN
(31) R^1 = R^2 = I

(32)

(33) R^1 = SCN, R^2 = I
(34) R^1 = NCS, R^2 = I
(35) R^1 = I, R^2 = SCN
(36) R^1 = I, R^2 = NCS
(37) R^1 = R^2 = I
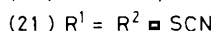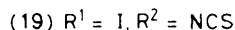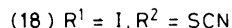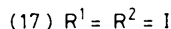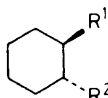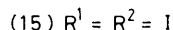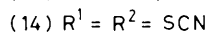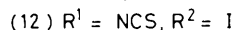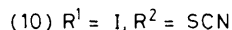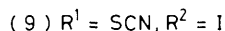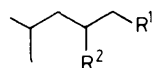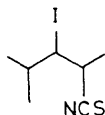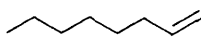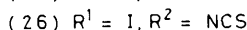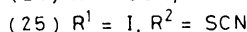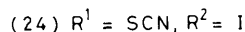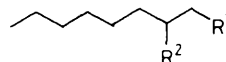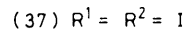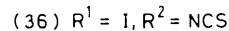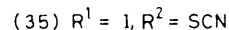
was associated with a triplet (J_R 24 Hz) at δ_C 28.9 due to C-2. The residual coupling constants (J_R) in the SFORD spectrum were consistent with the relative chemical shifts of the protons attached to these carbon atoms in the ^{1}H n.m.r. spectra;[9] all other proton-bearing carbon atoms which resonated in the same region showed signals with smaller J_R values. In the ^{1}H n.m.r. spectrum the downfield signals due to the regioisomers partially overlapped, but nevertheless integration could still be used for quantification. A doublet at δ_H 3.35 was assigned to the iodomethylene protons of (11) (cf. ref. 10) but the signal due to the CHNCS proton of (11) ($\delta_{calc.}$ ca. 4.0) overlapped with those (δ_H 3.59—4.63) of the CHI ($\delta_{calc.}$ ca. 4.3) and CH$_2$NCS ($\delta_{calc.}$ ca. 3.6) protons of the isomer (12) so that individual chemical shifts could not be measured. Proof of the assigned structures was provided by conversion of the mixture into separable five-membered heterocycles.[1]

Another iodoisothiocyanate obtained in low yield was identified from its spectral parameters as the compound (22). Thus, the i.r. spectrum showed isothiocyanate absorption (2 070 cm^{-1}) while both the ^{13}C and ^{1}H n.m.r. spectra indicated the presence of three methyl groups, two of which (δ_H 1.07 and 1.10) were coupled to only one proton (δ_H 1.62—2.10) and thus corresponded to an isopropyl group. The remaining methyl group resonated as a doublet (J 6 Hz) at δ_H 1.48 while two protons appeared as overlapping multiplets at δ_H 3.37—4.00, this region of the spectrum resembling that of erythro-3-iodo-4-isothiocyanatohexane (4).[2] The mass spectrum showed a molecular ion at m/z 269, peaks at m/z 211 ($M^{+\cdot}$ − NCS·) and 142 ($M^{+\cdot}$ − I·), and a base peak at m/z 86 (Scheme 1) consistent with structure (22).

The compound presumably arises from iodine- or thiocyanogen-catalysed isomerisation [11] of (8) followed by reaction of iodine–thiocyanogen with the resulting 4-methylpent-2-ene.

Unlike other alkenes which have been examined,[2,12] treatment of 4-methylpent-1-ene (8) with iodine–potassium thiocyanate under the previously employed conditions gave no vic-iodothiocyanates or iodoisothiocyanates but afforded a 76% yield of 1,2-di-iodo-4-methylpentane (15). The structure of the di-iodide (15) followed from a spectral comparison with an authentic sample prepared by iodination of 4-methyl-pent-1-ene. In its ^{1}H n.m.r. spectrum the methyl groups appeared as two discrete three-proton doublets ($\Delta\delta$ 0.16) consistent with their diastereoisotopic relationship [13] notwithstanding the fact that the chiral centre is two carbon

atoms distant from the prochiral isopropyl methine carbon atom.* The relatively large non-equivalence may be explained in terms of a conformational preference (cf. ref. 14) and the anisotropic effects of iodine.[9] The SFORD ^{13}C n.m.r. spectrum showed a triplet of δ_C 14.8 indicative of a primary iodide,[7] while use of appropriate substituent chemical-shift parameters for the iodo and methyl substituents [7] permitted unequivocal assignment of most of the signals (see Experimental section). Some decomposition of the di-iodide to the parent alkene occurred after 24 h at 0—3 °C in the dark while treatment of the freshly prepared di-iodide with anhydrous sodium thiosulphate in [^{2}H$_6$]dimethyl sulphoxide (in order to study the reaction by ^{1}H n.m.r.[15]) effected quantitative reversion to compound (8). In contrast to trans-1,2-di-iodocyclohexane (17) which was converted mainly into the iodothiocyanate (18) when treated with potassium thiocyanate in the presence of the phase-transfer catalyst Adogen 464,[2] similar treatment of the di-iodide (15) gave only a low yield (8%) of the regioisomeric vic-iodothiocyanates (9) and (10).

Products from the reaction of iodine–thiocyanogen with oct-1-ene (23) (Table 2) were similar to those from analogous reactions with 4-methylpent-1-ene, those arising by addition of thiocyanogen itself, viz. (28), (29), and (30), being identified by comparison of their ^{1}H n.m.r. spectra with data reported for the products of addition of thiocyanogen to hex-1-ene.[16] However, whereas the di-iodide (15) was obtained from the alkene (8) in only 1% yield (Table 1, entry 1), under identical conditions the di-iodide (31) was obtained from oct-1-ene (23) in 8% yield. [1] H N.m.r. studies of the formation of the di-iodides (15) and (31) by iodination of the respective alkenes indicated similar equilibrium positions for the reactions and thus the lower yield of (15) was ascribed to its greater ease of decomposition during isolation by silica-gel chromatography.

In contrast to the lack of isomerization of simple primary thiocyanates [17] and of vic-bromothiocyanates,[18] prolonged (46 h) treatment of the iodothiocyanate (24) with an excess of boron trifluoride–diethyl ether [2] gave a mixture (3 : 1) of the vic-iodoisothiocyanates (26) and (27). Treatment of the iodothiocyanate (9) with a catalytic amount of trifluoromethane-

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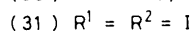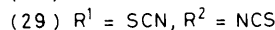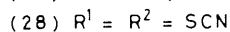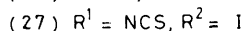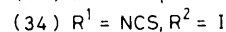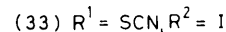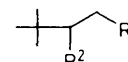* The isopropyl methyl groups of 1,2-dibromo-4-methylpentane also appear as pair of doublets.

Table 2. Reactions of oct-1-ene with I_2–$(SCN)_2$

Reaction conditions [a,b]	Products and yields (%) [c]						
	(24) (25)	(26) (27)	(28)	(29)	(30)	(31)
N_2, dark, 18 h	14 (1.3 : 1)	52 (2 : 1)		3		8
$N_2(O_2$-free), dark, 0.5 h	9 (1.7 : 1)	38 (2 : 1)		2		9
$N_2(O_2$-free), dark, 18 h	18 (1.5 : 1)	55 (2 : 1)		5		4
O_2, dark, 18 h	14 (1.8 : 1)	45 (2 : 1)				6
$N_2(O_2$-free), u.v. (254 nm), 1 h, 40 °C	71	21 (2 : 1)				5
$N_2(O_2$-free), u.v. (300 nm), 1 h, 40 °C	87	8 (2 : 1)				3

[a] Molar ratio (23) : I_2 : $(SCN)_2$ = 2 : 1.2 : 1.2. [b] In benzene at room temperature. [c] Yields after p.l.c.; ratios by ^1H n.m.r. analysis.

Table 3. Reactions of 3,3-dimethylbut-1-ene with I_2–$(SCN)_2$

Reaction conditions [a,b]	Products and yields (%) [c]		
	(33)	(34)	(38)
O_2, dark, 18 h	10	40	2 [d]
$N_2(O_2$-free), u.v., 17 h	77	12	2

[a] Molar ratio (32) : I_2 : $(SCN)_2$ = 2 : 1.2 : 1.2. [b] In benzene at room temperature under anhydrous conditions. [c] Yields after p.l.c. [d] ca. 20 : 1 Mixture with (34).

sulphonic acid in dichloromethane gave a 50% yield of a mixture (2 : 1) of the iodoisothiocyanates (11) and (12) whereas in nitromethane a 73% yield of a mixture (6 : 1) of the same products was obtained; however, isolated yields were low.

The products from reactions of iodine–thiocyanogen with 3,3-dimethylbut-1-ene (32) are given in Table 3. As in the case of additions of iodine(I) isocyanate,[19] iodine(I) azide,[20] and iodine(I) nitrate [21] to this substrate, attack of the nucleophile in an ionic reaction occurs exclusively at the less sterically hindered primary carbon atom of a bridged iodonium ion rather than at the electronically favoured secondary centre. Neither the regioisomeric vic-iodothiocyanate (35) nor the regioisomeric vic-iodoisothiocyanate (36) were formed in either reaction, and in accord with the unfavourable equilibrium between the alkene (32) and the di-iodide (37) none of the latter was detected. Compounds (33) and (34), each of which were malodorous and caused skin irritation (cf. ref. 16), were characterised by elemental analyses and from their spectral properties. The rearranged compound (38) had a broad isothiocyanate absorption (2 095 cm^{-1}) in the i.r. spectrum while the mass spectrum showed a molecular ion at m/z 269 and peaks at m/z 142 ($M^{+\cdot}$ — I·) and 211 ($M^{+\cdot}$ — NCŚ). The latter was the base peak in the 70 eV spectrum, suggesting a tertiary and therefore rearranged isothiocyanate structure. This inference was supported by the ^1H n.m.r. spectrum since the characteristic singlet due to a t-butyl group was replaced by two three-proton doublets at δ_H 0.98 and 1.03, and by another methyl singlet at δ_H 1.45. A two-proton singlet at δ_H 3.42 was assigned to the CH$_2$I group.

The data in Tables 1, 2, and 3 represent primary, and thus kinetically controlled, product distributions for the following reasons. Firstly, the same distributions were obtained (Table 1) after incomplete reaction (0.5 h). Secondly, when the pure regioisomeric iodothiocyanates (9) and (10) were treated separately with boron trifluoride–diethyl ether, in benzene, isomerization was only partially complete after 68 h. Each vic-iodothiocyanate is thermodynamically unstable with respect to both of the vic-iodoisothiocyanates (11) and (12); the thiocyanate (9) isomerizes to (10) also, but the reverse of the latter reaction does not occur. The ratio of (11) : (12) obtained, viz. 5 : 1, differed from that (2 : 1) generally found in Table 1. The ratio of (9) : (10) (1.5 : 1) was similar to that found in Table 1 but the possibility of the iodothiocyanate (9) isomerizing to (10) in situ with iodine–thiocyanogen was discounted when it was recovered unchanged when subjected to the original reaction conditions (Table 1, entry 2). Earlier [2] we proposed that the reaction of iodine–potassium thiocyanate with alkenes involves the initial addition of iodine in a pre-equilibrium step, conversion into the products occurring by subsequent nucleophilic attack on an intermediate iodonium
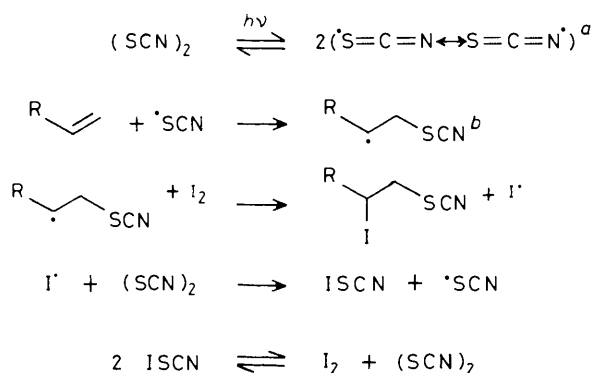
ion.[22] This is supported by the fact that products are not observed initially (t.l.c.) when this reagent system is used. Since the addition of iodine–thiocyanogen to the terminal alkenes (8) and (23) in the dark is not regiospecific, it is likely that a bridged iodonium ion is also an intermediate in these cases. However, since there is a preference for formation of the Markownikov vic-iodoisothiocyanate, the involvement of an open-carbocation cannot be discounted. Alternatively, the bridged iodonium ion may be unsymmetrical with only a partial bond to C-2, such asymmetry being favoured by steric factors. In contrast to the iodine–potassium thiocyanate reactions, adducts were detected (t.l.c.) soon after 4-methyl-pent-1-ene (8) was added to iodine–thiocyanogen mixtures, suggesting that the latter system, which is homogeneous, is more efficient in the product-forming step. A measure of the relative nucleophilicity of the two reagent mixtures was obtained by treatment of 1,2-di-iodo-4-methylpentane (15) with each system. In the presence of potassium thiocyanate, stirred rapidly in chloroform–water–Adogen 464 at room temperature for 24 h, the di-iodide was only converted into sulphur-containing adducts to a small extent (8%). In contrast, treatment of (15) with thiocyanogen in benzene for 18 h gave vic-iodoisothiocyanates (25%) and vic-iodothiocyanates (11%) in proportions similar to those obtained by treatment of the alkene (8) with iodine–thiocyanogen. Although the reaction with thiocyanogen was too slow to support the notion that the di-iodide is an intermediate in the latter reaction, the similar product distribution suggests that both reactions proceed via the action of thiocyanogen or free thiocyanate [from heterolysis of $(SCN)_2$] on an intermediate iodonium ion. This does not exclude the possibility that iodine (from decomposition of the di-iodide) could react with thiocyanogen to form iodine(I) thiocyanate which then reacts with the alkene. However, if as the results of Nelson and Pullin [4] suggest, iodine(I) thiocyanate contains an I–N bond, this species should be a sulphur nucleophile which is not consistent with it being a major product-forming species. The predominance of vic-iodoisothiocyanates as products from reactions in the dark is consistent with attack of ISCN or of thiocyanogen, or another nitrogen nucleophile such as I_2SCN^-,[2,3] on an intermediate bridged iodonium ion, the nitrogen end of the nucleophile being freely available. If free thiocyanate from heterolysis of thiocyanogen was the major nucleophile, attack via the more nucleophilic [24] sulphur terminus would predominate under kinetically controlled conditions. That the thiocyanate ion is not significantly involved in the formation of vic-iodoisothiocyanates is supported by studies on the isomerization of organic thiocyanates by the thiocyanate anion.[25] On the other hand, formation of vic-iodothiocyanates as minor products requires that the thiocyanate ion is involved in their formation. As mentioned earlier,[2] reaction via an S-cyano-thiiranium ion could provide a minor indirect pathway to the iodothiocyanates, but cannot account for iodoisothiocyanate formation.

