vic-Iodothiocyanates and Iodoisothiocyanates.   Part 1.   Preparation and Isomerization †
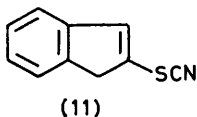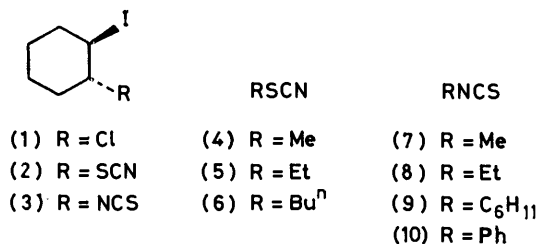
By **Richard C. Cambie, Ho H. Lee, Peter S. Rutledge,** and **Paul D. Woodgate,*** Department of Chemistry, University of Auckland, Auckland, New Zealand

Treatment of alkenes with iodine(I) thiocyanate gives high yields of vic-iodothiocyanates and vic-iodoisothiocyanates.   The ratio of the adducts varies with the reagents used. the conditions employed. and the nature of the alkene.   The products are consistent with the intermediacy of an iodonium ion for cyclohexene and 5α-androst-2-ene and an open or asymmetric cation for α-arylalkenes.   The rate of addition is accelerated by phase-transfer catalysts. especially in the case of 5α-androst-2-ene.   The iodothiocyanate is the kinetically formed product which may be rearranged to the thermodynamically more stable iodoisothiocyanate by boron trifluoride–ether. either in situ or separately. thereby providing a simple route to the latter derivatives.

ALTHOUGH the reactions of a variety of alkenes with iodine(I) thiocyanate have been reported [1-3] and kinetic data [4] support an ionic pathway via a free carbocation, few products have been conclusively identified.   With one exception,[5] iodine(I) thiocyanate has been prepared by treatment of thermally unstable thiocyanogen with iodine.   We have investigated alternative syntheses of vic-iodothiocyanates and vic-iodoisothiocyanates which do not involve the prior formation of thiocyanogen.

Initial reactions were carried out with cyclohexene using preformed iodine(I) thiocyanate generated from potassium thiocyanate and iodine(I) chloride.   The addition was affected (see Experimental section) by both the polarity of the solvent and the relative molar ratios of the reagents.   For example, using a 1 : 1 : 1.2 ratio of substrate to reagents, the products varied from a 95% yield of the undesired adduct trans-1-chloro-2-iodocyclohexane (1) [6a,7] in chloroform as solvent to a moderate yield (43%) of the trans-iodothiocyanate (2)

(1) R = Cl	(4) R = Me	(7) R = Me
(2) R = SCN	(5) R = Et	(8) R = Et
(3) R = NCS	(6) R = Bu^n	(9) R = C_6H_{11}
		(10) R = Ph

(11)

and a low yield (1%) of the trans-iodoisothiocyanate (3) in the more polar solvent tetramethylene sulphone (sulpholan) which is known to be a good ionising solvent for alkali thiocyanates.[8]   From a practical viewpoint the reaction was cheaper, and the work-up easier, if a combination of chloroform and sulpholan was used as solvent.   Doubling the amount of potassium thiocyanate and carrying out the reaction in chloroform–sulpholan (1 : 1) at 0 °C for 4 h (optimum conditions) gave a 67% yield of the iodothiocyanate, a 1% yield of the isomer (3), and only a trace of the iodochloride (1).

† Preliminary communications, ref. 6.

Control experiments showed that compounds (2) and (3) were primary products and were stable under the reaction conditions.   However, both were sensitive to heat and light and were unstable on preparative layer chromatography (p.l.c.) and hence the isolated yields were lower than the crude yields.

Treatment of cyclohexene with potassium thiocyanate (3 mol. equiv.) and the weaker electrophile iodine (2.4 mol. equiv.) in chloroform–sulpholan (1 : 1) at 0—3 °C for 21 h (optimum conditions) gave a 96% yield of the iodothiocyanate (2).   An identical result was obtained when the reaction was carried out under nitrogen in the presence of the free-radical inhibitor galvinoxyl, indicating that the reaction proceeded via an ionic pathway.   Use of thallium(I) thiocyanate instead of potassium thiocyanate also gave a high conversion (96%) to adducts but in this case the iodoisothiocyanate (3) (60%) predominated over the iodothiocyanate (2) (15%).   When chloroform alone was used as solvent in the latter reaction, compounds (3) and (2) were formed in the ratio 2 : 1, respectively.   Thus, variation of the metal thiocyanate allows formation of either the iodothiocyanate or the iodoisothiocyanate as the major product.   The enhanced yield of iodoisothiocyanate when thallium(I) thiocyanate is used is presumably due to retention of thallium–sulphur bonding [9] resulting in an increased availability of nucleophilic nitrogen in the potential ambident anion.   The reaction probably follows a pathway similar to that suggested [10] for the iodocarboxylation of alkenes with thallium(I) carboxylates and iodine: carrying out the reaction under irradiation by u.v. light in n-pentane gave a complex mixture consisting mainly of di-iodide.   When the reaction using thallium(I) thiocyanate was carried out at 20 °C the rate of addition of iodine(I) thiocyanate to cyclohexene was accelerated if water was used as a second phase and was further increased by addition of either of the phase-transfer catalysts Adogen 464 [methyltrialkyl (C_8—C_{10}) ammonium chloride] or 18-crown-6.   Thus, for example, under comparable conditions, cyclohexene gave an 84% conversion to a mixture of (2) (77%) and (3) (7%) in the presence of 18-crown-6 but only an 11% conversion in its absence, the iodoisothiocyanate (3) then being the major component.

The structures of the products were determined from microanalytical and spectroscopic data and were sup-

