

vic-Iodothiocyanates and Iodoisothiocyanates. Part 3.† Further Preparations, and the Formation of 2-Alkoxy-2-thiazolines

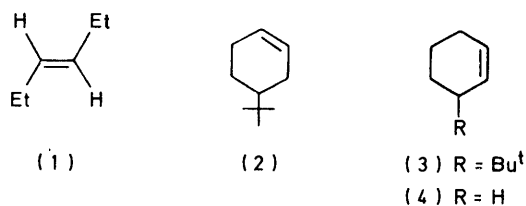
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The reactions of (*E*)-hex-3-ene, 4-*t*-butylcyclohexene, and 3-*t*-butylcyclohexene with iodine and potassium thiocyanate are examined. The action of iodine and thiocyanogen with (*E*)-hex-3-ene gives different results from those reported in the literature. Isomerizations of the *vic*-iodoethiocyanates to *vic*-iodoethioisothiocyanates and formation of 2-alkoxy-2-thiazolines from the latter adducts are reported.

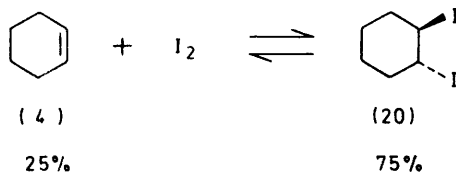
IN Part 1¹ we reported the preparation of *vic*-iodoethiocyanates and *vic*-iodoethioisothiocyanates from the reaction of iodine and potassium thiocyanate with alkenes. The former were products of kinetic control and could be isomerized into the thermodynamically more stable iodoisothiocyanates by treatment, either *in situ* or separately, with boron trifluoride-ether. Treatment of the *trans*-*vic*-iodoethioisothiocyanates with anhydrous methanol or amines gave convenient methods for the preparation of thiazolidin-2-ones and 2-amino-2-thiazolines, respectively.² We now report the formation of further *vic*-iodoethiocyanates and *vic*-iodoethioisothiocyanates and reactions of the latter with oxygen nucleophiles.

RESULTS AND DISCUSSION

Reactions of iodine and potassium thiocyanate with (*E*)-hex-3-ene (1), 4-*t*-butylcyclohexene (2), and 3-*t*-



butylcyclohexene (3) are summarized in Table 1 and isomerizations of the *vic*-iodoethiocyanates to *vic*-iodoethioisothiocyanates by reaction with boron trifluoride-ether ‡ are given in Table 2. As before,¹ the reagent



mixture was prepared from iodine and commercial (*i.e.* hydrated) potassium thiocyanate. In the current study it was found that reaction of cyclohexene (4) with iodine and *anhydrous* potassium thiocyanate gave only *trans*-1,2-diiodocyclohexane (20) which, as expected,³ readily

† Part 2 is ref. 2.

‡ In earlier work,¹ the isomerizations were carried out in the presence of chloroform or ether but in the present work it was found that boron trifluoride-ether was more effective in the absence of co-solvents.

reverted to cyclohexene and iodine. Presumably water is essential for iodoethiocyanation in providing a liquid-liquid interface in which the hydrated anion may attack a cationic intermediate. It was also shown by ¹H n.m.r. analysis that an equimolar mixture of cyclohexene and

TABLE 1

Reactions with iodine and potassium thiocyanate ^{a,b}

Alkene	Reaction time/h	Products	Yield (%) ^c
(1)	26	(5) (6)	66 18
(2)	20	(9) (10) ^d (11) (12) ^d	65 12
(3)	16	(13) (14) (15)	34 27 36

^a Molar ratio alkene : KSCN : I₂ = 1 : 3 : 2.4. ^b In ethanol-free CHCl₃ at 20 °C. ^c After p.l.c. ^d 5 : 4 ratio.

iodine in deuteriochloroform rapidly (<10 min) established an equilibrium which favoured the di-iodide (20) and which remained unchanged after 24 h. When iodine was treated with an excess of cyclohexene, displacement of the equilibrium to the right was shown by decolourization of the initial brown solution over several hours. Treatment of the latter solution with hydrated potassium thiocyanate in the presence of the phase-transfer catalyst Adogen 464 at ambient temperature for 13 h gave the iodoethiocyanate (18) and a small amount of the iodoisothiocyanate (19). It is likely therefore, that the iodoethiocyanation pathway involves initial formation of an

TABLE 2

Isomerizations of *vic*-iodoethiocyanates

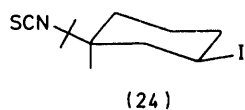
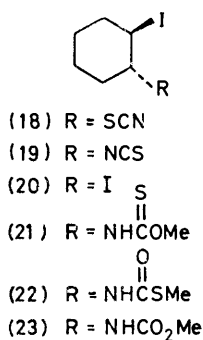
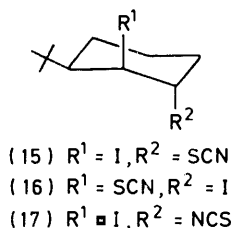
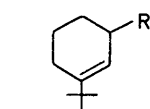
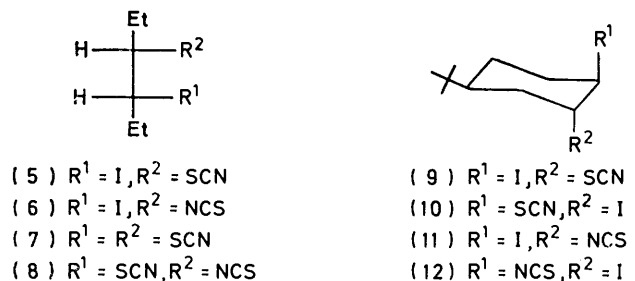
Iodoethiocyanate	Reaction time/h	Products	Yield (%)
(18) (ref. 1)	24	(19)	88 ^a
(5)	0.8	(6)	93
(9) (10) ^b	26	(11) (12) ^b	61 ^{c,d}
(15)	15	(24)	26 ^{c,e}

^a Isolated by column chromatography. ^b 5 : 4 ratio. ^c Isolated by p.l.c. ^d Plus starting material (9%). ^e Plus 3-*t*-butylcyclohexene.

iodonium ion which rapidly equilibrates with the di-iodide (20). Subsequent reaction of the thiocyanate anion or of a complex⁴ such as (I₂SCN)⁻ with the iodonium ion then shifts the equilibrium.