The results of reactions of the alkenes under irradiation by

Scheme 2. (a), Ref. 27; (b) ref. 28.

(38)

(39)

(40) R = SCN
(41) R = N_3

(42) R^1 = I, R^2 = SCN
(43) R^1 = SCN, R^2 = I
(44) R^1 = I, R^2 = NCS
(45) R^1 = NCS, R^2 = I

(46)

(47)

(48) R = H
(49) R = NCS

(50)

(51) R^1 = SCN, R^2 = I
(52) R^1 = NCS, R^2 = I
(53) R^1 = SCN, R^2 = NCS

(54)

(55) R^1, R^2 = CH$_2$NCS, I
(56) R^1 = CH$_2$I, R^2 = NCS
(57) R^1 = NCS, R^2 = CH$_2$I
(58) R^1 = CH$_2$I, R^2 = SCN
(59) R^1 = I, R^2 = CH$_2$SCN
(60) R^1 = CH$_2$I, R^2 = N$_3$
(61) R^1 = CH$_2$SCN, R^2 = I

(62) R^1 = NCS, R^2 = I
(63) R^1 = I, R^2 = NCS
(64) R^1 = R^2 = I
(65) R^1 = I, R^2 = SCN
(66) R^1 = SCN, R^2 = I
(67) R^1 = SCN, R^2 = NCS

Table 4. Reactions of cyclohexene with I_2–(SCN)$_2$

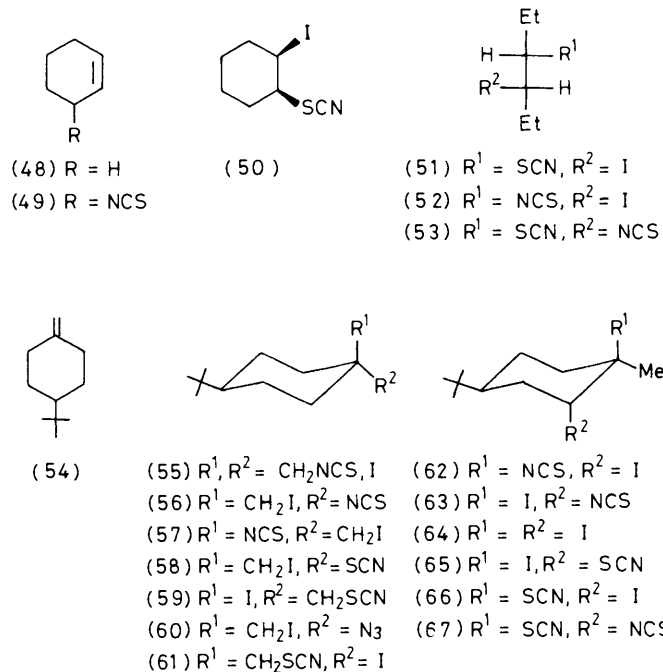| Reaction conditions [a,b]	Products and yields (%) [c]					
	(18)	(19)	(20)	(21)	(49)	(50)
N$_2$, dark, 18 h	16	69	2			
N$_2$, dark, 1 h	19	55	3			
N$_2$, u.v., 1 h	29	44	4		3	2

[a] Molar ratio (48) : I$_2$: (SCN)$_2$ = 2 : 1.2 : 1.2. [b] In benzene at room temperature. [c] Yields after p.l.c.

u.v. light are consistent with the occurrence of a free radical process [26] (Scheme 2) initiated by dissociation of thiocyanogen. Quantitative recovery of the major vic-iodothiocyanate (9) after it had been subjected to the reaction conditions established that the product distribution reflected kinetic control. The regioisomeric vic-iodoisothiocyanates probably arise via a competing ionic process even under irradiation by u.v. light. Since the addition of thiocyanogen alone to alkenes under homolytic conditions to form 1,2-dithiocyanates is a rapid process,[28] the formation of iodothiocyanates must occur even more rapidly since dithiocyanates were only minor products in the present work. The predominance of the vic-iodothiocyanates (9), (24), and (33) under homolytic conditions is consistent with initial attack of the thiocyanato-radical on the terminal carbon of the alkene to give an open thiocyanato-alkyl radical.[28] Product formation may then occur by a displacement reaction of the alkyl radical with iodine (or, in a sterically less favourable reaction, with thiocyanogen to generate a vic-dithiocyanate [28]). Since the thiocyanato-radical is not regenerated in the displacement step the only source is photochemical initiation, unless an iodo-radical reacts with thiocyanogen to liberate this species. Alternatively, displacement with a molecule of iodine(I) thiocyanate would provide thiocyanato-radicals. However, on changing the wavelength from 254 to 300 nm the yield of the radical product (24) from oct-1-ene increased from 71 to 87%. It is likely therefore that homolysis of thiocyanogen is the major source of thiocyanato-radicals in this and related reactions.

Further evidence for a radical pathway was obtained from the formation of the cis-adduct (40) (8%) along with mixtures of the known [12] compounds (42) and (43) (37%), and of (44)

and (45) (9%), when 5α-androst-2-ene (39) was treated with iodine–thiocyanogen in u.v. light. The structure of compound (40) was assigned as 2α-iodo-3α-thiocyanato-5α-androstane on the basis of its spectral properties. In particular, the occurrence of the 19-H signal at δ_H 0.90 indicated that iodine was not subtended from the 2β-position. Of the two downfield signals, viz. δ_H 4.28 ($W_{\frac{1}{2}}$ 9 Hz, CHSCN) and 4.85 ($W_{\frac{1}{2}}$ 24 Hz CHI) only one showed large coupling constants and a cis-iodothiocyanate structure was therefore required. The breadth of the signal at δ_H 4.85 is attributed to coupling between CHI and a vicinal 1α-H or 4β-H proton, depending on the regiochemistry of the adduct. In either case, the coupling vicinal protons must have a trans-diaxial orientation. Of the two possibilities (40) and (46), the former is favoured since a C-2β axial thiocyanate group, as in structure (46), would be expected to cause a slight downfield shift of the 19-H$_3$ signal. The analogous cis-iodoazide (41) has been obtained from the free radical addition of iodine(I) azide to the androstene (39).[29] In the present work, reversal of the relative proportions of the androstanes (42) and (43) from reactions carried out in the dark and under irradiation with u.v. light also support a radical pathway in the latter case. Thus, initial attack of the thiocyanato-radical occurs preferentially at C-3 from the α-face of the alkene to give an intermediate thiocyanato-alkyl radical (47). Attack at C-2 of (47) in a displacement reaction with iodine may occur along a pseudo-axial direction to give the iodothiocyanate (42), or along a pseudo-equatorial direction to give its isomer (40), with the former predominat-

Table 5. Reactions of hex-3-enes with I_2–$(SCN)_2$

Reaction conditions (E)-Isomer (1)	Products and yields (%) [a]							
	(3)	(51)	(4)	(52)	(5)	(6)	(53)	(7)
N_2, dark, 17 h [b]	20		38		4	8		
N_2(O_2-free), u.v., 80 min [b]	25		22					11
N_2, u.v., 1 h [c]	25	Trace	66				5	
(Z)-Isomer (2)								
N_2, dark, 18 h [c]		14	71 (braced)				6 (braced)	
N_2, u.v., 1 h [c]	Trace	19	65 (braced) 1 : 4.6				6 (braced)	

[a] Yields after p.l.c. [b] In acetic acid. [c] In benzene.

ing. The minor components (44) and (45) probably arise by competing ionic reactions.

In order to examine whether a conformationally flexible cyclic system would afford a *cis*-product with iodine–thiocyanogen, the reactions of this reagent with cyclohexene (48) were studied (Table 4). With one exception, products were identified by comparison with literature data. The new compound, which was isolated from a reaction carried out under irradiation by u.v. light, and which was assigned the structure *cis*-1-iodo-2-thiocyanatocyclohexane (50), showed a broad one-proton multiplet at δ_H 3.08 ($W_{\frac{1}{2}}$ 12 Hz), and another one-proton multiplet at δ_H 4.82 ($W_{\frac{1}{2}}$ 9 Hz), corresponding to an axial CHSCN proton and an equatorial CHI proton, respectively.

Although the yield of *trans*-1-iodo-2-thiocyanatocyclohexane (18) from reactions in the dark was lower after 18 h than after 1 h, and thus it was partially converted into *trans*-1-iodo-2-isothiocyanatocyclohexane (19) under the reaction conditions, the yield was increased under the influence of u.v. light. This compound was accompanied by the allylic isothiocyanate (49) and the *cis*-adduct (50), each of which could be formed by a radical reaction involving a conformationally mobile cyclohexyl radical (*cf.* ref. 30).

In Part 3 [2] we examined the action of iodine–thiocyanogen with (E)-hex-3-ene (1) and obtained results which differed from those recorded by Maxwell and Silbert [22] for the same substrate. In order to ascertain if the incursion of a radical pathway could account for the discrepancies, the reaction in acetic acid was carried out under u.v. irradiation (Table 5). The results were similar to our earlier ones and indicated that the formation of compound (5) in the dark cannot be explained by a radical pathway operating under Maxwell and Silbert's conditions. Indeed, although there is a reversal in the ratio of the hexane derivatives (3) and (4) when the reaction is carried out under u.v. irradiation, the poor yields from the latter reaction suggest that the radical reaction is sluggish in acetic acid. Also, the formation of significant amounts of compounds (4) and (7) indicated that the ionic pathway was competing effectively with the radical process, consistent with the fact that dissociation of iodine(ı) thiocyanate is promoted in acetic acid.[5] Under the influence of u.v. light no isomerization of (E)-hex-3-ene to the thermodynamically less stable (Z)-hex-3-ene (2) occurred since the *vic*-iodoisothiocyanate (4) recovered from the reaction mixture was stereochemically pure. However, some radical addition did in fact occur as evidenced by the slight increase in the yield of *vic*-iodothiocyanates compared with that from the dark reaction, and the appearance of a small amount of the *threo*-adduct (51).