ported by subsequent chemical transformations (see following paper). The isomers were well separated by p.l.c. and were clearly distinguishable by their i.r. spectra, the iodoisothiocyanate (3) exhibiting a strong broad band at 2 060 cm^{-1} and the iodothiocyanate (2) showing a strong sharp peak at 2 160 cm^{-1}. Mass spectra of both isomers showed a strong peak (>70%) at m/e 81 implying that expulsion of the elements of ISCN or INCS together with a hydrogen atom readily occurred. The ^{1}H n.m.r. spectrum of the iodothiocyanate showed multiplets at δ 3.52 and 4.34 due to the protons geminal to the thiocyanato- and iodo-groups, respectively, while that of the iodoisothiocyanate showed corresponding multiplets at δ 3.88 and 4.21. The magnitude of the coupling constants or half-height widths indicated that the protons in question were axial and thus both derivatives existed in chair conformations. The chemical shifts of the thiocyanato- and iodoisothiocyanato-carbon atoms in the ^{13}C n.m.r. spectra of the iodothiocyanate (2) and -isothiocyanate (3), respectively, corresponded with those of simple organic thiocyanates and isothiocyanates (Table 1).[11] For a pair of isomers
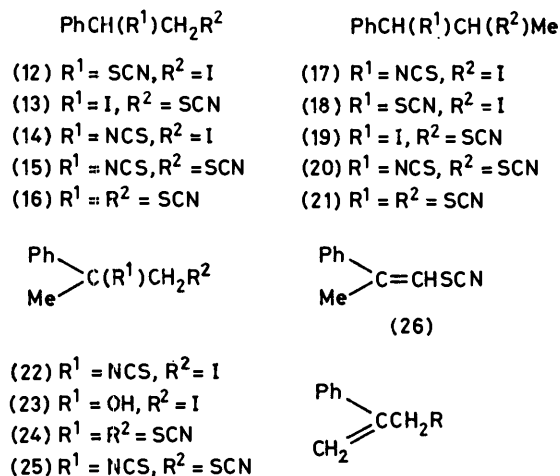
TABLE 1

^{13}C N.m.r. data [chemical shift δ (p.p.m.)]

Compound		Compound	
(4)	113.5	(7)	128.6
(5)	112.1	(8)	130.7
(6)	112.1	(9)	132.3
(2)	110.4	(10)	135.7
		(3)	133.1

it was noted that the isothiocyanato-group exerts a larger deshielding effect on the carbon atom directly attached to the group than does the thiocyanato-group. The iodoisothiocyanate (3) has been isolated previously by Raby [2a,12] who erroneously assigned to it the structure of the isomeric iodothiocyanate (2).

Reactions similar to the above were also carried out using styrene, 1-phenylpropene, 2-phenylpropene, indene, acenaphthylene, and 5α-androst-2-ene as the substrates. As expected,[4] the reactions of the α-aryl-alkenes were much slower and the products less stable than those of cyclohexene. Consequently extended reaction times were needed in order to achieve appreciable conversion of these alkenes, resulting in the formation of mixtures of products from secondary reactions. The yields of secondary products became more pronounced when more polar solvents were used and, in the case of 2-phenylpropene and indene, products of elimination [e.g. (11)] were also obtained. The reagents added trans-stereospecifically to acenaphthylene, regiospecifically to styrene and indene, and with high regioselectivity to 1-phenylpropene. The products from 2-phenylpropene were diverse, reflecting the partitioning of a tertiary carbocationic intermediate among several pathways.

In the case of styrene the best yield (72%) of the Markownikov adduct, 2-iodo-1-phenyl-1-thiocyanato-ethane (12) was obtained using potassium thiocyanate (4 mol. equiv.) and iodine(I) chloride (2 mol. equiv.) in

chloroform–sulpholan (1 : 9) at 0—3 °C for 22 h. Reaction with potassium thiocyanate (3.75 mol. equiv.) and iodine (3 mol. equiv.) in the same solvent mixture for 48 h gave only 36% of the iodothiocyanate (12) together with 3% of its regioisomer (13), suggesting that the

PhCH(R^1)CH$_2$R^2

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

PhCH(R^1)CH(R^2)Me

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

Ph,Me>C(R^1)CH$_2$R^2

(22) R^1 = NCS, R^2 = I
(23) R^1 = OH, R^2 = I
(24) R^1 = R^2 = SCN
(25) R^1 = NCS, R^2 = SCN

Ph,Me>C=CHSCN

(26)

Ph,CH$_2$>CCH$_2$R

(27) R = SCN
(28) R = NCS

cationic intermediate may be iodonium-like when iodine is used but carbocation-like when iodine(I) chloride is used. With thallium(I) thiocyanate and iodine, styrene gave a mixture of the iodoisothiocyanate (14) (27%) and iodothiocyanate (12) (61%) when the reaction was carried out in chloroform at 0 °C for 5 h. The products (12) and (14) were formed in lower yield, together with trace amounts of (15) and (16) and the anti-Markownikov adduct (13) (6%) when the reaction time was extended to 24 h. It was shown that, independently, neither (12) nor (14) was convertible into the anti-Markownikov adduct (13) under the reaction conditions. No anti-Markownikov products were formed when the reaction was carried out in chloroform–sulpholan (1 : 9) but in this case the products (15) (9%) and (16) (9%) were also formed, showing that under more polar homogeneous conditions the iodine-containing adducts reacted further.

The ^{1}H n.m.r. spectrum of the iodoisothiocyanate (14) showed a doublet (J 7 Hz) centred at δ 3.50, which was assigned to the protons geminal to the iodo-group, and a triplet (J 7 Hz) at δ 4.95 due to the proton geminal to the isothiocyanate group. In contrast, the spectrum of the iodothiocyanate (12) showed a multiplet at δ 3.84 for the protons geminal to the iodo-group and a doublet of doublets (J 10.5 and 5.5 Hz) at δ 4.62 for the proton geminal to the thiocyanate group. The complexity of the signals for the iodothiocyanate (12) can be rationalized since the two protons on the prochiral C-1 atom are diastereotopic [13] and observably anisochronous and hence couple with each other as well as with the adjacent methine proton. The simpler ^{1}H n.m.r. spectral pattern for the iodoisothiocyanate must then be due to accidental equivalence of the two diastereotopic methylene protons. This accidental degeneracy was not
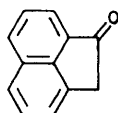
removed when the solvent was changed to [$^2H_6$]benzene or [$^2H_6$]dimethyl sulphoxide. Using the gated decoupling technique,[14] a doublet (J 3 Hz) in the ^{13}C n.m.r. spectrum of the iodothiocyanate (12) due to the thiocyanato-carbon atom was shown to arise by long range coupling with the benzylic proton. This was confirmed by collapse of the doublet to a singlet of higher relative intensity when the dual technique [15] of selective irradiation of the proton geminal to the thiocyanato-group combined with gated noise decoupling was employed. No similar $^3J_{C-H}$ bond coupling was observed for the iodoisothiocyanate (14).

In the reactions of 1-phenylpropene, pairs of *erythro*- and *threo*-isomers of each product were isolated except for 2-iodo-1-isothiocyanato-1-phenylpropane (17). Differentiation between the stereoisomers was achieved by comparison of the relative sizes of the coupling constants of the benzylic proton signals in the ^1H n.m.r. spectra. With 1-phenylpropene, the iodine–thallium(i) thiocyanate reagent was regiospecific in its formation of the iodoisothiocyanate (17) but only regioselective for the iodothiocyanato-products (18) and (19) and the substitution products (20) and (21). The Markownikov adduct (18) was not isolated but its structure was assigned from ^1H n.m.r. data of the crude products from various runs. The majority of products, *viz.* (22), (23), (24), and (25), from 2-phenylpropene were those of Markownikov attack of electrophilic iodine followed by capture of an anion and then further substitution of the iodo-group. As expected,[16] the allylic thiocyanate (27) isomerized readily into iodoisothiocyanate (28), even on storage at 0 °C.