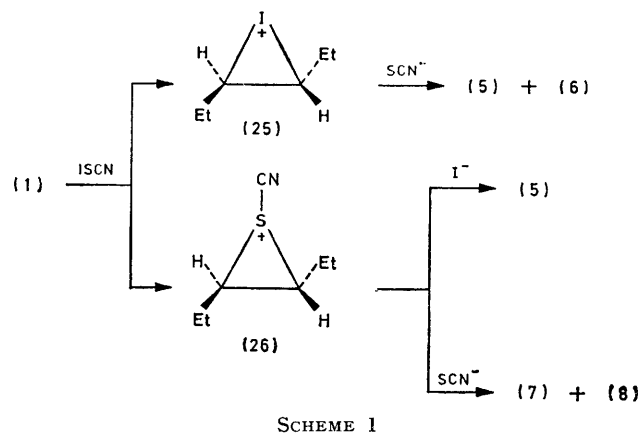
Formation of only the *erythro*-isomers (5) and (6) from

the reaction of iodine and potassium thiocyanate with (*E*)-hex-3-ene (1) is consistent with a reaction pathway involving a bridged iodonium ion which does not undergo ring-opening prior to attack by the thiocyanate anion. Maxwell and Silbert⁵ have recently isolated by preparative g.l.c. the compounds (6) and (8) from (*E*)-hex-3-ene using iodine and thiocyanogen in benzene, and have suggested that the formation of dithiocyanates and diisothiocyanates in our earlier work¹ results from the presence of thiocyanogen due to the equilibrium, $2 \text{ ISCN} \rightleftharpoons \text{I}_2 + (\text{SCN})_2$. Maxwell and Silbert discussed the formation of the possible products from (*E*)-hex-3-ene via the pathways shown in Scheme 1. Since they did



not detect any of the iodothiocyanate (5) or dithiocyanate (7) they apparently rejected the possibility that these compounds could have been present as intermediates. However, under their reaction conditions, kinetic-thermodynamic relationships could exist. The iodothiocyanate (5) may indeed have been produced but isomerized rapidly *in situ* to the iodoisothiocyanate (6), and we have therefore reinvestigated the reactions of (*E*)-hex-3-ene with iodine and thiocyanogen under carefully controlled conditions (see Experimental section; cf. ref. 5). Our results are presented in Table 3.

Contrary to the results of Maxwell and Silbert⁵ we isolated not only the *erythro*-iodoisothiocyanate (6) but also the *erythro*-iodothiocyanate (5) by p.l.c. from all reactions. Moreover, the dithiocyanate (7) was isolated in <10% yield from reactions carried out in acetic acid, which contrasts with the 74% yield recorded by Maxwell



and Silbert. These workers did not record a reaction time for their experiments but t.l.c. analysis during the present work indicated that the compounds (5), (6), and (8) were all present shortly after reaction commenced. Also, the iodothiocyanate was shown (t.l.c.) to be stable to thiocyanogen, thiocyanogen-iodine, and thiocyanogen-iodine-iron powder⁶ in both benzene and ethanol-free chloroform solutions. Since Maxwell and Silbert analysed their products after isolation by g.l.c., the discrepancy in the results may be due to the fact that the adduct (5) reverted thermally to (*E*)-hex-3-ene during g.l.c. and therefore went undetected, or that it isomerized to the iodoisothiocyanate (6). However, although thermally-induced isomerizations of thiocyanates to isothiocyanates have been reported,⁷ the latter explanation

TABLE 3

Reactions of (*E*)-hex-3-ene with iodine-thiocyanogen

Solvent	Radical inhibitor (%)	Products and yield (%) ^{a, b}			
		(5)	(6)	(7)	(8)
PhH		11	72		5
PhH	15	11	62		5
AcOH		21	40		2
AcOH ^c		20	38	4	8 ^d
AcOH	15	21	38	7	6
CH ₂ Cl ₂ ^e		17	71		2
CHCl ₃ ^e		12	69		2

^a Isolated by p.l.c. In each case conversion of alkene was quantitative. ^b Reaction time 17 h. ^c Mol. ratio of $\text{I}_2 - (\text{SCN})_2$: alkene = 1.2 : 1. In all other cases the ratio was 4.8 : 1. ^d Ca. 1 : 1 mixture with *erythro*-2-isothiocyanato-1-ethylbutyl acetate. ^e In these experiments ca. 15 mol % excess of iodine was used in the preparation of ISCN.

would not account for Maxwell and Silbert's failure to detect *any* iodine-containing products when acetic acid was used as the solvent. In their experiments Maxwell and Silbert used a 1.2 : 1 ratio of iodine(i) thiocyanate to alkene and reported that doubling the ratio to 2.4 : 1 had little effect on the product distribution. In the present

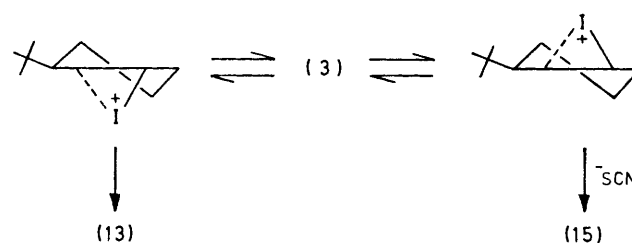
study since both the compounds (5) and (6) were obtained with a 1.2 : 1 ratio in acetic acid, a higher ratio (4.8 : 1) was used in subsequent experiments in order to determine if the discrepancy in the results could be attributed to further transformations of the primary products. However, no significant change in the ratio of products resulted.