The stereochemistry of the *threo*-compounds (Table 5) isolated from the reaction of iodine–thiocyanogen with (Z)-hex-3-ene (2) was established by comparison of their ^1H n.m.r. spectra with those of the corresponding *erythro*-adducts.
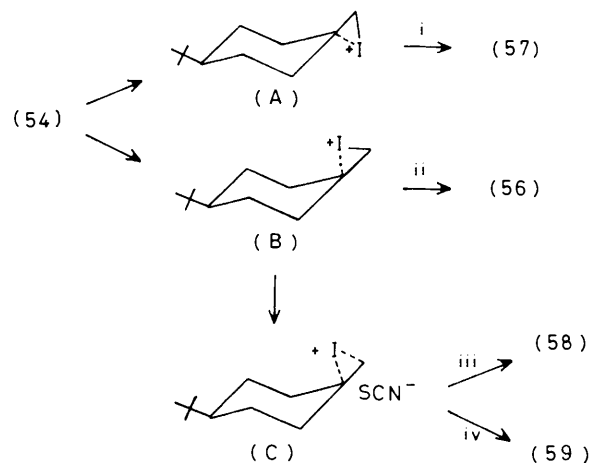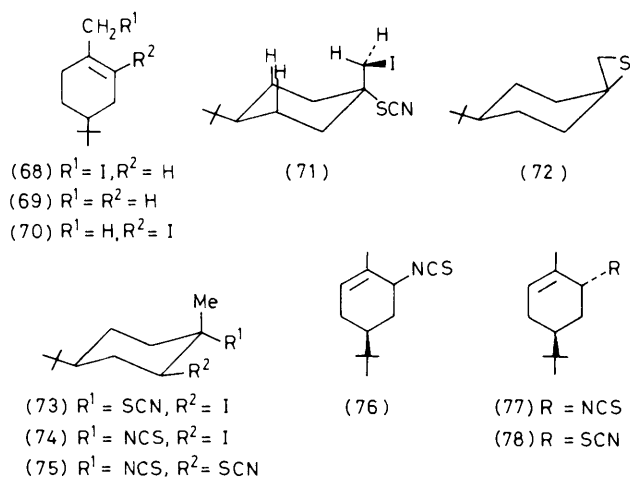
Table 6. Reactions of 1-methylene-4-t-butylcyclohexane with I_2–$(SCN)_2$

Reaction conditions [a,b]	Products and yields (%) [c]				
	(55) (56) (57)	(58)	(59)	(62) (63)	(68)
O_2, dark, r.t., 18 h [d]	48 (1.2 : 3 : 1)	8	7	3 (3 : 1)	1
N_2(O_2-free), u.v., r.t., 18 h	52 (1.2 : 3.5 : 1)	10	7	5 (3 : 1)	3
N_2(O_2-free), u.v., 37 °C, 40 min	63 (1.3 : 4 : 1)	12	15	10 (braced)	

[a] Molar ratio alkene (54) : I_2 : $(SCN)_2$ = 2 : 1.2 : 1.2. [b] In benzene under anhydrous conditions. [c] By p.l.c. and ^1H n.m.r. analysis. [d] Plus *ca.* 1% of 3 unidentified thiocyanogen adducts.

Thus, the ^1H n.m.r. spectrum of *threo*-3-iodo-4-thiocyanatohexane (51) exhibited an eight-line multiplet at δ_H 3.26 due to CHSCN and another eight-line multiplet at δ_H 4.35 due to CHI, the coupling constant between 3-H and 4-H being only 2.9 Hz compared with $J_{3,4}$ 9 Hz for the *erythro*-isomer. The ^1H n.m.r. spectrum of the isothiocyanate (52) showed multiplets at δ_H 3.32 and 4.05 but these were not sufficiently resolved to determine coupling constants. This was in contrast to the spectrum of the *erythro*-isomer which showed a clear eight-line pattern at δ_H 3.69 and a multiplet at δ_H 4.05 ($J_{3,4}$ 6.3 Hz).[2] Only one stereoisomer of each product was formed in the ionic reaction, consistent with a pathway involving a symmetrical bridged iodonium ion intermediate. The formation of both *erythro*- and *threo*-iodoisothiocyanates under the influence of u.v. light is consistent with a pathway involving an open thiocyanato-alkyl radical in which there is free rotation about the C(3)–C(4) bond (*cf.* ref. 28).

In order to gain insight into the stereochemical aspects of the addition to terminal alkenes, 1-methylene-4-t-butylcyclohexane (54) [29] was also treated with iodine–thiocyanogen under a variety of conditions (Table 6). A complex mixture of unstable compounds of almost identical product distribution was obtained in each case. The major fraction was a mixture of the isomeric *vic*-iodoisothiocyanates (55), (56), and (57). The ^1H n.m.r. spectrum showed singlets at δ_H 0.87 and 0.92 which were assigned to the methyl protons of t-butyl groups, these signals together integrating for nine protons. Of three singlets at δ_H 3.31, 3.47, and 4.02 integrating for a total of two protons, that at δ_H 3.47 was more intense than the other two which were of approximately equal intensity. The signals at δ_H 3.31 and 3.47 were assigned to CH_2I protons in accord with the appearance of two upfield triplets (δ_C 13.5 and 17.5) in the SFORD ^{13}C n.m.r. spectrum. The complexity of the latter spectrum was in accord with the presence of three components in the mixture, although the data for one component was obscured. Axial iodomethyl protons have been shown to be

(68) $R^1 = I, R^2 = H$
(69) $R^1 = R^2 = H$
(70) $R^1 = H, R^2 = I$

(71)

(72)

(73) $R^1 = SCN, R^2 = I$
(74) $R^1 = NCS, R^2 = I$
(75) $R^1 = NCS, R^2 = SCN$

(76)

(77) R = NCS
(78) R = SCN

Scheme 3. i, Axial attack of $(SCN)_2$; ii, equatorial attack of $(SCN)_2$ iii, collapse at C-2; iv, collapse at C-1

deshielded relative to equatorial iodomethyl protons and an inverse relationships exists for the corresponding carbon atoms.[29,31] On the assumption that the nature of the substituent geminal to an iodomethyl group does not affect these relationships, the major component (δ_C 13.5) was assigned the structure (56) while the isomer (57) contains an equatorial iodomethyl group (δ_C 17.5). As expected, the iodomethyl protons (δ_H 3.47) of the iodomethyl isothiocyanate (56) resonated downfield from those (δ_H 3.31) of its isomer (57) in the ^1H n.m.r. spectrum. The remaining signals in the ^1H and ^{13}C n.m.r. spectra were consistent with the assigned structures. In particular, the C-1 signal of compounds (55), (56), and (57) occurred as singlets near δ_C 60.0 in the SFORD ^{13}C n.m.r. spectrum. The remaining component (55), which did not show an iodomethyl carbon resonance, was one of the other vic-iodoisothiocyanates regioisomeric with the stereoisomers (56) and (57) but from present evidence it was not possible to define its stereochemistry.

1-Iodomethyl-t-4-t-butyl-r-1-thiocyanatocyclohexane (58) was identified similarly. Thus, the ^1H n.m.r. spectrum showed a two-proton singlet at δ_H 3.62 which was assigned to the protons of an iodomethyl group since the SFORD ^{13}C n.m.r. spectrum showed a triplet at δ_C 12.5. Because of steric factors the signals at δ_H 3.62 and δ_C 12.5 resonate at unusually low and high fields, respectively. In the favoured rotamer (71), repulsive interaction of one of the methylene protons with axial ring protons at C-3 and C-5 will polarise the local electron clouds such that the electron density on the iodomethyl carbon will be increased and that on the protons of this group will be decreased, the 1,3-diaxial interaction being increased by the bulky geminal thiocyanato-group. Thus, the axial iodomethyl carbon is shielded relative to the equatorial carbon of compounds (56) and (60)[29] and the iodomethyl protons are more deshielded.

A further product was identified as r-1-iodo-c-4-t-butyl-1-thiocyanatomethylcyclohexane (59). Although a two-proton singlet at δ_H 3.78 in the ^1H n.m.r. spectrum was uncharacteristically far downfield for CH_2SCN protons, the SFORD ^{13}C n.m.r. spectrum showed that the compound was not a primary iodide since an upfield triplet was absent. The stereochemistry could not be established from spectral evidence since the isomer (61) was not available for comparison. However, the equatorial conformation and thus α-configuration of the CH_2SCN group of (59) was established by its conversion into the trans-thiiran (72) in a stereospecific manner.[32]

In addition to a mixture of six minor compounds which were not examined further but which were recognised from their spectral properties as resulting from the addition of

thiocyanogen to the alkene, three further compounds with high R_F values were isolated. One, obtained pure by p.l.c., was the allylic iodide (68). The remaining high R_F band from p.l.c. contained a mixture (3 : 1) of r-1-iodo-t-2-isothio-cyanato-2-methyl-t-5-t-butylcyclohexane (62) and r-1-iodo-t-2-isothiocyanato-1-methyl-c-4-t-butylcyclohexane (63), the components of which were identified by comparison with the products from the addition of iodine-thiocyanogen to 1-methyl-4-t-butylcyclohexene (69) (see later). The compounds (62) and (63) arise by isomerization of the exocyclic alkene (54) to the thermodynamically more stable endocyclic alkene (69) and then addition of iodine-thiocyanogen. In an experiment designed to assess the stability of the di-iodide (64), treatment of the alkene (54) with an equimolar amount of iodine in carbon tetrachloride for 48 h gave, as the major product, the tetra-substituted vinylic iodide (70), which arose from (69) via an addition-elimination sequence.

Although the addition of iodine-thiocyanogen to compound (54) in the dark gave a complex mixture, a measure of regio- and stereo-selectivity was observed, the results being consistent with initial preferential delivery of electrophilic iodine from the axial direction to give the cis-iodonium ion (B) (Scheme 3). Equatorial attack would give the trans-iodonium ion (A), the intervention of bridged intermediates accounting for the observed lack of regiospecificity in the formation of compounds (56) and (57). Although the stereochemistry of (55) is not known, the compound must be formed by attack of thiocyanogen on the terminal carbon of an iodonium ion. However, compounds (58) and (59) could arise from attack of a thiocyanate ion on the cis-iodonium ion (B) in which the steric strain resulting from interaction of the axial iodine atom with the axial ring protons on C-3 and C-5 is relieved by formation of an ion pair (C). Collapse of the latter at C-2 and C-1 would give products (58) and (59) respectively. β-Elimination of the axial proton on C-2 (or C-6) in the cis-iodonium ion would account for formation of the allylic iodide (68).

Although the ionic reaction of iodine-thiocyanogen with 1-methylene-4-t-butylcyclohexane (54) occurs very rapidly, almost to the exclusion of the radical pathway, reaction under more intense u.v. radiation for a shorter period resulted in a significant increase in the proportion of compound (59). Thus, some of this product is likely to arise via a competing radical process. Since none of the axial thiocyanatomethyl derivative (61) was formed, delivery of the iodine atom on a 4-t-butylcyclohexyl radical at C-1 must occur exclusively
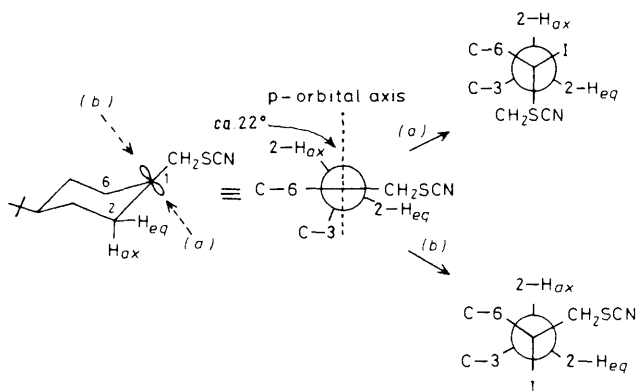
Scheme 4. (a) Pseudo-equatorial attack; (b) pseudo-axial attack

Scheme 5. i, Axial attack; ii, equatorial attack

Table 7. Reactions of 1-methyl-4-t-butylcyclohexene with I_2–$(SCN)_2$

| Reaction conditions[a,b]	Products and yields (%)[c]							
	(62) (63)	(73)	(76) (77)	(74)	(65) (66)	(67)	(75)
N_2, dark, 1 h	78 (1.8 : 1)	Trace	3 (1 : 1)	5	4 (1.2 : 1)	2	2
N_2, u.v., 1 h	48 (1.8 : 1)	2	2 (1 : 1)	4	17 (4 : 1)	2	0.5

[a] Molar ratio alkene (69) : I_2 : $(SCN)_2$ = 2 : 1.2 : 1.2. [b] In benzene under anhydrous conditions. [c] By p.l.c. and ^1H n.m.r. analysis.

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from the pseudo-axial face. As in the case of halogen transfer to the 4-t-butylcyclohexyl radical,[33] and of addition of iodine(I) azide to the alkene (54) under free radical conditions,[29]* this preferred attack along a pseudo-axial direction to a planar site can be attributed to torsional effects.[34] Pseudo-equatorial approach of iodine(I) thioycanate requires that the thiocyanato-group on C-1 must eclipse the equatorial proton on C-2 as rehybridisation to tetrahedral geometry occurs, thereby introducing torsional strain along the pathway leading to (61) (Scheme 4). In contrast, an analogous interaction is not predicted when iodine(I) thiocyanate approaches from the pseudo-axial direction.