Structures of the *cis*- and *trans*-adducts (29), (30), (31), (32), (33), and (34) of indene * were determined by

(29)	R^1 = NCS, R^2 = H, R^3 = I
(30)	R^1 = NCS, R^1 = H, R^3 = SCN
(31)	R^1 = NCS, R^2 = SCN, R^3 = H
(32)	R^1 = R^3 = SCN, R^2 = H
(33)	R^1 = SCN, R^2 = I, R^3 = H
(34)	R^1 = SCN, R^2 = H, R^3 = I

| (35) | R^1 = SCN, R^2 = H, R^3 = NCS |
(36)	R^1 = R^3 = SCN, R^2 = H
(37)	R^1 = NCS, R^2 = H, R^3 = I
(38)	R^1 = SCN, R^2 = H, R^3 = I
(39)	R^1 = NCS, R^2 = SCN, R^3 = H

(40)

comparison of the coupling constants in the ^1H n.m.r. spectra of pairs of isomers or from the spectral patterns of the benzylic methylene protons. In general, *cis*-1,2-vicinal coupling was greater than *trans*-1,2-vicinal

* Products from indene are reported incorrectly in the preliminary communication.[6a]

coupling. The methylene signals of a *trans*-isomer were two sets of doublets (8 lines; J_{gem} 15—18 Hz) while those of a *cis*-isomer were two sets of doublets (4 lines; J_{gem} 0) (*cf.* ref. 17).

Acenaphthylene, in particular, gave products [*e.g.* (35) and (36)] where further substitution of the initial adducts had occurred. Although the unstable product *trans*-1-iodo-2-isothiocyanatoacenaphthene (37) was isolated in 16% yield from the reaction with thallium(i) thiocyanate–iodine, the isomeric *trans*-1-iodo-2-thiocyanatoacenaphthene (38) was too unstable to be isolated, its formation being verified from ^1H n.m.r. analysis of the crude products. Likewise, *cis*-1-isothiocyanato-2-thiocyanatoacenaphthene (39) was also unstable, undergoing partial conversion (Scheme) into the ketone (40) during p.l.c.
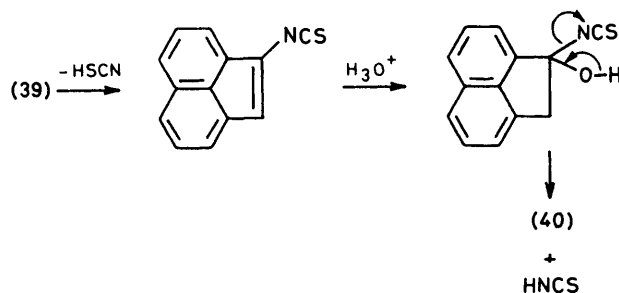
SCHEME

The practical advantage of addition of the phase transfer catalyst Adogen 464 to the potassium thiocyanate–iodine system was particularly evident with 5α-androst-2-ene, where the ratios of products to alkene after 94 h at 20 °C were 0.4 : 1 (chloroform), 1.7 : 1 (chloroform–water), and 15 : 1 (chloroform–water–Adogen 464). These reactions gave mixtures of regioisomers (41) and (42) (23%), (43) and (44) (34%), and
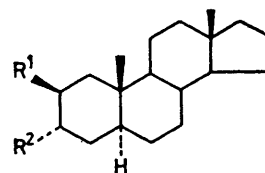
| (41) R^1 = NCS, R^2 = I |
| (42) R^1 = I, R^2 = NCS |
| (43) R^1 = SCN, R^2 = I |
| (44) R^1 = I, R^2 = SCN |
| (45) R^1 = Cl, R^2 = I |
| (46) R^1 = I, R^2 = Cl |

(45) and (46) (2%) from which pure samples of the major components (41) and (43) were obtained after crystallization. Compounds (43) and (44) each reverted to 5α-androst-2-ene on standing or during p.l.c.

Although the above methods gave high yields under optimum conditions, mixtures of iodothiocyanates and iodoisothiocyanates were usually formed. However, reaction of boron trifluoride–ether with the kinetically formed iodothiocyanate was found to effect isomerization

to the thermodynamically more stable iodoisothiocyanate in a manner similar to that of simple organic thiocyanates.[16] Moreover, with the exception of the adducts from cyclohexene and styrene, isomerization of the iodothiocyanates into the corresponding iodoisothiocyanates could be effected in high yield during the course of the reaction with thallium(I) thiocyanate and iodine if boron trifluoride–ether was added to the reaction mixtures.* With both cyclohexene and styrene, inclusion of the Lewis acid in the reaction mixture merely increased the proportion of the iodothiocyanate (2) or (12), presumably because complexation between boron and nitrogen (HASB principle[18]) allowed the sulphur terminus of the anion freedom to undergo kinetic attack on the cationic intermediate. Co-incidentally, the rate of isomerization of the iodothiocyanates (2) and (12) into the corresponding iodoisothiocyanates was slow under these conditions. Fewer products were formed from all the alkenes when boron trifluoride–ether was present in the reaction mixture. Thus, the Lewis acid has a dual role in that not only can it influence the ratio of primary adducts, but it can also catalyse isomerization to the thermodynamically more stable adduct.

EXPERIMENTAL

Unless otherwise indicated, i.r. spectra were recorded for solutions in carbon tetrachloride with a Perkin-Elmer 237 or 337 spectrophotometer. ¹H N.m.r. spectra were measured for solutions in carbon tetrachloride with a Varian T60 spectrometer (tetramethylsilane as internal reference) and ¹³C n.m.r. spectra for solutions in deuteriochloroform with a JEOL JNM-FX60 Fourier transform instrument. Low resolution mass spectra were determined with a Varian-MAT CH7 spectrometer. T.l.c. was carried out on Keiselgel DG (Riedel de Haen) (0.5 mm thickness); preparative t.l.c. (p.l.c.) was carried out on Keiselgel PF$_{254 + 366}$ (Merck) (1 mm thickness) with hexane–chloroform (2 : 1) as solvent. All solvents were purified by methods in ref. 19 and all alkenes were freshly distilled or recrystallized before use. Thallium(I) thiocyanate † was prepared [21] from potassium thiocyanate and thallium(I) nitrate and was recrystallized from water. Unless otherwise stated, all reactions were carried out in the absence of light and yields of products were calculated from ¹H n.m.r. analysis.