Treatment of (*E*)-hex-3-ene with iodine and potassium thiocyanate under standard conditions (see Table 1) in benzene, in order to provide a comparison with the iodine-thiocyanogen reagent, resulted in no detectable (t.l.c.) reaction after 15 min. This supports the supposition that the major process here is formation of the *trans*-*vic*-di-iodide, which decomposes to the alkene on the t.l.c. plate. After 1 h, water (0.5 ml) was added whereupon t.l.c. showed the formation of small amounts of the adducts (5) and (6); the reaction was accelerated by the further addition of Adogen 464. After stirring for a further 22.5 h, work-up and p.l.c. afforded the adducts (5) and (6) in yields of 20 and 51%, respectively. Again the inference is that the iodine-potassium thiocyanate reagent reacts primarily *via* a di-iodide, which is subsequently transformed into thiocyanato- or isothiocyanato-containing products.

The marked difference in the ratio of compounds (5) and (6) isolated from the reaction of (1) in chloroform with iodine-potassium thiocyanate (66 : 18), as opposed to iodine-thiocyanogen (12 : 69), demands a mechanistic distinction for the product-determining step for these kinetically-formed isomers. Since the iodoisothiocyanate (6) is the predominant isomer in the case of the iodine-thiocyanogen system the possible intermediacy of the *S*-cyanothiiranium ion (26) in the formation of the iodine-containing adducts can be rejected. Thus, the predominant initial ionic species is suggested to be the iodonium ion (25) with both systems, and therefore there must be a difference in the species which delivers the nucleophile to the cationic intermediate. Since this is clearly a thiocyanate anion or a complexed anion in the former case, we suggest that in the case of the iodine-thiocyanogen system, compound (6) is formed by delivery of the isothiocyanato-group to the iodonium ion from either iodine(t) thiocyanate or thiocyanogen. This in turn suggests that iodine(t) thiocyanate itself is not the major reactive species in the iodine-potassium thiocyanate system. Delivery of an isothiocyanate nucleophile from molecular thiocyanogen to an iodonium ion liberates an electrophilic complement capable of reacting with the alkene to form the *S*-cyanothiiranium ion (26), which could provide a minor indirect pathway to the iodothiocyanate (5) and also could lead to the dithiocyanate (7) and the isothiocyanatothiocyanate (8). However, cation (26) may also arise directly from interaction of the alkene (1) with thiocyanogen. Clearly, electrophilic attack by thiocyanogen must be slower (Table 3) than attack by species which deliver electrophilic iodine. The mixtures of inseparable (by p.l.c.) regioisomeric iodothiocyanates and iodoisothiocyanates from the reaction of iodine and potassium thiocyanate with

4-*t*-butylcyclohexene (2) arise by diaxial opening of *cis*- and *trans*-iodonium ions.* The ratio of products indicates that in contrast to 3-*t*-butylcyclohexene (see below), there is only a slight preference for reaction *via* the *cis*-iodonium ion. Similar results have been obtained for epoxidation,⁸ methoxybromination,⁹ oxymercuration,⁹⁻¹¹ and hydroboration¹² of 4-*t*-butylcyclohexene.

By analogy with earlier work,¹³ it is assumed that reaction of iodine and potassium thiocyanate with 3-*t*-butylcyclohexene (3) proceeds *via* the rapid and reversible formation of two diastereoisomeric cationic intermediates, *viz.* a *trans*-iodonium ion* and a sterically crowded and therefore less-stable *cis*-iodonium ion. These species are represented (Scheme 2) as closed ions in which the