In order to confirm the identity and source of products (62) and (63), the action of iodine–thiocyanogen on 1-methyl-4-t-butylcyclohexene (69) was also investigated (Table 7). The regioisomers (62) and (63) were identified from their spectral properties. The presence of two methyl singlets at δ_H 1.60 and 2.21 in the ^1H n.m.r. spectrum of the mixture indicated the presence of two regioisomers while narrow $W_{\frac{1}{2}}$ values (6 and 8 Hz) for downfield multiplets at δ_H 4.58 [CHI of (62)] and δ_H 4.18 [CHN of (63)] suggested that they arose from equatorial protons. The assignments are consistent with the relative positions of the methyl signals, that (δ_H 2.21) of compound (63) being shifted downfield relative to that (δ_H 1.60) of its isomer (62) in accord with similar shifts for corresponding products from the addition of iodine(I) acetate to the same substrate.[35] In the ^{13}C n.m.r. spectrum the methyl group carbon atoms resonated downfield at δ_C 32.3 and 35.7, suggesting that both groups were equatorial.

A minor product (74) had i.r. and mass spectra similar to those of the mixture of the iodoisothiocyanates (62) and (63).

* Although the Newman projections in Scheme 4 of ref. 29 are mistakenly represented as the enantiomers of the natural configuration, the argument remains valid.
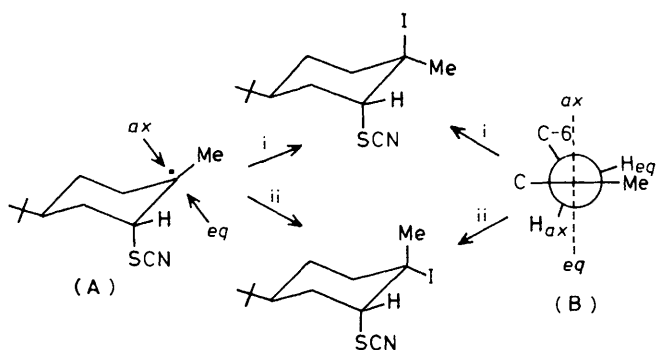
The ^1H n.m.r. spectrum showed a methyl singlet at δ_H 1.58 and a doublet of doublets at δ_H 4.37 (J 12 and 4 Hz) due to the proton geminal to the iodine atom. The methyl-group carbon atom resonated upfield in the ^{13}C n.m.r. spectrum at δ_C 23.9 suggesting that the group suffered 1,3-diaxial interactions with the C-3 and C-5 ring protons, and it was therefore assigned an axial conformation.

The iodothiocyanates (65) and (66) were obtained as an unstable inseparable oil, the stereochemistry assigned (see Experimental section) being that expected from *anti*-addition. The allylic isothiocyanates (76) and (77), formed as minor products, were also obtained as an inseparable mixture. The i.r. spectrum showed two isothiocyanate absorptions (2 050 and 2 070 cm^{-1}) while peaks at δ_H 1.82 (CH$_3$), 4.01 (CHNCS), and 5.57 (CH=) confirmed the allylic nature of these compounds.

A further minor product (73) gave i.r. and mass spectra which were consistent with its formulation as a *vic*-iodothiocyanate. In its ^1H n.m.r. spectrum, a methyl proton singlet resonated at δ_H 1.63, and the presence of an axial CHI proton was indicated by a doublet of doublets at δ_H 4.50 ($J_{ax;ax}$ 12 Hz and $J_{ax;eq}$ 4 Hz). Insufficient material was isolated to enable ^{13}C n.m.r. analysis to assist in the determination of the stereochemistry and it was assigned a diequatorial structure on the assumption of *anti*-addition. Even so, regardless of whether the thiocyanato-group was axial or equatorial, the presence of an equatorial iodo-group is unexpected if the compound arises by a radical mechanism. In the latter case, its formation would involve a secondary radical as an intermediate whereas formation of a more stable tertiary radical is possible. Moreover, torsional strain effects would favour axial attack at a planar radical site.

Two minor products, *viz.* (67) and (75) (see Experimental section), arising from the addition of thiocyanogen to the alkene were detected and again the stereochemistry about C-1 and C-2 was assigned on the basis that addition occurs in the expected *anti*-manner.

The increase in the yield of the *trans*-diaxial product (65) when the addition of iodine–thiocyanogen to the alkene (69) was carried out in u.v. light can be explained if a radical mechanism operates (*cf.* ref. 30). Attack by a thiocyanato-radical would give the more stable, conformationally biased, tertiary cyclohexyl radical. Approach to a planar radical site could occur from a pseudo-axial or -equatorial direction but the latter is not favoured since this would lead to strong eclipsing between the thiocyanato-group and the iodine atom [Scheme 5, conformation (A)]. Moreover, torsional strain is greatest when the methyl group eclipses the equatorial protons on the adjacent carbons during equatorial approach [Scheme 5, *e.g.* projection (B)].

The predominance of the *vic*-iodoisothiocyanates as products from reactions carried out both in the dark and under

i   ii

(SCN)₂   (62)

(A)

SCN⁻   (66)

(SCN)₂   (63)

SCN⁻   (65)

i   ii

(B)

SCN⁻   (SCN)₂

(73)   (74)
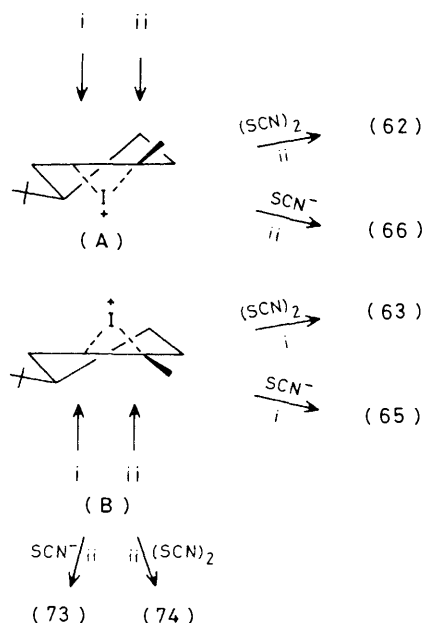
Scheme 6. i, Ring-opening at secondary site; ii, ring-opening at tertiary site

Table 8. Relative rates of ionic and radical reactions of I_2–$(SCN)_2$

Compound	Rel rate (in HOAc)	Radical/ionic
(32)	0.046	6
(8)	0.089	10
(23)	0.26	3
(1)	0.94	0.25
(48)	1.00	0.25
(2)	1.7	0.1
(39)	Slow	3.5

u.v. irradiation is consistent with an ionic reaction in each case wherein trans-diaxial opening by a nitrogen nucleophile would give compound (62) from a trans-iodonium ion (A) (Scheme 6) and its isomer (63) from a cis-iodonium ion (B). The predominance (1.8 : 1) of Markownikov over anti-Markownikov vic-iodoisothiocyanate formation is a consequence of preferred opening of the trans-iodonium ion at the tertiary site (pathway ii). A similar preference for trans-diaxial opening of a trans-onium ion is observed in the oxymercuriation,[30] methoxybromination,[36] and acetoxyiodination[36] of the same substrate (69). The vic-iodothiocyanates could also be formed from the intermediates (A) and (B) (Scheme 6) but in this case steric factors outweigh electronic considerations resulting in a slight predominance of the anti-Markownikov isomer (65) over the Markownikov isomer (66). Diequatorial attack on intermediates (A) and (B) is not favoured since this would involve a boat-like transition state. However, since equatorial opening of the cis-iodonium ion (B) could involve attack at a tertiary centre, this could overcome energy constraints leading to the formation of compounds (74) and (73) (cf. ref. 36).

The allylic isothiocyanates (76) and (77) may arise via rearrangement of the allylic thiocyanate (78) which in turn may be formed by elimination of hydrogen iodide from the vic-iodothiocyanate (65). If, as seems likely, compound (78) rearranges via a cyclic transition state directly to the stereoisomer (76), an equilibrium must then be established between (76) and (77). The alternative explanation that (78) rearranges

via an ion-pair mechanism to give both stereoisomers (76) and (77) is unlikely since allylic thiocyanates are known to undergo a 1,3-rearrangement.

Finally, the relative rates of Pritzkow et al.[37] for the addition[26] of ' ISCN ' in acetic acid to various alkenes (Table 8) show a trend which is roughly parallel to the ratio of radical to ionic products observed in the present work. Thus alkenes such as (Z)- and (E)-hex-3-ene and cyclohexene which react rapidly with iodine–thiocyanogen show little evidence of reaction by radical processes under the influence of u.v. light. However, radical reactions compete successfully in the cases of 3,3-dimethylbutene, 4-methylpent-1-ene, etc., where the ionic reactions are relatively sluggish.

Experimental

General experimental details are given in ref. 38. Ether refers to diethyl ether.

General Procedure for the Reactions of Alkenes with Iodine–Thiocyanogen.—Reactions were carried out under a dry atmosphere in three-necked flasks equipped with a magnetic stirrer bar, a septum, gas inlet, and a bubbler. All glassware was oven-dried, assembled hot, and allowed to cool under a dry gas stream before use. Dry deoxygenated nitrogen was obtained by sequential passage through two aqueous chromium-(II) chloride solutions, two wash bottles containing concentrated sulphuric acid, and then over solid potassium hydroxide. Where necessary, exposure to laboratory light was avoided by wrapping the flask in aluminium foil. Irradiation was carried out using an Engelhard Hanovia 125-W medium-pressure mercury lamp surrounded by a Pyrex cooling jacket placed at a distance of 15 cm from the reaction flask. Benzene and acetic acid were dried and redistilled before use; for reactions conducted under u.v. irradiation, solvents were deoxygenated by bubbling oxygen-free nitrogen through them for 15 min immediately prior to use. Alkenes were passed through a column of activated alumina and distilled before use.

Solutions of thiocyanogen were prepared by adding bromine (0.125 ml, 2.44 mmol) dropwise with stirring to a suspension of freshly prepared dry lead(II) thiocyanate[39] (1.5 g, 4.64 mmol) in dry benzene (11 ml) at room temperature under nitrogen in the dark. Stirring was stopped after 15 min, the solids were allowed to settle, and the supernatant solution was transferred by a nitrogen-flushed syringe bearing a stainless-steel needle. Iodometric analyses of 3-ml aliquots gave a value of 0.22 mmol ml⁻¹; therefore 7.5 ml contained 1.65 mmol of thiocyanogen. Larger-scale preparations were carried out by adjusting the above amounts and increasing the volume of solvent in proportion so that the concentration of thiocyanogen was maintained at 0.22 mmol ml⁻¹. The solution of thiocyanogen (pale yellow in benzene; pale burgundy in acetic acid) was transferred to another three-necked flask containing iodine (1 mol equiv.) under a dry atmosphere and the mixture was stirred for 15 min. The alkene was then added dropwise through the septum with a nitrogen-flushed syringe and stirring was continued for up to 18 h. The pre-mixing step and the reaction itself was carried out either in the dark, or under an atmosphere of oxygen-free nitrogen with irradiation by u.v. light. Reactions were worked up by diluting with benzene, washing the organic layer with water (some polymerisation of thiocyanogen occurred at this stage; filtration through silicone-treated paper facilitated separation of the polymer from the benzene solution), aqueous sodium hydrogen sulphite, aqueous saturated sodium hydrogen carbonate, and brine. Solvent was removed from the dried ($MgSO_4$) solution by evaporation under reduced pressure.