Solvent systems were: A, chloroform; B, chloroform–sulpholan; C, sulpholan; D, chloroform–hexamethylphosphoric triamide; E, chloroform–dimethyl sulphoxide (DMSO); F, dichloromethane; G, diethyl ether; H, carbon tetrachloride; I, pentane.

The i.r. spectra of all thiocyanato- and isothiocyanato-derivatives showed stretching frequencies in the regions 2 160 (SCN) and 2 060 cm⁻¹ (NCS), respectively.

Addition of Iodine(I) Thiocyanate to Cyclohexene.—(a) *Using potassium thiocyanate and iodine(I) chloride.* A solution of potassium thiocyanate (0.24 g, 2.5 mmol) in the appropriate solvent (10 ml) was added to iodine(I) chloride (0.24 g, 1.5 mmol) and the mixture was stirred at 0 °C for 1—2 h. Cyclohexene (0.10 g, 1.25 mmol) was then added to the blood-red solution and the stirring was continued for

* With potassium thiocyanate it was necessary to add the Lewis acid after adduct formation was completed. Even so, yields were low.

the time recorded. Products were isolated by work-up, extraction into pentane–ether (3 : 1), and p.l.c. Conditions and yields are shown in Table 2.

TABLE 2

Solvent	Temp./°C	Time/h	Conversion (%)	Yield (%) (1)	(2)	(3)
A	20	27	95 [a]	95	trace	trace
B (2 : 1)	20	17	90	28 [b]	39 [b]	4 [b]
C	20	24	78	13 [b]	43 [b]	1 [b]
B (1 : 1)	0	2	49	2 [b]	32 [b]	1 [b]
B (1 : 1)	0	4	84	trace	67 [b]	1 [b]
B (1 : 1)	0	6	83	trace	80	3
D	0	4	13		13	
E	0	4	59		59	

[a] Molar ratio cyclohexene : KSCN : ICl = 1 : 1 : 1.2.
[b] Yields after p.l.c.

(b) *Using potassium thiocyanate and iodine.* A cold solution of potassium thiocyanate (0.34 g, 3.75 mmol) in solvents A or B (10 ml) was added to iodine (0.76 g, 3.0 mmol) and the mixture was stirred at 0 °C for 2 h. Cyclohexene (0.10 g) was added and the stirring was continued for the time recorded. The mixture was worked up as in (a). Product yields are shown in Table 3.

TABLE 3

Solvent	Temp./°C	Time/h	Yield (%) (2)	(3)
B (1 : 9)	0	4	50 [a]	
B (1 : 1)	0	2	72	
B (1 : 1)	0—3	21	96	
A	0—3	24	24	20
A	20	24	96	4

[a] Molar ratio cyclohexene : KSCN : I$_2$ = 1 : 2 : 1.2.

(c) *Using thallium(I) thiocyanate and iodine.* A mixture of thallium(I) thiocyanate (0.615 g, 2.5 mmol) and iodine (0.315 g, 1.25 mmol) in the appropriate solvent (10 ml) was stirred at 0 °C for 2 h. Cyclohexene (0.10 g) was added over 10 min and the mixture was kept at the appropriate temperature for the time recorded. The mixture was

TABLE 4

Solvent	Temp./°C	Time/h	Conversion (%)	Yield (%) (2)	(3)
F	20	24	59	18	23
F	40	72	43	9	19
A	20	48	72	33	17
A	62	1	56	16	13
G	20	24	53	15	19
H	20	48	43	7	7 [a]
I	20	24	59	trace	7 [a]
C	20	1	35	6	9 [b]
E (2 : 1)	20	18	62	10	29 [b]
A	0—3 [c]	21	92	25	53
B (1 : 1)	0—3 [c]	21	96	15	60

[a] Also contained *trans*-1,2-di-iodocyclohexane. [b] Also contained *trans*-2-iodocyclohexanol.[9,22] [c] Molar ratio cyclohexene : TlSCN : I$_2$ = 1 : 3 : 2.4.

worked up as in (a). Yields were obtained after p.l.c. and are shown in Table 4.

(d) *Using potassium thiocyanate, iodine, and Adogen 464.*

† According to literature reports [8,20] it is possible to obtain thallium(I) isothiocyanate from the reaction of thallium(III) chloride with potassium thiocyanate. During the present study this compound was found to have an identical m.p. and i.r. spectrum with those of thallium(I) thiocyanate and to give identical results in its reaction with cyclohexene. Thus, the i.r. data, claimed to indicate and to differentiate between two thallium(I) compounds, appears to have been incorrectly interpreted.

A solution of potassium thiocyanate (0.61 g, 6.25 mmol) in water (1 ml) was added to a mixture of iodine (0.76 g) and Adogen 464 (29 mg, 0.06 mmol) in chloroform (10 ml). Cyclohexene (0.10 g) was added dropwise and the mixture was stirred at 20 °C for 22 h. Excess of iodine was then removed with aqueous sodium disulphite and the products were extracted into dichloromethane. Adogen 464 was removed by passing the organic solution through a short column of silica gel. Work-up gave a pale yellow oil (0.31 g, 91%) which was separated by p.l.c. into the adducts (2) (61%) and (3) (17%).

After 2 h the conversion was 43% and the ratio of adducts (2) to (3) was 1 : 2.2. In the absence of Adogen 464 the conversion was 24% and the ratio 1 : 1.5, and in the absence of water and Adogen 464 the conversion was 11%.

(e) *Using potassium thiocyanate, iodine, and* 18-*crown*-6. Iodine (0.76 g) was added to anhydrous potassium thiocyanate (0.61 g) and 18-crown-6 (0.33 g, 1.25 mmol) in chloroform (10 ml), and the mixture was stirred at 20 °C for 10 min. Cyclohexene (0.10 g) was added and the stirring was continued at 20 °C for 2 h in a dry atmosphere. Work-up as in (d) gave a pale yellow oil (0.30 g, 84%) containing the adducts (2) (77%) and (3) (7%). The conversion in the absence of 18-crown-6 was 11%.

(f) *In the presence of boron trifluoride–ether.* A mixture of thallium(I) thiocyanate (0.92 g, 3.75 mmol) and iodine (0.76 g) in chloroform (10 ml) was stirred at 0 °C for 2 h. Boron trifluoride–ether (0.53 g, 3.75 mmol) was added followed by cyclohexene (0.10 g) in chloroform (1 ml). The mixture was stirred at 0—3 °C for 22 h and worked up to give an oil (0.29 g, 88%) which was separated by p.l.c. into the adducts (2) (69%) and (3) (1%). *trans*-1-*Iodo*-2-*thiocyanatocyclohexane* (2) was a yellow oil, b.p. 110° at 0.7 mmHg (Found: C, 31.5; H, 3.6; H, 48.3; N, 5.3. $C_7H_{10}INS$ requires C, 31.5; H, 3.8; I, 47.5; N, 5.2%), δ 3.52 (m, CHS) and 4.34 (t of d, J 8, 8, and 4.5 Hz, CHI), m/e 267 ($M^{+\cdot}$), δ_C 24.67 (C-4), 26.23 (C-5), 32.34 (C-6)*, 32.73 (C-3)*, 38.57 (C-1), 55.58 (C-2), and 110.38 (SCN).