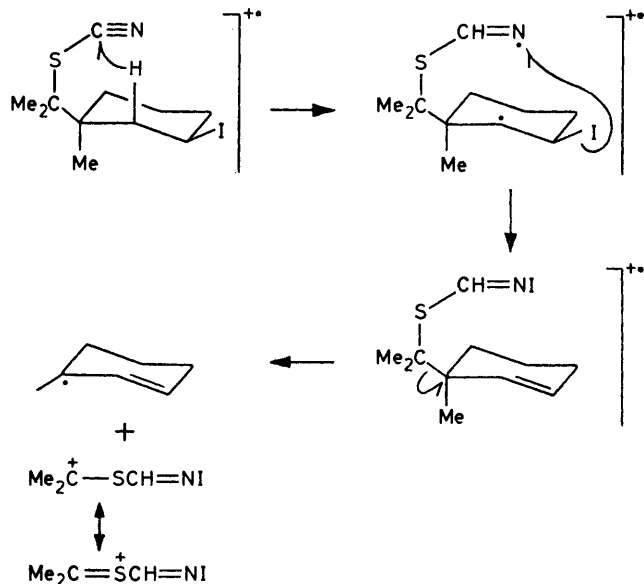
SCHEME 2

extent of bonding of the halogen to each of the carbon atoms may be different. Preferential attack of thiocyanate anion on the *cis*-iodonium ion at C-1 would result in formation of the adduct (15), while axial cleavage¹⁴ of the *trans*-iodonium ion with concomitant loss of a proton would result in formation of the allylic iodide (13). Equatorial cleavage of the *cis*-iodonium ion could also lead to the allylic iodide (13) although this pathway would involve a boat-like transition state. None of the regioisomer (16) was isolated, *trans*-diaxial opening of the *trans*-iodonium ion apparently being impeded by the contiguous *t*-butyl group. However, compound (16) may have been formed and may have undergone *anti*-elimination of thiocyanic acid to produce (13). Interestingly, no *c*-2-iodo-*t*-3-isothiocyanato-*r*-1-*t*-butylcyclohexane (17) [*cf.* (2)] was detected in the reaction mixture, although one of the isolated products was 3-isothiocyanato-1-*t*-butylcyclohexene (14). Isolation of the iodothiocyanate (15), and the fact that iodoisothiocyanates are more stable than iodothiocyanates, precludes the likelihood of the compound (14) arising by loss of hydroiodic acid from the iodoisothiocyanate (17). More likely pathways for its formation involve either the loss of hydroiodic acid from the iodothiocyanate (15) followed by rapid isomerization¹ of the resulting allylic thiocyanate, or *via* the allylic iodide (13).

Treatment of the iodothiocyanate (15) with boron trifluoride-ether did not give the expected product (17). Instead, a mixture (*ca.* 1 : 2) of 3-*t*-butylcyclohexene (3) and a compound identified as *r*-1-iodo-*c*-3-[2-(2-isothiocyanatopropyl)]-3-methylcyclohexane (24) was obtained. The new iodoisothiocyanate (24) showed the characteristic absorption of an isothiocyanate group (ν_{\max} .

* Relative to the *t*-butyl group.

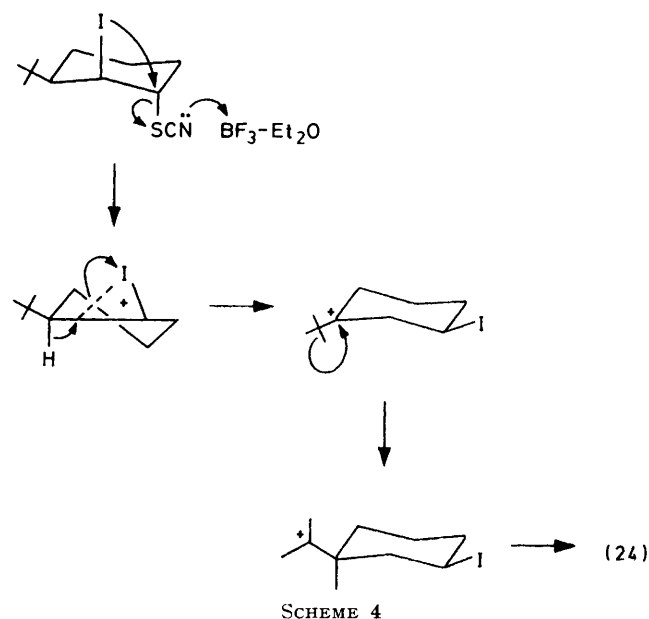
2060 cm^{-1} in its i.r. spectrum, while the molecular ion (m/e 323) and fragment peaks due to the expulsion of an isothiocyanate group (m/e 265) and an iodine atom (m/e 196) in the mass spectrum indicated the molecular formula and confirmed the functional groups present. The ^1H n.m.r. spectrum showed only one downfield multiplet (δ 4.26), with a half-height width of 17.5 Hz consistent with an axial proton geminal to an equatorial iodine atom in a cyclohexane ring; singlet resonances at δ 1.00 and 1.39 integrated in the ratio 3 : 6. The noise-decoupled ^{13}C n.m.r. spectrum confirmed the presence of eleven carbon atoms; interpretation of the SFORD spectrum identified three methyl carbon atoms (two of which were equivalent), four methylene carbon atoms, one methine carbon atom, and three quaternary carbon atoms. Chemical-shift data showed that the methine carbon was bound to iodine and that two of the quaternary signals were due to an isothiocyanato-carbon atom (δ_{C} 160.0, br) and the carbon atom bearing this group (δ_{C} 67.9). The relative *cis*-stereochemistry of the 2-(2-isothiocyanato)propyl substituent was deduced from the



SCHEME 3

mass spectrum which showed a significant (35% relative intensity) peak at m/e 228; high-resolution measurement confirmed the elemental composition of this fragment to be $\text{C}_4\text{H}_7\text{INS}$, while a metastable re-focusing experiment detected only one precursor (m^* 160.9) of this ion, indicating its formation directly and only from the molecular ion (Scheme 3). The formation of compound (24) by a concerted process is ruled out from a consideration of the stereochemistry of the starting material (15) relative to that of the rearranged product. Although the ionic pathway represented in Scheme 4 involves the same reactive *cis* iodonium ion previously implicated in the formation of iodothiocyanate (15) from alkene (3), the absence of an alternative good nucleophilic source concomitant with the use of boron trifluoride-ether