Reactions of 4-Methylpent-1-ene with Iodine–Thiocyanogen.—(a) In the dark under nitrogen. A mixture of a solution of thiocyanogen in benzene (30 ml, 0.22 mmol ml^{-1}), iodine (1.68 g, 6.62 mmol), and 4-methylpent-1-ene (8) (1.39 ml,10.95 mmol) was stirred in the dark at room temperature for 18 h. Work-up gave a yellow oil (2.80 g, 95%) which after p.l.c. (hexane–chloroform, 3 : 1) yielded (i) 1,2-di-iodo-4-methylpentane (15) (37 mg, 1%) (see below); (ii) a mixture (2 : 1) (1.43 g, 49%) of 1-*iodo-2-isothiocyanato-4-methylpentane* (11) and 2-*iodo-1-isothiocyanato-4-methylpentane* (12) as an oil, b.p. (Kugelrohr) 80 °C at 0.2 mmHg (Found: C, 31.6; H, 4.5; N, 5.2. C$_7$H$_{12}$INS requires C, 31.2; H, 4.5; N, 5.2%); $\nu_{max.}$ 2 060 cm^{-1} (NCS); δ_H 1.00 [d, J 5.5 Hz, overlapping 4-CH$_3$ and 5-H$_3$ of (11) and (12)], 1.35—2.30 [m, overlapping 3-H$_2$ and 4-H of (11) and (12)], 3.35 [d, J 5.5 Hz, CH$_2$I of (11)], and 3.59—4.36 [m, overlapping CHNCS of (11), and CH$_2$NCS and CHI of (12)]; δ_C (11) 9.1 (C-1), 21.5 (C-5), 22.8 (C-6), 25.1 (C-4), 45.0 (C-3), 57.1 (C-2), and 133 p.p.m. (NCS); δ_C (12) 20.8 (C-5), 22.7 (C-6), 28.1 (C-4), 28.9 (C-2), 46.0 (C-3), 53.7 (C-1), and 133 (NCS); m/z 269 ($M^{+\cdot}$), 211 ($M^{+\cdot}$ – NCS$^\cdot$), and 142 ($M^{+\cdot}$ – I$^\cdot$); (iii) 3-iodo-2-isothiocyanato-4-methylpentane (22) (41 mg, 1%) as a yellow oil; $\nu_{max.}$ 2 070 cm^{-1} (NCS); δ_H 1.07, 1.10 (2 d, J 6, 6 Hz, 5-H$_3$ and 4-CH$_3$), 1.48 (d, $J_{1,2}$ 6 Hz, 1-H$_3$), 1.62—2.10 (m, 4-H), and 3.37—4.00 (m, overlapping CHI and CHNCS); δ_C 22.2 and 22.5 (C-5 and 4-CH$_3$), 23.8 (C-1), 29.7 (C-3), 34.1 (C-4), and 52.4 p.p.m. (C-2); m/z 269 ($M^{+\cdot}$), 211 ($M^{+\cdot}$ – NCS$^\cdot$), 142 ($M^{+\cdot}$ – I$^\cdot$), and 86 (C$_3$H$_4$NS$^{+\cdot}$ 100%); (iv) a mixture (1.6 : 1) (0.49 g, 17%) of (9) and (10) which was separated by multiple elution p.l.c. (hexane–chloroform, 3 : 1) to give 2-*iodo-4-methyl-1-thiocyanatopentane* (9) as an oil, b.p. (Kugelrohr) 50 °C at 0.2 mmHg (Found: C, 31.5; H, 4.8; N, 5.2. C$_7$H$_{12}$INS requires C, 31.2; H, 4.5; N, 5.2%); $\nu_{max.}$ 2 160 cm^{-1} (SCN); δ_H 0.96, 1.06 (2 d, J 6, 6 Hz, overlapping 5-H and 4-CH$_3$), 1.45—2.16 (m, 3-H$_2$ and 4-H), 3.37, 3.68 [2 (d × d), $J_{1a,2}$ 8.5 Hz, $J_{1b,2}$ 5.7 Hz, $J_{1a,1b}$ 13.6 Hz, 1-H$_a$ and 1-H$_b$), and 4.29 (m, 2-H); δ_C 20.6 (C-5), 22.8 (C-6), 28.4 (C-4), 29.6 (C-2), 43.7 (C-1), 46.8 (C-3), and 111.1 p.p.m. (SCN); m/z 269 ($M^{+\cdot}$), 211 ($M^{+\cdot}$ – SCN$^\cdot$), and 142 ($M^{+\cdot}$ – I$^\cdot$); and 1-*iodo-4-methyl-2-thio-cyanatopentane* (10) as an oil, b.p. (Kugelrohr) 50 °C at 0.2 mmHg (Found: C, 31.4; H, 4.7; N, 5.5. C$_7$H$_{12}$INS requires C, 31.2; H, 4.5; N, 5.2%); $\nu_{max.}$ 2 160 cm^{-1} (SCN); δ_H 0.98, 1.04 (2 d, J 6, 5 Hz, 5-H$_3$ and 4-CH$_3$), 1.33—2.17 (m, 3-H$_2$ and 4-H), and 3.03—3.93 (m, CH$_2$I and CHSCN); δ_C 9.6 (C-1), 21.2 (C-5 and C-6), 25.7 (C-4), 43.0 (C-3), 49.1 (C-2), and 110.0 p.p.m. (SCN); m/z 269 ($M^{+\cdot}$), 211 ($M^{+\cdot}$ – SCN$^\cdot$), and 142 ($M^{+\cdot}$ – I$^\cdot$); and (v) a mixture (0.14 g, 7%) containing mainly 2-isothiocyanato-4-methyl-1-thiocyanatopentane (13) as a yellow oil, $\nu_{max.}$ 2 050 (NCS), and 2 160 cm^{-1} (SCN); δ_H 1.03 (d, J 6 Hz, 4-CH$_3$ and 5-H$_3$), 1.40—2.25 (m, 3-H$_2$ and 4-H), 3.00—3.32 (m, CH$_2$SCN), and 3.78—4.40 (m, CHNCS); δ_C 21.3; 22.9 (C-5 and 4-CH$_3$), 25.3 (C-4), 39.3 (C-1), 43.7 (C-3), and 56.4 p.p.m. (C-2).

Only the iodothiocyanate (9) (0.17 g) was recovered (58%) when it was stirred with iodine (0.42 g) and a solution of thiocyanogen in benzene (7.5 ml, 0.22 mmol ml^{-1}) in the dark at room temperature for 18 h. For other reactions in the dark, see Table 1.

(b) Under irradiation by u.v. light. A mixture of a solution of thiocyanogen in benzene (7.5 ml, 0.22 mmol ml^{-1}), iodine (0.42 g, 1.65 mmol), and 4-methylpent-1-ene (348 μl, 2.75 mmol) was stirred under u.v. light at room temperature for 18 h. Work-up gave a yellow oil (0.74 g), p.l.c. of which yielded (i) 1,2-di-iodo-4-methylpentane (15) (58 mg, 6%); (ii) a mixture (2 : 1) (56 mg, 8%) of 1-iodo-2-isothiocyanato-4-methylpentane (11) and 2-iodo-1-isothiocyanato-4-methyl-pentane (12); (iii) 3-iodo-2-isothiocyanato-4-methylpentane (22) (11 mg, 1%); (iv) 2-iodo-4-methyl-1-thiocyanatopentane

(9) (0.59 g, 80%); and (v) 4-methyl-1,2-dithiocyanatopentane (14) (14 mg, 3%).

The iodothiocyanate (9) (0.14 g) was recovered (99%) when it was treated with iodine (0.42 g) and a solution of thiocyanogen in benzene (7.5 ml) under the above conditions for 18 h.

1,2-Di-iodo-4-methylpentane (15).—A mixture of 4-methyl-pent-1-ene (8) (0.67 g, 8.0 mmol) and iodine (4.8 g, 18.9 mmol) in chloroform (30 ml) was stirred under laboratory fluorescent light at room temperature for 5 h. Work-up yielded 1,2-di-iodo-4-methylpentane (2.27 g, 84%) as a brown oil; δ_H 0.90, 1.03 (2 d, J 6, 6 Hz, 5-H$_3$ and 4-CH$_3$), 1.50—2.00 (m, 3-H$_2$ and 4-H), 3.61 (d × d, $J_{1a,1b}$ 12.5 Hz, $J_{1a,2}$ 9.5 Hz, 1-H$_a$), and 3.96—4.50 (m, 1-H$_b$ and 2-H); δ_C 14.8 (C-1), 20.3, 23.1 (C-5 and C-6), 28.6 (C-4), 32.1 (C-2), and 48.2 p.p.m. (C-3); m/z 127 (I$^+$) and 254 (I$_2^{+\cdot}$).

A heterogeneous mixture of the di-iodide (15) (99 mg, 0.29 mmol) and anhydrous sodium thiosulphate (88 mg, 0.56 mmol) in [^{2}H$_6$]dimethyl sulphoxide (1.0 ml) was shaken at room temperature for 15 min. ^{1}H N.m.r. analysis of the supernatant solution showed that only the alkene (8) was present.

Reaction of the Di-iodide (15) *with Potassium Thiocyanate.*— A mixture of the di-iodide (15) (0.32 g, 0.9 mmol), potassium thiocyanate (0.50 g, 5 mmol), and Adogen 464 (30 mg) in chloroform–water (4 : 1; 10 ml) was stirred rapidly at room temperature for 24 h. Work-up gave a yellow precipitate and an almond smell characteristic of polymeric thiocyanogen. Removal of the solvent gave a brown oil (0.11 g) which on p.l.c. (hexane–chloroform, 2 : 1) yielded a mixture (2.4 : 1) (20 mg, 8%) of 2-iodo-4-methyl-1-thiocyanatopentane (9) and 1-iodo-4-methyl-2-thiocyanatopentane (10) (correct ^{1}H n.m.r. and i.r. spectra), and three minor unidentified compounds.

Reactions of the Di-iodide (15) *with Thiocyanogen.*—1,2-Di-iodo-4-methylpentane (1.0 g) in benzene (0.5 ml) was added to a solution of thiocyanogen in benzene (7.5 ml, 0.22 mol l^{-1}) and the mixture was stirred in the dark under nitrogen for 18 h. Work-up gave an oil (0.24 g), p.l.c. of a portion (0.21 g) of which yielded (i) 1,2-di-iodo-4-methylpentane (15) (65 mg, 31%); (ii) a mixture (2 : 1) (40 mg, 25%) of 1-iodo-2-isothio-cyanato-4-methylpentane (11) and 2-iodo-1-isothiocyanato-4-methylpentane (12); and (iii) a mixture (1.9:1) (17 mg, 11%) of 2-iodo-4-methyl-1-thiocyanatopentane (9) and 1-iodo-4-methyl-2-thiocyanatopentane (10).

The reaction was repeated in the presence of activated silica gel D.G. (1.0 g). Work-up gave an oil (0.63 g), p.l.c. of a portion (0.53 g) of which yielded (i) a mixture (1.6 : 1) (0.11 g, 18.5%) of the *vic*-iodoisothiocyanates (11) and (12); (ii) a mixture (1.6:1) (0.33 g, 53%) of the *vic*-iodothio-cyanates (9) and (10); and (iii) 4-methyl-1,2-dithiocyanato-pentane (14) (26 mg, 6%).

Reactions of Oct-1-ene with Iodine–Thiocyanogen.—(a) In the dark under nitrogen. A mixture of a solution of thio-cyanogen in benzene (7.5 ml, 0.22 mmol ml^{-1}), iodine (0.42 g, 1.65 mmol), and oct-1-ene (23) (432 μl, 2.75 mmol) was stirred in the dark under oxygen-free nitrogen at room temperature for 18 h. Work-up gave a yellow oil (0.83 g), p.l.c. (hexane–chloroform, 3 : 1) of a portion (0.62 g) of which yielded (i) 1,2-di-iodo-octane (31) (33 mg, 4%); δ_H 0.63—2.27 (m, overlapping 3-, 4-, 5-, 6-, 7-H$_2$ and 8-H$_3$), 3.63 (d × d, $J_{1a,1b}$ 12.5 Hz, $J_{1a,2}$ 9.5 Hz, 1-H$_a$), and 3.93—4.61 (m, over-lapping 1-H$_b$ and 2-H); (ii) a mixture (2 : 1) (0.34 g, 55%) of 1-*iodo-2-isothiocyanato-octane* (26) and 2-*iodo-1-isothio-cyanato-octane* (27) as an oil, b.p. (Kugelrohr) 35 °C at 0.04 mmHg (Found: C, 36.4; H, 5.5; N, 4.8. C$_9$H$_{16}$INS requires C,