Addition of boron trifluoride–ether (0.53 g) to a solution of the iodothiocyanate (2) (0.34 g, 1.25 mmol) in chloroform (10 ml) followed by stirring at 20 °C for 30 h and work-up (p.l.c.) gave the iodoisothiocyanate (3) (65%) and starting material (25%). *trans*-1-*Iodo*-2-*isothiocyanatocyclohexane* (3) crystallized from pentane as pale yellow needles, m.p. 35.5—36° (Found: C, 31.6; H, 3.6; I, 48.2; N, 5.4. C_7-$H_{10}INS$ requires C, 31.5; H, 3.8; I, 47.5; N, 5.2%), δ 3.88 (m, $W_{1/2}$ 20 Hz, CHN), and 4.21 (t of d, J 7, 7, and 4 Hz, CHI), m/e 267 ($M^{+\cdot}$), δ_C 23.25 (C-4), 26.36 (C-5), 31.82 (C-6)*, 33.25 (C-3)*, 37.27 (C-1), 62.98 (C-2), and 133.11 (NCS).

Addition of Iodine(I) *Thiocyanate to Styrene.*—(a) *Using potassium thiocyanate and iodine*(I) *chloride.* A solution of potassium thiocyanate (0.49 g, 5.0 mmol) in solvent B (1 : 9) (8 ml) at 0 °C was added to a solution of iodine(I) chloride (0.41 g, 2.5 mmol) in the same solvent (2 ml), and the mixture was stirred at 0 °C for 2 h. Styrene (0.13 g, 1.25 mmol) in chloroform (0.5 ml) was added and the mixture was stirred at 0—3 °C for the time recorded. Products were isolated by work-up and extraction into chloroform–pentane (1 : 10). Details are shown in Table 5.

(b) *Using potassium thiocyanate and iodine.* A cold solution of potassium thiocyanate (0.37 g, 3.75 mmol) in

solvent A or B (10 ml) was added to iodine (0.76 g, 3.0 mmol) and the mixture was stirred at 0 °C for 2 h. Styrene

TABLE 5

Molar ratio Styrene : KSCN : ICl			Time/h	Conversion (%)	Yield (%) (12)
1	2	1.2	4	15	15 [a]
1	2	1.2	72	60	50 [b]
1	4	3	11	76	37 [c,d]
1	4	2	20	72	36 [c]
1	2.2	2	20	82	70
1	1.5	1	20	72	72 [d]

[a] Using solvent B (1 : 1). [b] Also contained iodoisothiocyanate (14) (10%). [c] Isolated by p.l.c. [d] Also contained 1-chloro-2-iodo-1-phenylethane (*ca.* 13%).

(0.13 g) in chloroform (0.5 ml) was added and the mixture was stirred for the time recorded. The mixture was worked up as in (a). Details as shown in Table 6.

TABLE 6

Solvent	Temp./°C	Time/h	(12)	Yield (%) (13)	(14)
B (1 : 1)	0—3	68	36	3	
B (1 : 9)	0—3	48	36	3	
A [a]	20	24	71		24

[a] Under N_2.

(c) *Using thallium*(I) *thiocyanate and iodine.* A mixture of thallium(I) thiocyanate (0.92 g, 3.75 mmol) and iodine (0.76 g) in solvent A or B (10 ml) was stirred at 0 °C for 1.5 h. Styrene (0.13 g) in chloroform (0.5 ml) was added over 10 min and the mixture was stirred at the appropriate temperature for the time recorded. Yields were obtained after p.l.c. and are shown in Table 7.

TABLE 7

Solvent	Temp./ °C	Time/ h	Conversion (%)	(12)	Yield (%) (13)	(14)	(15)	(16)
A	0—3	24	89	38	6	17	0.4	0.7
A	0	5	98	61		27		
B (1 : 9)	0—3	24	84	24		10	9	9
A [a]	20	70 [b]	67	12	6	21		

[a] Molar ratio styrene : TlSCN : I_2 = 1 : 2 : 1. [b] In daylight.

Repetition of the first experiment with the addition of boron trifluoride–ether (0.53 g, 3.75 mmol) gave 94% conversion and products (12) (64%) and (14) (12%).

(d) *Using potassium thiocyanate, iodine, and Adogen* 464. A mixture of styrene (0.13 g), potassium thiocyanate (0.61 g, 6.25 mmol), iodine (0.76 g), and Adogen 464 (29 mg, 0.06 mmol) was stirred in chloroform–water (10 : 1) (10 ml) at 20 °C for 24 h. Work-up gave a pale yellow oil (0.32 g, 90%) which was separated by p.l.c. into the adducts (12) (55%) (14) (14%) and 2-iodo-1-phenylethanol (1%) (i.r. and ¹H n.m.r. spectra[23]). 2-*Iodo*-1-*phenyl*-1-*thiocyanatoethane* (12) formed needles, m.p. 70.5—71° (Found: C, 37.2; H, 3.1; I, 43.6; N, 5.0. C_9H_8INS requires C, 37.4; H, 2.8; I, 43.9; N, 4.8%), δ 3.84 (m, CH_2I), 4.62 (d of d, J 10.5 and 5.5 Hz, CHS), and 7.40 (br s, ArH), m/e 289 ($M^{+\cdot}$), δ_C 5.58 (t, J_{C-H} 155 Hz, C-1), 53.24 (d, J_{C-H} 153 Hz, C-2), 110.64 (d, $^3J_{C-H}$ 3 Hz, SCN), 127.40 (d, J 155 Hz, *o*-C), 129.21 (d, J 164 Hz, *m*-C), 129.73 (d, J 164 Hz, *p*-C), and 135.40 (s, *ipso*-C).

Addition of boron trifluoride–ether (0.53 g) to the iodo-thiocyanate (12) (0.19 g, 0.66 mmol) in chloroform (15 ml) followed by stirring at 0—3 °C for 40 h and work-up gave the iodoisothiocyanate (14) (89%).