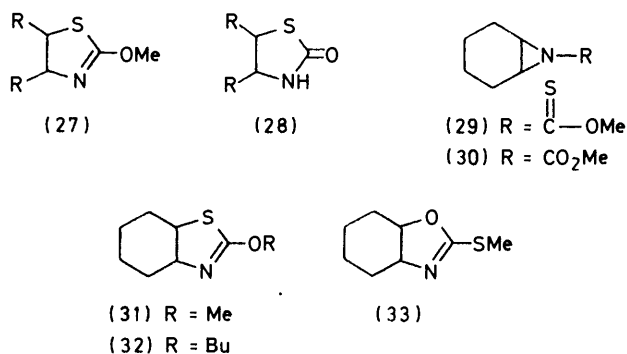
allows a hard acid-hard base complexation between boron and nitrogen. This interaction is sufficiently favourable to permit the iodonium ion apparently to undergo skeletal reorganization prior to re-capture by thiocyanate anion. In this respect it is noteworthy that



SCHEME 4

analogous rearranged products were not isolated from treatment of alkene (3) with iodine-thallium(I) acetate or iodine-silver(I) acetate.¹³

In Part 2² we suggested that the conjugate acids of the 2-methoxy-2-thiazoline (27) were intermediates in the formation of the thiazolidin-2-ones (28) from *vic*-iodoisothiocyanates. Attempts were therefore made to prepare a 2-methoxy-2-thiazoline. Treatment of the iodoisothiocyanate (19) with lithium methoxide at 0 °C for 3 h gave methyl 7-azabicyclo[4.1.0]heptane-7-thioxocarboxylate (29) (9%) and an inseparable mixture (63%) of *O*-methyl *N*-(*trans*-2-iodocyclohexyl)thiocarbamate (21) and *S*-methyl *N*-(*trans*-2-iodocyclohexyl)-



thiocarbamate (22). Formation of an isomeric mixture of (21) and (22) is presumably due to a Newman-Kwart thermal rearrangement¹⁵ since, contrary to our earlier surmise,² the compounds (21) and (22) are relatively stable even when subjected to multiple p.l.c.

Greibrokk¹⁶ has shown that refluxing the iodocarbamate (23) in a biphasic system with sodium hydroxide affords a high yield of methyl 7-azabicyclo[4.1.0]heptane-7-carboxylate (30). Application of this method to the iodothiocabamate (21) resulted in no significant formation of the *O*-methylthiocarbamoylaziridine (29). However, treatment of the mixture of *O*- and *S*-carbammates (21) and (22) with potassium carbonate in acetone at ambient temperature for 44 h gave the desired 2-methoxy-*cis*-3a,4,5,6,7,7a-hexahydrobenzothiazole (31) in 63% yield, in addition to a trace of the aziridine (29). No 2-(methylthio)-*cis*-3a,4,5,6,7,7a-hexahydrobenzoxazole (33) was isolated and thus the *O*-acid-*S*-acid carbamate equilibrium is presumably displaced on formation of the heterocycle (31). The 2-butoxy-analogue (32) of the thiazole (31) was formed directly from the iodoisothiocyanate (19) in 41% yield by treatment with lithium butoxide.

EXPERIMENTAL

General experimental details are given in ref. 1.

Reaction of Cyclohexene with Iodine-Anhydrous Potassium Thiocyanate.—A mixture of cyclohexene (5.0 g, 60.9 mmol), anhydrous (finely-ground and oven-dried) potassium thiocyanate (17.8 g, 0.18 mol), and iodine (37.2 g, 0.15 mol) was stirred in chloroform (200 ml) at 20 °C in the dark for 24 h. Work-up gave *trans*-1,2-di-iodocyclohexane (20) as a brown oil, which decomposed readily to cyclohexene and iodine.

Reaction of Cyclohexene with Iodine-Potassium Thiocyanate in the Presence of Adogen 464.—Iodine (*ca.* 0.40 g) was added to an excess of cyclohexene (5.0 g) to give a brown solution which decolorized after several hours. Potassium thiocyanate (0.20 g), water (1 ml), and Adogen 464 (30 mg) were added to the clear solution and the resulting suspension was shaken at 20 °C in the dark for 13 h. Work-up gave *trans*-1-iodo-2-thiocyanatocyclohexane (18) and a small amount of *trans*-1-iodo-2-isothiocyanatocyclohexane (19) (t.l.c. and ¹H n.m.r. analysis).

Reaction of (*E*)-Hex-3-ene with Iodine-Potassium Thiocyanate.—A mixture of (*E*)-hex-3-ene (1.0 g, 11.9 mmol), iodine 7.25 g, 28.5 mmol), and potassium thiocyanate (3.47 g, 35.7 mmol) was stirred in chloroform (50 ml) at 20 °C in the dark for 26 h. Work-up gave an oil (2.97 g, 93%). P.l.c. of a portion (1.46 g) in hexane yielded (*i*) erythro-3-iodo-4-isothiocyanatohexane (6) (0.29 g, 18%) as a clear oil, b.p. 78 °C at 0.6 mmHg (Found: C, 31.7; H, 4.5; N, 5.3; S, 12.0. C₇H₁₂INS requires C, 31.2; H, 4.5; N, 5.2; S, 11.9%); ν_{\max} 2 060 cm⁻¹ (NCS); δ 1.10 (t, *J* 7 Hz, overlapping 1-H₃ and 6-H₃), 1.88 (m, 2-H₂ and 5-H₂), 3.69 (ddd, *J*_{4,3} 6.3, *J*_{4,5a} 7.4, *J*_{4,5b} 4.5 Hz, CHNCS), and 4.05 (dt, *J*_{3,4} = *J*_{3,2} 6.6 Hz, CHI); *m/e* 269 (*M*⁺), 211 (*M*⁺ - NCS), and 142 (*M*⁺ - I); and (*ii*) erythro-3-iodo-4-thiocyanatohexane (5) (1.03 g, 66%) as an unstable oil, b.p. 80° at 0.6 mmHg (Found: C, 31.8; H, 4.5; N, 5.3. C₇H₁₂INS requires C, 31.2; H, 4.5; N, 5.2%); ν_{\max} 2 155 cm⁻¹ (SCN); δ 1.10, 1.16 (2 t, *J* 7 and 7 Hz, 1-H₃ and 6-H₃), 2.0 (m, 2-H₂ and 5-H₂), 3.10 (ddd, *J*_{4,3} 9, *J*_{4,5a} 3.6, *J*_{4,5b} 7.1 Hz, CHSCN), and 4.28 (q, *J*_{3,4} = *J*_{3,2} 6.5 Hz, CHI); *m/e* 269 (*M*⁺), 211 (*M*⁺ - SCN⁻), and 142 (*M*⁺ - I⁻).