36.4; H, 5.4; N, 4.7%); $\nu_{max.}$ 2 060 cm^{-1} (NCS); δ_H 0.91 (t, 8-H$_3$), 1.10—2.10 (m, overlapping 3-, 4-, 5-, 6-, and 7-H$_2$), 3.32 [d, J 6 Hz, CH$_2$I of (26)], and 3.50—4.30 [m, overlapping CHNCS of (26), CH$_2$NCS and CHI of (27)]; δ_C (26) 8.8 (C-1), 14.0 (C-8), 22.4 (C-7), 25,6 (C-4), 28.4 (C-5), 31.4 (C-6), 36.1 (C-3), 58.8 (C-2), and 133.4 p.p.m. (NCS); δ_C (27) 30.5 (C-2), 53.2 (C-1) and 133.4 p.p.m. (NCS); m/z 297 ($M^{+\cdot}$), 239 ($M^{+\cdot}$ — NCS$\cdot$), and 170 ($M^{+\cdot}$ — I$\cdot$); (iii) a mixture (1.5 : 1) (0.11 g, 18%) of (24) and (25) as a yellow oil which was separated by multiple elution p.l.c. [hexane ($\times$2), hexane–chloroform, 5 : 1 ($\times$2), and hexane–chloroform, 3 : 1] to give 2-*iodo*-1-*thiocyanato-octane* (24) as an oil, b.p. (Kugel-rohr) 90 °C at 0.2 mmHg (Found: C, 36.7; H, 5.4; N, 4.7. C$_9$H$_{16}$INS requires C, 36.4; H, 5.4; N, 4.7%); $\nu_{max.}$ 2 155 cm^{-1} (SCN); δ_H 0.90 (t, 8-H$_3$), 1.08—2.17 (m, 3-, 4-, 5-, 6-, and 7-H$_2$), 3.36, 3.62 (2 d $\times$ d, $J_{1a,1b}$ 13.3 Hz, $J_{1a,2}$ 8.5 Hz, $J_{1b,2}$ 5.5 Hz, 1-H$_a$ and 1-H$_b$), and 4.00—4.50 (m, 2-H); δ_C 14.0 (C-8), 22.4 (C-7), 28.1 (C-6), 29.0 (C-5), 31.2 (C-2), 31.4 (C-4), 37.5 (C-3), 43.0 (C-1), and 111.1 p.p.m. (SCN); m/z 297 ($M^{+\cdot}$), 239 ($M^{+\cdot}$ — SCN$\cdot$), and 170 ($M^{+\cdot}$ — I$\cdot$); and 1-*iodo*-2-*thiocyanato-octane* (25) as an oil, b.p. (Kugelrohr) 40 °C at 0.05 mmHg (Found: C, 36.5; H, 5.6; N, 4.8. C$_9$H$_{16}$-INS requires C, 36.4; H, 5.4; N, 4.7%); $\nu_{max.}$ 2 155 cm^{-1}; δ_H 0.92 (t, 8-H$_3$), 1.11—2.37 (m, 3-, 4-, 5-, 6-, and 7-H$_2$), and 3.00—3.86 (m, overlapping CH$_2$I and CHSCN); δ_C 8.9 (C-1), 14.0 (C-8), 22.4 (C-7), 26.5 (C-5), 28.4 (C-4), 31.3 (C-6), 34.1 (C-3), 50.9 (C-2), and 110.2 p.p.m. (SCN); m/z 297 ($M^{+\cdot}$), 239 ($M^{+\cdot}$ — SCN$\cdot$), and 170 ($M^{+\cdot}$ — I$\cdot$); (iv) a mixture (22 mg, 5%) containing *vic*-isothiocyanato-thiocyanates (29) and (30) and the *vic*-1,2-dithiocyanate (28); $\nu_{max.}$ 2 053 (NCS) and 2 157 cm^{-1} (SCN); δ_H 0.68—2.10 (m, overlapping 8-H$_3$ and 3-, 4-, 5-, 6-, and 7-H$_2$), and 3.05—4.30 (m, overlapping CHSCN, CH$_2$NCS, CHNCS, and CH$_2$SCN). The presence of all these compounds was deduced from the complexity of the spectrum, and by comparison with the ^{1}H n.m.r. and i.r. data of similar compounds.[16]

For other reactions in the dark see Table 2.

(b) *Under irradiation by u.v. light.* A mixture of a solution of thiocyanogen in benzene (7.5 ml, 0.22 mmol ml^{-1}), iodine (0.42 g, 1.65 mmol), and oct-1-ene (430 μl, 2.75 mmol) was stirred under u.v. light at room temperature for 19 h. Work-up gave an oil (0.86 g), p.l.c. of a portion (0.74 g) of which yielded (i), 1,2-di-iodo-octane (31) (5 mg, 1%); (ii) a mixture (2 : 1) (0.14 g, 20%) of the *vic*-iodo-isothiocyanates (26) and (27); (iii) 2-iodo-1-thiocyanato-octane (24) (0.45 g, 64%); and (iv) 1,2-dithiocyanato-octane (28) (29 mg, 5%); $\nu_{max.}$ 2 155 cm^{-1} (SCN); δ_H 0.70—2.30 (m, overlapping CH$_3$ and CH$_2$), 3.20—3.40 (m, overlapping CHSCN and CH$_2$SCN) (*cf.* ref. 16).

For other reactions under u.v. light see Table 2.

Reactions of 3,3-*Dimethylbut*-1-*ene with Iodine–Thiocyanogen.*—(a) *Under irradiation by u.v. light.* A mixture of a solution of thiocyanogen in benzene (7.5 ml, 0.22 mmol ml^{-1}), iodine (0.42 g, 1.65 mmol), and 3,3-dimethylbut-1-ene (32) (360 μl, 2.79 mmol) was stirred under u.v. light at room temperature for 17 h. Work-up gave a pale yellow oil (0.73 g), p.l.c. (hexane–chloroform, 2 : 1) of a portion (0.66 g) of which yielded (i) 1-iodo-2-isothiocyanato-2,3-dimethylbutane (38) as a yellow oil (14 mg, 2%); $\nu_{max.}$ 2 095 cm^{-1} (NCS); δ_H 0.98, 1.03 (2 d, J 6.5, 6.5 Hz, 4-H$_3$ and 3-CH$_3$), 1.45 (s, 2-CH$_3$), 2.02 (septet, J 6 Hz, 3-H), and 3.42 (s, CH$_2$I); m/z 269 ($M^{+\cdot}$), 211 ($M^{+\cdot}$ — NCS$\cdot$, 100%), and 142 ($M^{+\cdot}$ — I$\cdot$); (ii) 2-*iodo*-1-*isothiocyanato*-3,3-*dimethylbutane* (34) (79 mg, 12%) as a malodorous oil, b.p. (Kugelrohr) 35 °C at 0.04 mmHg (Found: C, 31.5; H, 4.5; N, 5.3. C$_7$H$_{12}$INS requires C, 31.2; H, 4.5; N, 5.2%); $\nu_{max.}$ 2 070 cm^{-1} (NCS); δ_H 1.17 (s, CMe$_3$) and 3.83—4.23 (m, overlapping CH$_2$NCS and CHI); δ_C 28.5 (C-4,

and 3-Me$_2$), 35.2 (C-3), 48.6 (C-2), 51.0 (C-1), and 133.2 p.p.m. (NCS); m/z 269 ($M^{+\cdot}$), 211 ($M^{+\cdot}$ — NCS$\cdot$), and 142 ($M^{+\cdot}$ — I$\cdot$, 100%); (iii) 2-*iodo*-3,3-*dimethyl*-1-*thiocyanato-butane* (33) (0.52 g, 77%), which crystallised from hexane as large malodorous plates, m.p. 38.5—39 °C (Found: C, 31.3; H, 4.6; N, 5.3. C$_7$H$_{12}$INS requires C, 31.2; H, 4.5; N, 5.2%); $\nu_{max.}$ 2 160 cm^{-1} (SCN); δ_H 1.18 (s, CMe$_3$), 3.26, 3.73 (2 d $\times$ d, $J_{1a,1b}$ 14 Hz, $J_{1a,2}$ 11 Hz and $J_{1b,2}$ 3 Hz, 1-H$_a$ and 1-H$_b$), and 4.18 (d $\times$ d, $J_{1a,2}$ 11 Hz and $J_{1b,2}$ 3 Hz, 2-H); δ_C 28.2 (C-4, 3-Me$_2$), 36.5 (C-3), 42.4 (C-1), 50.7 (C-2), and 111.5 p.p.m. (SCN); m/z 269 ($M^{+\cdot}$), 211 ($M^{+\cdot}$ — SCN$\cdot$), 142 ($M^{+\cdot}$ — I$\cdot$), and 83 (C$_6$H$_{11}^+$, 100%); and (iv) unidentified material (15 mg).

(b) *In the dark under oxygen.* A mixture of a solution of thio-cyanogen in oxygenated benzene (7.6 ml, 0.22 mmol ml^{-1}), iodine (0.43 g, 1.69 mmol), and 3,3-dimethylbut-1-ene (360 μl, 2.79 mmol) was stirred in the dark under dry oxygen for 18 h. Work-up gave a pale yellow oil (0.51 g), p.l.c. of a portion (0.42 g) of which yielded (i) a mixture (20 : 1) (0.26 g, 42%) of 2-iodo-1-isothiocyanato-3,3-dimethylbutane (33) and 1-iodo-2-isothiocyanato-2,3-dimethylbutane (38); and (ii) 2-iodo-3,3-dimethyl-1-thiocyanatobutane (33) (59 mg, 10%).

Reaction of 5α-*Androst*-2-*ene with Iodine–Thiocyanogen.*— (a) *In the dark.* A mixture of a solution of thiocyanogen in benzene (4.2 ml, 0.22 mmol ml^{-1}), iodine (0.24 g, 0.94 mmol), and 5α-androst-2-ene (39) (0.40 g, 1.55 mmol) was stirred in the dark for 18 h. Work-up gave an oil (0.62 g), p.l.c. (hexane-chloroform, 4 : 1) of a portion (0.38 g) of which yielded (i) 3α-iodo-2β-isothiocyanato-5α-androstane (45) (0.29 g, 68%), m.p. 124—126 °C (lit.,[12] 125—127 °C) (correct ^{1}H n.m.r. and i.r. spectra [12]); and (ii) a mixture (2.4 : 1) (43 mg, 10%) of 3α-iodo-2β-thiocyanato-5α-androstane (43) and 2β-iodo-3α-thiocyanato-5α-androstane (42) (correct ^{1}H n.m.r. and i.r. spectra).[12]

(b) *Under irradiation by u.v. light.* A mixture of a solution of thiocyanogen in benzene (4.2 ml, 0.22 mmol ml^{-1}), iodine (0.24 g, 0.94 mmol), and 5α-androst-2-ene (0.40 g, 1.55 mol) was stirred under irradiation by u.v. light for 50 min. The internal temperature did not exceed 40 °C. Work-up gave a viscous oil (0.58 g, 84%), p.l.c. (hexane–chloroform, 6 : 1) of a portion (0.51 g) of which yielded (i) a mixture (55 mg, 9%) containing mainly 3α-iodo-2β-isothiocyanato-5α-androstane (45) with a trace of 2β-iodo-3α-isothiocyanato-5α-androstane (44) (correct ^{1}H n.m.r. and i.r. spectra [12]); (ii) a mixture (4 : 1) (0.23 g, 37%) of 2β-iodo-3α-thiocyanato-5α-androstane (42) and 3α-iodo-2β-thiocyanato-5α-androstane (43); (iii) 2α-iodo-3α-thiocyanato-5α-androstane (40) (52 mg, 8%) which crystallized from ether as small needles, m.p. 218—221 °C (decomp.) (Found: C, 54.4; H, 6.9; N, 3.2. C$_{20}$H$_{30}$INS requires C, 54.2; H, 6.8; N, 3.2%); $\nu_{max.}$ (CHCl$_3$) 2 150 cm^{-1} (SCN); δ_H (CDCl$_3$) 0.71 (s, 18-H$_3$), 0.90 (s, 19-H$_3$), 4.28 (m, $W_{\frac12}$ 9 Hz, CHSCN), and 4.85 (m $W_{\frac12}$ 24 Hz, CHI); m/z 316 ($M^{+\cdot}$ — I$\cdot$), 258 ($M^{+\cdot}$ — I$\cdot$ — $\cdot$SCN), and four minor (25 mg) unidentified compounds.

Reactions of Cyclohexene with Iodine–Thiocyanogen.—(a) *In the dark under nitrogen.* A mixture of a solution of thio-cyanogen in benzene (7.5 ml, 0.22 mmol ml^{-1}), iodine (0.42 g, 1.65 mmol), and cyclohexene (47) (280 μl, 2.75 mmol) was stirred in the dark under oxygen-free nitrogen at room temperature for 18 h. Work-up gave a yellow oil (0.73 g), p.l.c. (hexane–chloroform, 3 : 1) of a portion (0.65 g) of which yielded (i) *trans*-1-iodo-2-isothiocyanatocyclohexane (19) (0.45 g, 69%), m.p. 35—36 °C (lit.[12] 35.5—36 °C) (correct ^{1}H n.m r. spectrum); (ii) *trans*-1-iodo-2-thiocyanatocyclohexane (18) (0.10 g, 16%) (correct ^{1}H n.m.r. spectrum [12]); and (iii) a mixture (12 mg, 2%) of *trans*-2-isothiocyanato-1-thiocyan-

atocyclohexane (21) and *trans*-1,2-dithiocyanatocyclohexane (26) (correct [1]H n.m.r. spectrum [16]) (see also Table 4).

(b) *Under irradiation by u.v. light.* A mixture of a solution of thiocyanogen in benzene (7.5 ml, 0.22 mmol ml^{-1}), iodine (0.42 g, 1.65 mmol), and cyclohexene (280 µl, 2.75 mmol) was stirred under u.v. light (300 nm) for 1 h. Work-up gave an oil (0.67 g), p.l.c. of a portion (0.62 g) of which yielded (i) 3-isothiocyanatocyclohexene (49) (10 mg, 3%); $v_{max.}$ 2 060 cm^{-1} (NCS); δ_H 1.09—2.42 (m, CH$_2$), 3.97—4.36 (m, $W_{\frac{1}{2}}$ 11 Hz, CHNCS), and 5.72—5.93 (m, $W_{\frac{1}{2}}$ 3.5 Hz, 1- and 2-H); m/z 139 ($M^{+\cdot}$), and 81 ($M^{+\cdot}$ — NCS$\cdot$); (ii) *trans*-1-iodo-2-isothiocyanatocyclohexane (19) (0.30 g, 44%); (iii) *trans*-1-iodo-2-thiocyanatocyclohexane (18) (0.19 g, 29%); (iv) *cis*-1-*iodo-2-thiocyanatocyclohexane* (50) (12 mg, 2%) as an oil (Found: $M^{+\cdot}$ 266.9590. C$_7$H$_{16}$INS requires M 266.9581); $v_{max.}$ 2 150 cm^{-1} (SCN); δ_H 1.45—2.47 (m, CH$_2$), 3.08 (m, $W_{\frac{1}{2}}$ 12 Hz, CHSCN), and 4.82 (m, $W_{\frac{1}{2}}$ 9 Hz, CHI); m/z 267 ($M^{+\cdot}$), 140 ($M^{+\cdot}$ — I$\cdot$), and 81 (C$_6$H$_9$$^+$); and (v) a mixture (19 mg, 4%) of *trans*-2-isothiocyanato-1-thiocyanatocyclohexane (21) and *trans*-1,2-dithiocyanatocyclohexane (20).