1-Iodo-1-phenyl-2-thio-cyanatoethane (13) was an un-

* Assignments may be reversed.

stable oil, δ 3.77 (m, CH₂S) and 5.30 (d of d, J 10.5 and 6 Hz, CHI), m/e 289 ($M^{+\cdot}$). 2-*Iodo-1-isothiocyanato-1-phenylethane* (14) was a pale yellow oil, b.p. 132° at 0.1 mmHg (Found: C, 37.9; H, 2.8; I, 43.7; N, 5.1. C_9H_8INS requires C, 37.4; H, 2.8; I, 43.9; N, 4.8%), δ 3.51 (d, J 7 Hz, CH₂I), 4.95 (t, J 7 Hz, CHN), and 7.39 (s, ArH), m/e 289 ($M^{+\cdot}$), $δ_C$ 9.48 (t, J_{C-H} 153 Hz, C-1), 63.11 (d, J_{C-H} 148 Hz, C-2), 125.84 (d, J_{C-H} 159 Hz, o-C), 129.08 (d, J_{C-H} 164 Hz, m- and p-C; s, $ipso$-C), and 137.52 (s, NCS). 1-Isothiocyanato-1-phenyl-2-thiocyanatoethane (15) was a yellow oil, b.p. 145° at 0.1 mmHg (lit.,[24] 150—152° at 0.4 mmHg), δ(CDCl₃) 3.28 (m, CH₂S), 5.10 (d of d, J 7.5 and 5.5 Hz, CHN), and 7.40 (s, ArH), m/e 220 ($M^{+\cdot}$). 1,2-Dithiocyanato-1-phenyl-ethane (16) formed pale yellow needles, m.p. 98—100° (from carbon tetrachloride) (lit.,[24] 101—102°) (Found: C, 54.9; H, 3.9; N, 12.4. Calc. for $C_{10}H_8N_2S_2$: C, 54.6; H, 3.6; N, 12.7%), δ(CDCl₃) 3.67 (m, CH₂S), 4.66 (d of d, J 8.5 and 6.5 Hz, CHS), and 7.43 (s, ArH), m/e 220 ($M^{+\cdot}$).

Addition of Iodine(I) *Thiocyanate to* 1-*Phenylpropene.*—(a) *Using thallium*(I) *thiocyanate and iodine.* A mixture of thallium(I) thiocyanate (0.92 g, 3.75 mmol) and iodine (0.76 g, 3.0 mmol) in chloroform (15 ml) was stirred at 0 °C for 2 h. 1-Phenylpropene (0.15 g, 1.25 mmol) was added dropwise and the mixture was stirred at 0—3 °C for 46 h. Work-up gave an oil (0.32 g) which was separated by p.l.c. into (i) 2-*iodo-1-isothiocyanato-1-phenylpropane* (17) (39%) as a pale yellow oil, b.p. 120° at 0.1 mmHg (Found: C, 39.9; H, 3.3; I, 41.9; N, 4.8. $C_{10}H_{10}INS$ requires C, 39.6; H, 3.3; I, 41.9; N, 4.6%), δ 1.84 (d, J 6.5 Hz, Me), 4.35 (m, CHI), 5.06 (d, J 4.5 Hz, CHN), and 7.34 (s, ArH), m/e 303 ($M^{+\cdot}$); (ii) *erythro*- and *threo*-1-iodo-1-phenyl-2-thiocyanatopropane (19) (1.3 : 1; 6%), unstable oil, δ 1.54 (d, J 6.5 Hz, *threo*-Me), 1.96 (d, J 6.5 Hz, *erythro*-Me), 3.36—4.05 (m, *threo*- and *erythro*-CHS), 5.08, 6.01 (2 × d, J 10 and 6.5 Hz, *erythro*- and *threo*-CHI), and 7.32 (br s, ArH), m/e 244 ($M^{+\cdot}$ − HSCN); (iii) threo-1-*isothio-cyanato-1-phenyl-2-thiocyanatopropane* (20) (10%, with a trace of the *erythro*-isomer), pale yellow oil, b.p. 137° at 0.1 mmHg (Found: C, 56.3; H, 4.4; N, 12.1. $C_{11}H_{10}N_2S_2$ requires C, 56.4; H, 4.3; N, 12.0%), δ 1.50 (d, J 6.5 Hz, Me), 3.59 (m, CHS), 5.12 (d, J 5.0 Hz, CHN), and 7.39 (s, ArH), m/e 234 ($M^{+\cdot}$), *erythro*-isomer, δ 4.86 (d, J 7.0 Hz, CHN); (iv) erythro- and threo-1-*phenyl-1,2-bisthiocyanato-propane* (21) (1.7 : 1; 3%), needles, m.p. 90—101° (from carbon tetrachloride) (Found: C, 56.6; H, 4.4; N, 12.3. $C_{11}H_{10}N_2S_2$ requires C, 56.4; H, 4.3; N, 12.0%), δ(CDCl₃) 1.52, 1.88 (2 × d, J 7 and 7 Hz, *threo*- and *erythro*-CH), 3.50—4.10 (m, *threo*- and *erythro*-2-CHS), 4.45, 4.58 (2 × d, J 9.5 and 7.5 Hz, *erythro*- and *threo*-1-CHS), and 7.43 (s, ArH), m/e 234 ($M^{+\cdot}$); and (v) erythro- and threo-2-iodo-1-phenyl-1-thiocyanatopropane (18) (2 : 1, 20%), δ 2.15 (d, J 6.5 Hz, CH₃), 4.32 (d, J 10.5 Hz, *erythro*-CHS), 4.55 (d, J 6.5 Hz, *threo*-CHS), 4.50—5.20 (m, *erythro*- and *threo*-CHI), and 7.35 (s, ArH).

Repetition of the reaction with the addition of boron trifluoride–ether (0.53 g, 3.75 mmol) gave compounds (17) (74%) and (21) (12.5 : 1; 15%). After 5 h the products were (17) (38%), (18) (34%), and (19) (5%).

Repetition of the reaction in solvent B (1 : 9) for 41 h gave compounds (17) (18%), (18) (25%), (19) (trace), (20) (21%), and (21) (9%).

(b) *Using potassium thiocyanate and iodine*(I) *chloride.* A cold solution of potassium thiocyanate (0.29 g, 2.75 mmol) in solvent B (1 : 9) (10 ml) was added to iodine(I) chloride (0.41 g, 2.5 mmol) and the mixture was stirred at 0 °C for

2 h. 1-Phenylpropene (0.15 g) was added and the stirring was continued at 0—3 °C for 20 h. Work-up gave an oil (0.27 g) containing compounds (18) (51%) and (19) (3%).

(c) *Using potassium thiocyanate, iodine, and Adogen 464.* A mixture of 1-phenylpropene (0.15 g), potassium thiocyanate (0.61 g, 6.25 mmol), iodine (0.76 g), and Adogen 464 (29 mg, 0.06 mmol) was stirred in chloroform–water (1 : 1) (20 ml) at 20 °C for 46 h. Work-up gave an oil (0.31 g) which was separated by p.l.c. into compounds (17) (31%), (18) (13%), (19) (18%), and 2-iodo-1-phenyl-propan-1-ol (2%) (i.r. and ¹H n.m.r. spectra [23]).