A mixture of erythro-3-iodo-4-thiocyanatohexane (0.42 g, 1.57 mmol) and boron trifluoride-ether (0.69 g, 4.8 mmol) was stirred at 20 °C in the dark for 50 min. Work-up gave

erythro-3-iodo-4-isothiocyanatohexane (6) (0.39 g, 93%), pure by t.l.c.

Reactions of (*E*)-Hex-3-ene with Iodine-Thiocyanogen.—All reactions were carried out under nitrogen in three-necked flasks equipped with a magnetic stirrer bar, a septum, a gas inlet, and a condenser. All glassware was oven-dried and the flasks were wrapped in aluminium foil to avoid exposure of the reagents to light. Before use, the nitrogen was passed through two aqueous chromium(II) chloride solutions to remove oxygen, through concentrated sulphuric acid, and then over solid potassium hydroxide. All solvents were dried and redistilled under dry nitrogen before use; acetic acid was distilled from a solution containing *ca.* 5% of acetic anhydride and a catalytic amount of toluene-*p*-sulphonic acid.¹⁷ (*E*)-Hex-3-ene was distilled from lithium aluminium hydride and stored over molecular sieves.

Solutions of thiocyanogen were prepared in batch lots from freshly prepared dry lead(II) thiocyanate (1.5 g) and bromine (0.125 ml) in the appropriate solvent (11 ml). Solutions of thiocyanogen were yellow in colour; in acetic acid they were a pale burgundy. Stirring was stopped after 1 h, and when solids had settled an aliquot (7.5 ml) of the supernatant liquid was transferred by a nitrogen-flushed glass syringe with a stainless steel needle to another three-necked flask. Iodometric analysis¹⁸ of 3-ml aliquots from a batch prepared in benzene gave a value of 0.22 mmol ml⁻¹; therefore, 7.5 ml contained 1.65 mmol.

Iodine (0.419 g, 1.65 mmol) was added to the thiocyanogen solution in one portion and the mixture was stirred at room temperature for 10 min. (*E*)-Hex-3-ene (85 μ l, 58 mg, 0.69 mmol) was then injected through the septum and the stirring was continued for 17 h. T.l.c. analyses showed that the iodothiocyanate (5), the iodoisothiocyanate (6), and the isothiocyanatothiocyanate (8) were present after 10 min, and after 17 h. Reactions were worked up by dilution with dichloromethane, washing the organic layer with water (some polymerisation of thiocyanogen occurred at this stage), aqueous sodium hydrogensulphite, aqueous sodium hydrogencarbonate, and brine. Solvent was removed from the dried (Na₂SO₄) solution and the resulting pale yellow oil was separated into its constituents by p.l.c. (*cf.* ref. 5) in hexane-chloroform (3 : 1).

In one case where acetic acid was the solvent the ratio of ISCN : alkene was reduced to 1.2 : 1. Although a stoichiometric ratio of thiocyanogen : iodine was usually employed, several experiments were conducted with an *ca.* 15 mol% excess of iodine;⁵ only minor changes in product distribution resulted. Similarly, the addition of 15 mol% of the radical inhibitor 2,6-di-*t*-butyl-4-methylphenol⁶ to the ISCN solutions in either benzene or acetic acid had no significant effect (Table 3). Authentic samples of the erythro-dithiocyanate (7) and the erythro-isothiocyanatothiocyanate (8) were prepared by the reaction of thiocyanogen with (*E*)-hex-3-ene in acetic acid.^{6 19}

Reaction of 4-*t*-Butylcyclohexene with Iodine-Potassium Thiocyanate.—A mixture of 4-*t*-butylcyclohexene (1.0 g, 7.2 mmol), iodine (4.4 g, 17.3 mmol), and potassium thiocyanate (2.1 g, 26.1 mmol) was stirred in chloroform (30 ml) at 20 °C in the dark for 20 h. Work-up yielded an oil (2.12 g). P.l.c. [hexane-chloroform (9 : 1)] of a portion (0.91 g), gave: (*i*) a mixture (5 : 4) of *c*-4-iodo-*t*-3-isothiocyanato-*r*-1-*t*-butylcyclohexane (11) and *t*-3-iodo-*c*-4-isothiocyanato-*r*-1-*t*-butylcyclohexane (12) (0.13 g, 12%); ν_{\max} 2 042 cm⁻¹ (NCS); δ 0.93 [s, overlapping CMe₃ of (11) and (12)], 1.79 (m, CH₂, CH), 4.01 and 4.28 [2 m, *W*_{1/2} 5 and 5 Hz, CHNCS of

(11) and (12)], and 4.67 [m, $W_{\frac{1}{2}}$ 12 Hz, overlapping CHI of (11) and (12)]; and (ii) a mixture (ca. 5 : 4) of *c*-4-iodo-*t*-3-thiocyanato-*r*-1-*t*-butylcyclohexane (9) and *t*-3-iodo-*c*-4-thiocyanato-*r*-1-*t*-butylcyclohexane (10) (0.69 g, 65%); ν_{\max} 2 160 cm^{-1} (SCN); δ 0.92 [s, overlapping CMe_3 of (9) and (10)], 1.71 (m, CH_2 , CH), 4.18 [m, $W_{\frac{1}{2}}$ 11 Hz, overlapping CHSCN of (9) and (10)], and 4.96 [m, $W_{\frac{1}{2}}$ 13 Hz, overlapping CHI of (9) and (10)].