Reaction of (E)-*Hex-3-ene with Iodine–Thiocyanogen under U.v. Light.*—A mixture of a solution of thiocyanogen in benzene (7.5 ml, 0.22 mmol ml^{-1}), iodine (0.42 g, 1.65 mmol), and (*E*)-hex-3-ene (1) (342 µl, 2.75 mmol) was stirred under irradiation by u.v. light for 1 h. Work-up gave an oil (0.74 g), p.l.c. of a portion (0.60 g) of which yielded (i) *erythro*-3-iodo-4-isothiocyanatohexane (4) (0.43 g, 66%) (correct [1]H n.m.r. spectrum [32]); (ii) a mixture (0.16 g, 25%) containing mainly *erythro*-3-iodo-4-thiocyanatohexane (3) with a trace of *threo*-3-iodo-4-thiocyanatohexane (51); and (iii) *threo*-3-isothiocyanato-4-thiocyanatohexane (53) (24 mg, 5%) (correct [1]H n.m.r. and i.r. spectrum [3]).

For reaction in acetic acid see Table 5.

Reaction of (Z)-*Hex-3-ene with Iodine.*—(a) *In the dark under nitrogen.* A mixture of a solution of thiocyanogen in benzene (7.5 ml, 0.22 mmol ml^{-1}), iodine (0.42 g, 1.65 mmol), and (*Z*)-hex-3-ene (2) (343 µl, 2.75 mmol) was stirred in the dark under nitrogen for 18 h. Work-up gave an oil (0.69 g), p.l.c. (hexane–chloroform, 3 : 1) of a portion (0.62 g) of which yielded (i) threo-3-*iodo-4-isothiocyanatohexane* (52) (0.47 g, 71%) as an oil, b.p. (Kugelrohr) 40 °C at 0.1 mmHg (Found: C, 31.4; H, 4.5; N, 5.0. C$_7$H$_{12}$INS requires C, 31.2; H, 4.5; N, 5.2%); $v_{max.}$ 2 070 cm^{-1} (NCS); δ_H 1.09 (t, J 7 Hz, overlapping 1-H$_3$ and 6-H$_3$), 1.32—2.43 (m, overlapping 2- and 5-H$_2$), 3.32 (d × d × d, $W_{\frac{1}{2}}$ 16 Hz, CHNCS), and 4.05 (d × d × d, $W_{\frac{1}{2}}$ 18 Hz, CHI); m/z 269 ($M^{+\cdot}$), 211 ($M^{+\cdot}$ — NCS$\cdot$), and 142 ($M^{+\cdot}$ — I$\cdot$); and (ii) threo-3-*iodo-4-thiocyanatohexane* (51) (94 mg, 14%) as an oil, b.p. (Kugelrohr) 40 °C at 0.09 mmHg (Found: C, 31.4; H, 4.3; N, 5.0. C$_7$H$_{12}$INS requires C, 31.2; H, 4.5; N, 5.2%); $v_{max.}$ 2 150 cm^{-1} (SCN); δ_H 1.10, 1.13 (2 t, J 7 and 7 Hz, overlapping 1- and 6-H$_3$), 1.49—2.23 (m, 2- and 5-H$_2$), 3.26 (d × d × d, $J_{3,4}$ 2.9 Hz, $J_{4,5a}$ 8.5 Hz, $J_{4,5b}$ 5.3 Hz, CHSCN), and 4.35 (d × d × d, $J_{3,4}$ 2.9 Hz, $J_{2a,3}$ 6.0 Hz, $J_{2b,3}$ 7.8 Hz, CHI); m/z 269 ($M^{+\cdot}$), 211 ($M^{+\cdot}$ — SCN$\cdot$), and 142 ($M^{+\cdot}$ — I$\cdot$); and (iii) *threo*-3-isothiocyanato-4-thiocyanatohexane (53) (30 mg, 6%) (correct [1]H n.m.r. and i.r. spectra).

(b) *Under irradiation by u.v. light.* A mixture of a solution of thiocyanogen in benzene (7.5 ml, 0.22 mmol ml^{-1}), iodine (0.42 g, 1.65 mmol) and (*Z*)-hex-3-ene (343 µl, 2.75 mmol) was stirred under u.v. light (300 nm) for 1 h. Work-up gave an oil (0.73 g), p.l.c. of a portion (0.68 g) of which yielded a mixture (4.6 : 1) (0.45 g, 65%) of *threo*-3-iodo-4-isothiocyanatohexane (52) and *erythro*-3-iodo-4-isothiocyanatohexane (4); (ii) a mixture (0.13 g, 19%) containing mainly *threo*-3-iodo-4-thiocyanatohexane (51) with some *erythro*-3-iodo-4-

thiocyanatohexane (3); and (iii) a mixture (30 mg, 6%) of *threo*-3-isothioycanato-4-thiocyanatohexane (53) and *erythro*-3-isothiocyanato-4-thiocyanatohexane (6).

Isomerisation of 1-*Iodo-4-methyl-2-thiocyanatopentane.*—A solution of the iodothiocyanate (10) (50 mg, 0.19 mmol) and boron trifluoride–ether (0.10 g, 0.71 mmol) in dry benzene (1 ml) was allowed to stand, with occasional shaking, in the dark at 0—3 °C for 68 h. Work-up gave an oil (43 mg, 86%), p.l.c. of which yielded (i) a mixture (5 mg, 10%) containing mainly 1-iodo-2-isothiocyanato-4-methylpentane (11) with a trace of 2-iodo-1-isothiocyanato-4-methylpentane (12); and (ii) starting material (23 mg, 46%).

Isomerisation of 2-*Iodo-4-methyl*-1-*thiocyanatopentane.*—(a) *Using boron trifluoride–ether.* A solution of the iodothiocyanate (9) (0.16 g, 0.61 mmol) and boron trifluoride–ether (0.26 g, 1.84 mmol) in dry benzene (1 ml) was allowed to stand, with occasional shaking, in the dark at 0—3 °C for 68 h. Work-up gave an oil (0.14 g, 87%), p.l.c. of which yielded (i) a mixture (5 : 1) (30 mg, 18%) of 1-iodo-2-isothiocyanato-4-methylpentane (11) and 2-iodo-1-isothiocyanato-4-methylpentane (12); and (ii) a mixture (3 : 2) (84 mg, 52%) of 2-iodo-4-methyl-1-thiocyanatopentane (9) and 1-iodo-4-methyl-2-thiocyanatopentane (10).

(b) *Using trifluoromethanesulphonic acid.* (i) Redistilled trifluoromethanesulphonic acid (1 drop) was added to a solution of the iodo-thiocyanate (9) (93 mg, 0.35 mmol) in nitromethane (1 ml) and the mixture was allowed to stand with occasional shaking in the dark at room temperature for 6 h. Further acid (two drops) was added after 3 h. The mixture was extracted into dichloromethane, washed with saturated aqueous sodium hydrogen carbonate, aqueous sodium hydrogen sulphite, saturated aqueous sodium hydrogen carbonate, and brine. Removal of solvent from the dried solution gave a brown oil (68 mg, 73%) containing mainly ([1]H n.m.r.) the iodoisothiocyanate (11). P.l.c. of a portion (51 mg) gave (i) a mixture (6 : 1) (21 mg, 30%) of 1-iodo-2-isothiocyanato-4-methylpentane (11) and 2-iodo-1-isothiocyanato-4-methylpentane (12); and (ii) starting material (5 mg, 7%). (ii) Trifluoromethanesulphonic acid (1 drop) was added to a solution of the iodothiocyanate (9) (87 mg, 0.32 mmol) in dichloromethane (1 ml) and the mixture was allowed to stand, with occasional shaking, in the dark at room temperature for 7 h. Work-up gave a brown oil (43 mg, 50%) shown ([1]H n.m.r.) to be a mixture (2 : 1) containing the iodoisothiocyanates (11) and (12), and unidentified compounds.

Isomerisation of 2-*Iodo-1-thiocyanato-octane.*—Boron trifluoride–ether (0.32 g, 2.25 mmol) was added dropwise with stirring to the iodothiocyanate (24) (0.11 g, 0.38 mmol) and the mixture was left to stand in the dark at room temperature for 46 h. Work-up gave a mixture (3 : 1) (93 mg, 83%) of 1-iodo-2-isothiocyanato-octane (26) and 2-iodo-1-isothiocyanato-octane (27) as an oil.

Reactions of 1-*Methylene-4-t-butylcyclohexane with Iodine–Thiocyanogen.*—(a) *Reactions under irradiation by u.v. light.* A mixture of a solution of thiocyanogen in benzene (7.6 ml, 0.22 mmol ml^{-1}), iodine (0.43 g, 1.69 mmol), and 1-methylene-4-t-butylcyclohexane (b.p. 58—60 °C at 8 mmHg) (54) (0.42 g, 2.76 mmol) was stirred under u.v. light at room temperature for 17.5 h. Work-up gave a yellow oil (0.84 g), p.l.c. (hexane–chloroform, 1 : 1) of a portion (0.79 g) of which yielded (i) 1-iodomethyl-4-t-butylcyclohexene (68) (20 mg, 3%), as an oil; $v_{max.}$ 1 650 cm^{-1} (C=C); δ_H 0.88 (s, CMe$_3$), 1.00—2.40 (m, overlapping 3-, 5-, 6-H$_2$ and 4-H), 3.85 (br s, $W_{\frac{1}{2}}$ 3 Hz, CH$_2$I), and 5.97 (m, $W_{\frac{1}{2}}$ 13 Hz, 2-H); m/z 278 ($M^{+\cdot}$, not detected at

70 eV or 12 eV), 151 ($M^{+ \cdot}$ — I˙); (ii) a mixture (3 : 1) (42 mg, 5%) of r-1-iodo-t-2-isothiocyanato-2-methyl-t-5-t-butylcyclohexane (62) and r-1-iodo-t-2-isothiocyanato-1-methyl-c-4-t-butylcyclohexane (63) as an oil (correct i.r. ^{1}H n.m.r., and mass spectra, see below); (iii) a mixture (1.2 : 3.5 : 1) (0.45 g, 52%) of 1-iodo-4-t-butyl-1-thiocyanatomethylcyclohexane (55), 1-iodomethyl-r-1-isothiocyanato-t-4-t-butylcyclohexane (56), and 1-iodomethyl-r-1-isothiocyanato-c-4-t-butylcyclohexane (57) as a yellow oil; ν_{max} 2 090 cm^{-1} (NCS); δ_H 0.87 and 0.92 [2 × s, overlapping 4-CMe$_3$ of (55), (56), and (57)], 1.00—2.50 [m, overlapping CH and CH$_2$ of (55), (56), and (57)], 3.31 [s, CH$_2$I of (57)], 3.47 [s, CH$_2$I of (56)], and 4.02 [s, CH$_2$NCS of (55)]; δ_C (56) 13.5 (CH$_2$I), 23.2 (C-3 and -5), 27.4 (CMe$_3$), 32.1 (CMe$_3$), 37.8 (C-2 and -6), 46.8 (C-4), 62.3 (C-1), and 133.2 p.p.m. (NCS); δ_C (57) 17.4 (CH$_2$I), 23.3 (C-3 and -5), 27.4 (CMe$_3$), 32.2 (CMe$_3$), 38.0 (C-2 and -6), 46.8 (C-4), 63.0 (C-1), and 133.2 p.p.m. (NCS); δ_C (55) obscured; m/z 337 ($M^{+ \cdot}$), 336 ($M^{+ \cdot}$ — H˙), 279 ($M^{+ \cdot}$ — SCN˙), and 210 ($M^{+ \cdot}$ — I˙); (iv) 1-iodomethyl-t-4-t-butyl-r-1-thiocyanatocyclohexane (58) (83 mg, 10%) as an oil, b.p. 40 °C at 0.04 mmHg (Found: $M^{+ \cdot}$ 337.0352. C$_{12}$H$_{20}$INS requires M, 337.0362); ν_{max} 2 160 cm^{-1} (SCN); δ_H 0.91 (s, 4-CMe$_3$), 1 00—2.50 (m, overlapping 2-, 3-, 5-, and 6-H$_2$, and 4-H), and 3.62 (s, CH$_2$I); δ_C 12.5 (CH$_2$I), 23.8 (C-3 and -5), 27.4 (CMe$_3$), 32.3 (CMe$_3$), 37.0 (C-2 and -6), 46.7 (C-4), 57.7 (C-1), and 111.4 p.p.m. (SCN); m/z 337 ($M^{+ \cdot}$), 279 ($M^{+ \cdot}$ — SCN˙), and 209 ($M^{+ \cdot}$ — HI); and (v) r-1-iodo-c-4-t-butyl-1-thiocyanatomethylcyclohexane (59) (61 mg, 7%) which crystallised from hexane as needles, m.p. 60—61 °C (Found: C, 43.0; H, 6.3; N, 4.2. C$_{12}$H$_{20}$INS requires C, 42.7; H, 6.0; N, 4.2%); ν_{max} 2 160 cm^{-1} (SCN); δ_H 0.93 (s, 4-CMe$_3$), 1.00—2.50 (m, overlapping 2-, 3-, 5-, and 6-H$_2$, and 4-H), and 3.78 (s, CH$_2$SCN); δ_C 25.5 (C-3 and -5) 27.4 (CMe$_3$), 32.3 (CMe$_3$), 41.8 (C-2 and -6), 46.9 (C-4), 52.8 (CH$_2$SCN), 59.8 (C-1), and 112.6 p.p.m. (SCN); m/z 337 ($M^{+ \cdot}$), 279 ($M^{+ \cdot}$ — SCN˙), and 210 ($M^{+ \cdot}$ — I˙).