Addition of Iodine(I) *Thiocyanate to* 2-*Phenylpropene.*—(a) *Using potassium thiocyanate and iodine*(I) *chloride.* A cold solution of potassium thiocyanate (0.29 g, 2.75 mmol) in solvent B (1 : 9) (8 ml) was added to iodine(I) chloride (0.41 g, 2.5 mmol) in the same solvent (2 ml) and the mixture was stirred at 0 °C for 2 h. 2-Phenylpropene (0.15 g, 1.25 mmol) was added and the stirring was continued at 0—3 °C for 20 h. Work-up gave an oil (0.24 g) which, after p.l.c., yielded (i) 1-*iodo-2-isothiocyanato-2-phenylpropane* (22) (8%), pale yellow oil, b.p. 155° at 0.10 mmHg (Found: C, 39.7; H, 3.2; I, 42.3; N, 4.5. $C_{10}H_{10}INS$ requires C, 39.6; H, 3.3; I, 41.9; N, 4.6%), δ 2.00 (s, CH₃), 3.61 (s, CH₂I), and 7.40 (s, ArH), m/e 303 ($M^{+\cdot}$), $δ_C$ 18.44 (t, J_{C-H} 152 Hz, C-1), 29.74 (q, J_{C-H} 132 Hz, C-3), 66.10 (s, C-2), 124.67 (d, J_{C-H} 158 Hz, o-C), 128.43 (s, $ipso$-C), 128.82 (d, J_{C-H} 160 Hz, m- and p-C), and 140.51 (br s, NCS); (ii) 2-*phenyl-1-thiocyanatopropene* (26) (2%), pale yellow oil (Found: C, 68.85; H, 5.5; N, 7.5. $C_{10}H_9NS$ requires C, 68.5; H, 5.1; N, 8.0%), δ 2.25 (s, Me), 6.31 (br s, CHS), and 7.37 (s, ArH), m/e 175 ($M^{+\cdot}$); (iii) 2-phenyl-3-thiocyanato-propene (27) (13%), unstable yellow oil, b.p. 110° at 0.05 mmHg, δ 3.97 (d, CH₂S), 5.41 (br s, C=CH *trans* to Ph), 5.57 (s, C=CH *cis* to Ph), and 7.33 (br s, ArH), m/e 175 ($M^{+\cdot}$). After 4 months at 0 °C the compound had isomerised (28%) to 3-*isothiocyanato-2-phenylpro-pene* (28), pale yellow oil (Found: C, 68.3; H, 5.2; N, 7.9. $C_{10}H_9NS$ requires C, 68.5; H, 5.1; N, 8.0%), δ 4.52 (3 lines, CH₂N), 5.43 (3 lines, C=CH *trans* to Ph), 5.54 (2 lines, C=CH *cis* to Ph), and 7.35 (s, ArH); (iv) 1-iodo-2-phenylpropan-2-ol (23) (9%), $ν_{max.}$ 3 555 and 3 466 cm⁻¹ (OH), (¹H n.m.r. spectrum [23]); (v) 2-*isothiocyanato-2-phenyl-1-thiocyanatopropane* (25) (7%), pale yellow oil, b.p. 140° at 0.1 mmHg (Found: C, 56.6; H, 4.4; N, 11.7. $C_{11}H_{10}N_2S_2$ requires C, 56.4; H, 4.3; N, 12.0%), δ 1.98 (s, Me), 3.43 (s, CH₂S), and 7.39 (s, ArH), m/e 176 ($M^{+\cdot}$ − SCN˙); and (vi) 2-*phenyl-1,2-dithiocyanatopropane* (24) (7%), pale yellow needles, m.p. 51—52° (from carbon tetrachloride) (Found: C, 56.4; H, 4.3; N, 11.7. $C_{11}H_{10}-N_2S_2$ requires C, 56.4; H, 4.3; N, 12.0%), δ 2.21 (s, Me), 3.69, 4.05 (2 × d, J_{gem} 14 Hz, CH₂S), and 7.50 (s, ArH), m/e 176 ($M^{+\cdot}$ − SCN˙).

(b) *Using potassium thiocyanate and iodine.* A mixture of 2-phenylpropene (0.15 g), potassium thiocyanate (0.37 g, 3.75 mmol), and iodine (0.76 g, 3.0 mmol) in solvent B (1 : 9) (10 ml) was stirred at 0 °C for 2 h. The mixture was stirred at 0—3 °C for a further 48 h and then worked up by extraction into chloroform–pentane (1 : 19) and p.l.c., to yield the products (22) (6%), (26) (0.2%), (27) (15%), (23) (1%), (25) (1%), and (24) (2%).

(c) *Using thallium*(I) *thiocyanate and iodine.* A mixture of thallium(I) thiocyanate (0.92 g, 3.75 mmol) and iodine (0.76 g) in solvent B (1 : 9) (10 ml) was stirred at 0 °C for 1 h. 2-Phenylpropene (0.15 g) was added over 10 min and the mixture was stirred at 0—3 °C for 48 h. Work-up as in

(b) gave an oil (0.27 g) which was separated by p.l.c. into (22) (16%), (26) (2%), (27) (12%), (25) (22%), and (24) (13%).

Repetition of the reaction in solvent C gave an oil (0.32 g) which yielded (22) (53%), (25) (14%), and (24) (6%). Repetition of the latter experiment with the addition of boron trifluoride–ether (0.58 g, 4.13 mmol) gave (22) (68%), (27) (15%), (25) (1%), and (24) (2%). After 2 h the products were (22) (76%) and (24) (3%).

(d) *Using potassium thiocyanate, iodine, and Adogen* 464. A mixture of 2-phenylpropene (0.15 g), potassium thiocyanate (0.61 g, 6.25 mmol), iodine (0.76 g), and Adogen 464 (29 mg, 0.06 mmol) was stirred in chloroform–water (10 : 1) (11 ml) at 20 °C for 49 h. Work-up gave a pale yellow oil (0.36 g, 95%) which was separated by p.l.c. into compounds (22) (71%), (26) (0.6%), (27) (2%), (23) (4%), (25) (3%), and (24) (1%).

In the absence of Adogen 464 the conversion was 67% and the products were (22) (57%), (27) (3%), and (23) (11%).