Treatment of the mixture of (9) and (10) (0.56 g, 1.54 mmol) with boron trifluoride-ether (1.1 g, 7.8 mmol) at 20 °C in the dark for 26 h gave an oil (0.49 g) which was separated by p.l.c. [hexane-chloroform (9 : 1)] into a mixture (5 : 4, 0.35 g, 61%) of *c*-4-iodo-*t*-3-isothiocyanato-*r*-1-*t*-butylcyclohexane (11) and *t*-3-iodo-*c*-4-isothiocyanato-*r*-1-*t*-butylcyclohexane (12), and a mixture of recovered iodothiocyanates (9) and (10) (50 mg, 9%).

Reaction of 3-*t*-Butylcyclohexene with Iodine-Potassium Thiocyanate.—A mixture of 3-*t*-butylcyclohexene (1.0 g, 7.2 mmol), iodine (4.4 g, 17.3 mmol), and potassium thiocyanate (2.1 g, 21.6 mmol) was stirred in chloroform (30 ml) at 20 °C in the dark for 16 h. Work-up yielded an oil (1.96 g). P.l.c. [hexane-ether (9 : 1)] of a portion (0.24 g) gave: (i) 3-iodo-1-*t*-butylcyclohexene (13) (81 mg, 34%), b.p. 90 °C at 0.2 mmHg (Found: C, 45.5; H, 6.8. $\text{C}_{10}\text{H}_{17}\text{I}$ requires C, 45.5; H, 6.5%); δ 1.04 (s, CMe_3), 2.10 (m, 5- H_2 and 6- H_2), 2.66 (m, 4- H_2), 4.40 (m, $W_{\frac{1}{2}}$ 14.5 Hz, CHI), and 5.52 (m, $W_{\frac{1}{2}}$ 6.5 Hz, 2-H); m/e 264 (M^{+}), 137 ($M^{+} - \text{I}$), and 57 (CMe_3^{+}); (ii) 3-isothiocyanato-1-*t*-butylcyclohexene (14) (48 mg, 27%) as an unstable oil; ν_{\max} 2 060 cm^{-1} (NCS); δ 1.08 (s, CMe_3), 1.88 (m, CH_2), 4.20 (m, $W_{\frac{1}{2}}$ 12 Hz, CHNCS), and 5.54 (m, $W_{\frac{1}{2}}$ 6.5 Hz, 2-H); m/e 195 (M^{+}), 153 ($M^{+} - \text{C}_3\text{H}_6$), and 137 ($M^{+} - \text{NCS}$); and (iii) *c*-2-iodo-*t*-3-thiocyanato-*r*-1-*t*-butylcyclohexane (15) (0.11 g, 36%), m.p. 46–50 °C, b.p. 100 °C at 0.2 mmHg; ν_{\max} 2 155 cm^{-1} (SCN); δ 1.00 (s, CMe_3), 1.72 (m, CH_2), 2.58 (m, CHBu^t), 4.25 (m, $W_{\frac{1}{2}}$ 6.5 Hz, CHSCN), and 4.89 (m, $W_{\frac{1}{2}}$ 5.5 Hz, CHI); m/e 323 (M^{+}), 265.043 ($M^{+} - \text{SCN}^{\cdot}$), 196.1163 ($M^{+} - \text{I}$), 137 ($M^{+} - \text{HI} - \text{SCN}^{\cdot}$), and 57 (CMe_3^{+}).

The iodothiocyanate (9) (0.30 g, 0.92 mmol) was stirred with boron trifluoride-ether (1.1 g, 7.8 mmol) at 20 °C in the dark for 15 h. ^1H N.m.r. analysis of the crude product showed several minor unidentified alkenes (δ 5.50), together with two major components (ca. 1 : 2), viz. 3-*t*-butylcyclohexene, δ 5.55 (m, $W_{\frac{1}{2}}$ 3 Hz, 1-H and 2-H), and, after p.l.c. (hexane), *r*-1-iodo-*c*-3-[2-(2-isothiocyanatopropyl)]-3-methylcyclohexane (24) (78 mg, 26%), b.p. 117 °C at 0.4 mmHg (Found: C, 41.4; H, 5.5; N, 4.4. $\text{C}_{11}\text{H}_{18}\text{INS}$ requires C, 40.9; H, 5.6; N, 4.3%); ν_{\max} 2 060 cm^{-1} (NCS); δ 1.00 (s, 3-Me), 1.38 (m, 4- H_2 and 5- H_2), 1.39 (s, Me_2CNCS), 2.09 (m, 2- H_2 and 6- H_2), and 4.27 (m, $W_{\frac{1}{2}}$ 17.5 Hz, CHI), m/e 323.0214 (M^{+} , $\text{C}_{11}\text{H}_{18}\text{INS}$ requires M , 323.0206), 265.0460 ($M^{+} - \text{NCS}^{\cdot}$), 227.9343 ($M^{+} - \text{C}_7\text{H}_{11}$), 222.9997 ($M^{+} - \text{C}_3\text{H}_6\text{NCS}^{\cdot}$), 196.1164 ($M^{+} - \text{I}$), 137.1327 [$M^{+} - (\text{HI} + \text{NCS}^{\cdot})$], 136.1247 ($\text{C}_{10}\text{H}_{16}^{+}$), 121.1011 (C_9H_{13}), 100.0216 (Me_2CNCS), 95.0858 ($\text{C}_7\text{H}_{11}^{+}$), and 81.0704 (C_6H_9^{+}); δ_{C} 17.3 (3-Me), 24.0 (C-5), 24.5 (Me_2CNCS), 26.2 (C-1), 29.7 (C-4), 39.7 (C-6), 44.0 (C-3), 45.6 (C-2), 67.9 (Me_2CNCS), and 160.0br (NCS).