In another experiment 1-methylene-4-t-butylcyclohexane (0.42 g, 2.75 mmol), iodine (0.42 g, 1.65 mmol), and a solution of thiocyanogen in benzene (7.5 ml, 0.22 mmol ml^{-1}) were stirred together at 37 °C for 40 min under u.v. light with the lamp 1 cm from the reaction flask. Work-up gave an oil (0.64 g, 69%) containing (^{1}H n.m.r. analysis) 1-iodo-1-iso-thiocyanatomethyl-4-t-butylcyclohexane (55) (13%), 1-iodo-methyl-r-1-isothiocyanato-t-4-t-butylcyclohexane (56) (40%), 1-iodomethyl-r-1-isothiocyanato-c-4-t-butylcyclohexane (57) (10%), 1-iodomethyl-t-4-t-butyl-r-1-thiocyanatocyclohexane (58), 12%), r-1-iodo-c-4-t-butyl-1-thiocyanatomethylcyclo-hexane (59) (15%), and minor compounds (62), (63), and (68) (10%).

(b) *In the dark under oxygen.* A solution of thiocyanogen in oxygenated benzene (7.6 ml, 0.22 mmol ml^{-1}), iodine (0.43 g, 1.69 mmol), and 1-methylene-4-t-butylcyclohexane (0.41 g, 2.70 mmol) were stirred together at 20 °C in the dark under oxygen for 18 h. Work-up gave a yellow oil (0.79 g), p.l.c. (hexane–chloroform, 2 : 1) of a portion (0.72 g) of which yielded (i) 1-iodomethyl-4-t-butylcyclohexane (68) (5 mg, 1%); (ii) a mixture (3 : 1) (29 mg, 3%) of compounds (62) and (63); (iii) a mixture (1.2 : 3 : 1) (0.40 g, 48%) of the *vic*-iodoiso-thiocyanates (55), (56), and (57); (iv) the *vic*-iodothiocyanate (58) (67 mg, 8%); and (v) the *vic*-iodothiocyanate (59) (59 mg, 7%).

Reactions of 1-Methyl-4-t-butylcyclohexene with Iodine–Thiocyanogen.—(a) *In the dark under nitrogen.* A mixture of a solution of thiocyanogen in benzene (7.5 ml, 0.22 mmol ml^{-1}), iodine (0.42 g, 1.65 mmol), and 1-methyl-4-t-butylcyclo-hexene (69) (0.42 g, 2.75 mmol) was stirred in the dark under nitrogen for 17 h. Work-up gave an oil (0.90 g), p.l.c. (hexane–

chloroform, 3 : 1) of a portion (0.69 g) of which yielded (i) a mixture (1.8 : 1) (0.55 g, 78%) of r-1-*iodo*-t-2-*isothiocyanato*-2-*methyl*-t-5-*t-butylcyclohexane* (62) and r-1-*iodo*-t-2-*isothio-cyanato*-1-*methyl*-c-4-*t-butylcyclohexane* (63) as an oil, b.p. (Kugelrohr) 60 °C at 0.07 mmHg (Found: C, 43.5; H, 6.2; N, 4.2. C$_{12}$H$_{20}$INS requires C, 42.7; H, 6.0; N, 4.15%); ν_{max} 2 060 cm^{-1} (NCS); δ_H 0.94 [s, CMe$_3$ of (9) and (10)], 1.17—2.38 [m, overlapping CH$_2$ and CH of (62) and (63)], 1.60 [s, CH$_3$ of (62)], 2.21 [s, CH$_3$ of (63)], 4.18 [m, $W_{\frac{1}{2}}$ 8 Hz, CHNCS of (63)], and 4.58 [m, $W_{\frac{1}{2}}$ 6 Hz, CHI of (62)]; δ_C (63) 25.3 (C-5), 27.3 (CMe$_3$), 31.0 (C-3), 31.9 (CMe$_3$), 35.7 (Me) 39.7 (C-6), 40.8 (C-4), 51.5 (C-1), 65.6 (C-2), and 133.5 p.p.m. (NCS); δ_C (62) 22.7 (C-4), 27.5 (CMe$_3$), 32.0 (CMe$_3$), 32.2 (Me), 34.0 (C-3),* 34.4 (C-6),* 39.8 (C-1), 42.0 (C-5), 63.4 (C-2), and 133.5 p.p.m. (NCS); m/z 337 ($M^{+ \cdot}$), 279 ($M^{+ \cdot}$ — NCS˙), 210 ($M^{+ \cdot}$ — I˙), and 151 ($M^{+ \cdot}$ — I˙ — HNCS); (ii) a mixture (1 : 1) (14 mg, 3%) of cis-6-*isothiocyanato*-1-*methyl*-4-*t-butylcyclohexene* (76) and trans-6-*isothiocyanato*-1-*methyl*-4-*t-butylcyclohexene* (77) as an oil, b.p. (Kugelrohr) 40 °C at 0.2 mmHg (Found: C, 68.7; H, 9.8; N, 6.6. C$_{12}$H$_{19}$NS requires C, 68.85; H, 9.15; N, 6.7%); ν_{max} 2 050 and 2 070 cm^{-1} (NCS); δ_H 0.93 (s, CMe$_3$), 1.13—2.33 (m, CH$_2$ and 4-H), 1.82 (br s, CH$_3$), 4.01 (m, $W_{\frac{1}{2}}$ 6 Hz, CHNCS), and 5.57 (m, $W_{\frac{1}{2}}$ 9 Hz, 2-H); m/z 209 ($M^{+ \cdot}$), and 151 ($M^{+ \cdot}$ — NCS˙); (iii) r-1-*iodo*-t-2-*isothiocyanato*-2-*methyl*-c-5-*t-butylcyclohexane* (74) (36 mg, 5%) as an oil, b.p. (Kugelrohr) 50 °C at 0.01 mmHg (Found: $M^{+ \cdot}$ 337.0347. C$_{12}$H$_{20}$INS requires M, 337.0362); ν_{max} 2 045 cm^{-1} (NCS); δ_H 0.90 (s, CMe$_3$), 1.00—2.63 (m, CH$_2$ and 5-H), 1.58 (s, CH$_3$), and 4.37 (d × d, $J_{1,6ax}$ 12 Hz, $J_{1,6eq}$ 4 Hz, CHI); δ_C 22.7 (C-4), 23.9 (Me), 27.4 (CMe$_3$), 32.3 (CMe$_3$), 37.9 (C-3),* 38.7 (C-6),* 41.6 (C-1), 50.3 (C-5), 64.2 (C-2), and 133.3 p.p.m. (NCS); m/z 337 ($M^{+ \cdot}$), 279 ($M^{+ \cdot}$ — NCS˙), 210 ($M^{+ \cdot}$ — I˙), and 151 (C$_{11}$H$_{19}$+); (iv) a mixture (1.2 : 1) (28 mg, 4%) of r-1-iodo-1-methyl-c-4-t-butyl-t-2-thiocyanatocyclohex-ane (65) and r-1-iodo-2-methyl-t-5-t-butyl-t-2-thiocyanato-cyclohexane (66) as an unstable oil; ν_{max} 2 150 cm^{-1} (SCN); δ_H 0.94 (s, CMe$_3$), 1.00—2.47 (m, CH$_2$ and CH), 1.87 [s, CH$_3$ of (66)], 2.34 [s, CH$_3$ of (65)], 4.23 [m, $W_{\frac{1}{2}}$ 8 Hz, CHSCN of (65)], and 4.93 [m, $W_{\frac{1}{2}}$ 6 Hz, CHI of (66)]; m/z 337 ($M^{+ \cdot}$), 279 ($M^{+ \cdot}$ — SCN˙), 210 ($M^{+ \cdot}$ — I˙), and 151 (C$_{11}$H$_{19}$+). This mix-ture contained a trace of (73); (v) r-2-isothiocyanato-1-methyl-t-4-t-butyl-t-1-thiocyanatocyclohexane (67) (11 mg, 2%) as an oil; ν_{max} 2 160 (SCN) and 2 060 cm^{-1} (NCS); δ_H 0.94 (s, CMe$_3$), 1.00—2.27 (m, CH$_2$ and CH), 1.61 (s, CH$_3$), and 3.82 (m, $W_{\frac{1}{2}}$ 7 Hz, CHNCS); m/z 268 ($M^{+ \cdot}$), 210 ($M^{+ \cdot}$ — NCS˙), and 151 (C$_{11}$H$_{19}$+); and (vi) t-2-isothiocyanato-2-methyl-c-5-t-butyl-r-1-thiocyanatocyclohexane (75) (11 mg, 2%) as an oil; ν_{max} 2 150 (SCN) and 2 040 cm^{-1} (NCS); δ_H 0.93 (s, CMe$_3$), 1.07—2.43 (m, overlapping CH$_2$ and CH), 1.52 (s, CH$_3$), and 3.30 (d × d, $J_{1,6ax}$ 12 Hz, $J_{1,6eq}$ 4 Hz, CHSCN); m/z 268 ($M^{+ \cdot}$), 210 ($M^{+ \cdot}$ — NCS˙), and 151 (C$_{11}$H$_{19}$+).

(b) *Under irradiation by u.v. light.* A mixture of a solution of thiocyanogen in benzene (7.5 ml, 0.22 mmol ml^{-1}), iodine (0.42 g, 1.65 mmol), and 1-methyl-4-t-butylcyclohexane (0.42 g, 2.75 mmol), was stirred under u.v. light (300 nm) for 1 h. Work-up gave an oil (0.89 g), p.l.c. of a portion (0.87 g) of which yielded (i) a mixture (1.8 : 1) (0.43 g, 48%) of r-1-iodo-t-2-isothiocyanato-2-methyl-t-5-t-butylcyclohexane (62) and r-1-iodo-t-2-isothiocyanato-1-methyl-c-4-t-butylcyclohexane (63); (ii) a mixture (1 : 1) (12 mg, 2%) of the allylic isothio-cyanates (76) and (77); (iii) r-1-iodo-t-2-isothiocyanato-2-methyl-c-5-t-butylcyclohexane (74) (32 mg, 4%); (iv) a mixture (4 : 1) (0.15 g, 17%) of the *vic*-iodothiocyanates, (65) and (66); (v) r-1-*iodo*-2-*methyl*-c-5-*t-butyl*-t-2-*thiocyanatocyclohexane* (73) (20 mg, 2%) as an oil (Found: $M^{+ \cdot}$ 337.0370. C$_{12}$H$_{20}$INS requires M, 337.0362); ν_{max} 2 150 cm^{-1} (SCN); δ_H (CDCl$_3$)

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* Assignments may be reversed.

0.87 (s, CMe$_3$), 1.00—2.83 (m, overlapping CH$_2$ and CH) 1.63, (s, CH$_3$), and 4.50 (d × d, $J_{1,6ax}$ 12 Hz, $J_{1,6eq}$ 4 Hz, CHI); m/z 337 ($M^{+\cdot}$), 279 ($M^{+\cdot}$ — SCN$^{\cdot}$), 210 ($M^{+\cdot}$ — I$^{\cdot}$), and 152 ($M^{+\cdot}$ — ISCN); (vi) the vic-isothiocyanatothiocyanate (67) (11 mg, 2%); and (vii) the vic-isothiocyanatothiocyanate (75) (3 mg, 0.5%).

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