Reaction of trans-1-Iodo-2-isothiocyanatocyclohexane with Lithium Methoxide.—Butyl-lithium (1.8 ml, 2.88 mmol) was added slowly to anhydrous methanol at 0 °C followed after 5 min by *trans*-1-iodo-2-isothiocyanatocyclohexane (19) (0.40 g, 1.5 mmol), and the mixture was stirred at 0 °C for 3 h. Work-up yielded an oil (0.38 g) which after p.l.c. [hexane-chloroform (1 : 1)] gave: (i) methyl 7-azabicyclo-

[4.1.0]heptane-7-*O*-thiocarboxylate (29) (22 mg, 9%), b.p. 65 °C at 0.25 mmHg (Found: C, 56.3; H, 8.1; N, 8.2. $\text{C}_8\text{H}_{13}\text{NOS}$ requires C, 56.1; H, 7.7; N, 8.2%); δ 1.38 (m, 3- H_2 and 4- H_2), 1.96 (m, 2- H_2 and 5- H_2), 2.68 (m, $W_{\frac{1}{2}}$ 5.5 Hz, 1-H and 6-H), and 3.97 (s, OMe); m/e 171 (M^{+}); and (ii) an inseparable mixture (0.29 g, 63%) of *O*-methyl *N*-(*trans*-2-iodocyclohexyl)thiocarbamate (21) and *S*-methyl *N*-(*trans*-2-iodocyclohexyl)thiocarbamate (22); ν_{\max} 3 400 and 3 250br cm^{-1} (NH); δ 1.87 (m, CH_2), 4.06 (m, CHI, CHN, and Me), 6.43 and 7.78 (2br s, NH); m/e 299 (M^{+}), and 172 ($M^{+} - \text{I}$). Reaction at 20 °C gave many side-products.

2-Methoxy-cis-3a,4,5,6,7,7a-hexahydrobenzothiazole (31).—The mixture of thiocarbamates (21) and (22) (0.15 g, 0.48 mmol) and potassium carbonate (0.36 g) in acetone (5 ml) was kept at 20 °C for 44 h. Work-up gave an oil (0.10 g) which after p.l.c. [hexane-ether (1 : 1)] yielded: (i) 2-methoxy-cis-3a,4,5,6,7,7a-hexahydrobenzothiazole (53 mg, 63%), b.p. 65 °C at 0.25 mmHg (Found: C, 56.4; H, 7.8; N, 8.3; S, 18.4. $\text{C}_8\text{H}_{13}\text{NOS}$ requires C, 56.1; H, 7.7; N, 8.2; S, 18.7%); ν_{\max} 1 615 (C=N) and 1 230 cm^{-1} (C-O); δ 1.62 (m, CH_2), 3.75 (m, CHS and CHN), and 3.84 (s, OMe); m/e 171 (M^{+}), and 128 ($M^{+} - \text{HNCO}$); and (ii) the thiocarbamoylaziridine (29) (trace).

2-Butoxy-cis-3a,4,5,6,7,7a-hexahydrobenzothiazole (32).—Butyl-lithium (0.65 ml, 0.9 mmol) was added over 10 min in the presence of air to *trans*-1-iodo-2-isothiocyanatocyclohexane (19) (0.10 g, 0.37 mmol) in ether (5 ml) and the mixture was kept at –78 °C for 3 h, and then at 20 °C for 15 h. Work-up afforded an oil (90 mg) which after p.l.c. [hexane-chloroform (1 : 1)] gave 2-butoxy-cis-3a,4,5,6,7,7a-hexahydrobenzothiazole (30 mg, 41%), b.p. 74 °C at 0.25 mmHg (Found: C, 61.7; H, 9.2; N, 6.4; S, 15.0. $\text{C}_{11}\text{H}_{19}\text{NOS}$ requires C, 61.9; H, 9.0; N, 6.6; S, 15.0%); ν_{\max} 1 601 cm^{-1} (C=N); δ 1.37 (m, CH_2), 0.93 (t, J 7 Hz, Me), 3.73 (m, $W_{\frac{1}{2}}$ 14.5 Hz, CHS and CHN), and 4.17 (t, J 7 Hz, OCH_2Pr); m/e 213.1191 (M^{+} requires 213.1187), 180.1384 ($M^{+} - \text{HS}^{\cdot}$ requires 180.1389), 171.0699 ($M^{+} - \text{C}_3\text{H}_6$ requires 171.0718), 157.0577 ($M^{+} - \text{C}_4\text{H}_8$ requires 157.0562), and 114.0503 ($\text{C}_6\text{H}_{10}\text{S}^{+}$ requires 114.0518); δ_{C} 13.8 (C-4'), 19.1 (C-3'), 21.6 (C-6), 22.7 (C-5), 29.2 (C-7), 29.5 (C-2'), 31.0 (C-4), 53.5 (C-7a), 68.7 (C-1'), 70.4 (C-3a), and 168.1 (C-2).

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