Addition of Iodine(I) Thiocyanate to Indene.—(a) *Using thallium(I) thiocyanate and iodine.* A mixture of thallium(I) thiocyanate (0.92 g, 3.75 mmol) and iodine (0.76 g, 3.0 mmol) in solvent B (1 : 9) (10 ml) was stirred at 0° for 2 h. Indene (0.14 g, 1.25 mmol) in chloroform (0.5 ml) was added over 10 min and the mixture was stirred at 0—3 °C for 23 h. Work-up gave an oil (0.27 g) which was separated by p.l.c. into (i) trans-2-*iodo*-1-*isothiocyanatoindane* (29) (8%), needles, m.p. 135—136.5° (from dichloromethane) (Found: C, 40.1; H, 2.7; I, 42.8; N, 4.6. $C_{10}H_8INS$ requires C, 39.9; H, 2.7; I, 42.1; N, 4.7%), $\delta(CDCl_3)$ 3.26 (d of d, J 17 and 8.5 Hz, CH *trans* to I), 3.61 (d of d, J 17 and 7 Hz, CH *cis* to I), 4.35 (m, CHI), 5.36 (d, J 7 Hz, CHN), and 7.29 (m, ArH), m/e 301 ($M^{+\cdot}$); (ii) 2-thiocyanato-indene (11) (2%), δ 3.71 (br s, CH$_2$), 7.03 (br s, C=CH), and 7.23 (m, ArH); (iii) trans-1-*isothiocyanato*-2-*thiocyanato-indane* (30) (11%), pale yellow oil (Found: C, 57.1; H, 3.5; N, 12.2. $C_{11}H_8N_2S_2$ requires C, 56.9; H, 3.5; N, 12.1%), δ 3.27 (d of d, J 17.5 and 6.5 Hz, CH), 3.3—4.0 (m, CH and CHS), 5.29 (d, J 6.5 Hz, CHN), and 7.00—7.67 (m, ArH), m/e 232 ($M^{+\cdot}$); (iv) cis-1-*isothiocyanato*-2-*thiocyanatoindane* (31), pale yellow oil (Found: C, 57.7; H, 3.7. $C_{11}H_8N_2S_2$ requires C, 56.9; H, 3.5%), δ 3.39, 3.40 (2 × d, J 7.5 and 5.5 Hz, CH$_2$), 4.27 (m, CHS), 5.21 (d, J 6 Hz, CHN), and 7.34 (m, ArH), m/e 174 ($M^{+\cdot}$ − SCN$^{\cdot}$); (v) trans-1,2-*dithiocyanatoindane* (32) (6%), yellow oil, b.p. 175° at 0.05 mmHg (Found: C, 56.9; H, 4.1; N, 12.7. $C_{11}H_8N_2S_2$ requires C, 56.9; H, 3.5; N, 12.1%), δ 3.12 (d of d, J 17 and 4.5 Hz, CH), 3.77 (d of d, J 17 and 7 Hz, CH), 4.15 (m, 2-CHS), 4.83 (d, J 4 Hz, 1-CHS), and 7.37 (m, ArH), m/e 174 ($M^{+\cdot}$ − SCN$^{\cdot}$); (vi) cis-2-iodo-1-thiocyanatoindane (33) (4%), unstable yellow oil, δ 3.38 (2 × d, CH$_2$), 4.99 (m, CHI), 5.05 (d, J 6.5 Hz, CHS), and 7.37 (m, ArH), m/e 243 ($M^{+\cdot}$ − SCN$^{\cdot}$); and (vii) trans-2-iodo-1-thiocyanatoindane (34) (11%), unstable oil which decomposed completely on p.l.c., δ 3.33 (d of d, J 17.5 and 3 Hz, CH), 3.85 (d of d, J 17.5 and 5.5 Hz, CH), 4.82 (m, CHI), and 5.14 (d, J 2 Hz, CHS).

Repetition of the reaction in solvent C for 2 h gave an oil (0.37 g, 98%) containing the adducts (19) and (20) in the ratio 1 : 2.6. Repetition of the reaction with the addition of boron trifluoride–ether (0.53 g, 3.75 mmol) gave a solid (0.36 g, 97%) which was separated by p.l.c. into (29) (43%) and (34) (26%). After 23 h the product was mainly (29) (88%).

(b) *Using potassium thiocyanate and iodine(I) chloride.* A

solution of potassium thiocyanate (0.24 g, 2.5 mmol) in solvent B (1 : 9) (10 ml) was added to iodine(I) chloride (0.24 g, 1.5 mmol) and the mixture was stirred at 0 °C for 2 h. Indene (0.14 g) was added and the stirring was continued at 0—3 °C for 22 h. Work-up gave an oil (0.21 g) containing indene (67%), (34) (25%), and (29) (trace).

(c) *Using potassium thiocyanate and iodine.* A mixture of indene (0.14 g), potassium thiocyanate (0.37 g, 3.75 mmol), and iodine (0.76 g) in chloroform (10 ml) was stirred at 20 °C for 23 h. Work-up gave an oil (0.32 g) containing (29) (66%), (32) (17%), (33) (7%), (31) (trace), and (34) (trace).

Addition of Iodine(I) Thiocyanate to Acenaphthylene.—(a) *Using thallium(I) thiocyanate and iodine.* Acenaphthylene (0.19 g, 1.25 mmol) in chloroform (1 ml) was added dropwise to a cold mixture of thallium(I) thiocyanate (0.37 g, 1.5 mmol) and iodine (0.38 g, 1.5 mmol) in chloroform (15 ml). The mixture was stirred at 0 °C for 2 h and worked up to give an oil (0.30 g) which after p.l.c. afforded (i) trans-1-iodo-2-isothiocyanatoacenaphthene (37) (16%), unstable oil, δ 5.81 (d, J 2.5 Hz, CHN), 5.92 (d, J 2.5 Hz, CHI), and 7.35—7.90 (m, ArH), m/e 210 ($M^{+\cdot}$ − I$^{\cdot}$); (ii) trans-1-*isothio-cyanato*-2-*thiocyanatoacenaphthene* (35) (21%), pale yellow crystals, m.p. 118.5—119° (from carbon tetrachloride) (Found: C, 62.5; H, 2.75; N, 10.2. $C_{14}H_8N_2S_2$ requires C, 62.6; H, 3.0; N, 10.4%), $\delta(CDCl_3)$ 5.13 (d, J 3.5 Hz, CHS), 5.81 (d, J 3.5 Hz, CHN), and 7.3—8.0 (m, ArH), m/e 268 ($M^{+\cdot}$); (iii) cis-1-isothiocyanato-2-thiocyanatoacenaphthene (39) (1.6%), unstable yellow solid, $\delta(CDCl_3)$ 5.48 (d, J 6.5 Hz, CHS), 6.06 (d, J 6.5 Hz, CHN), and 7.4—8.0 (m, ArH), m/e 268 ($M^{+\cdot}$); (iv) trans-1,2-*dithiocyanatoacenaphthene* (36) (4%), pale yellow needles, m.p. 141—142° (from chloroform) (Found: C, 62.3; H, 3.1; N, 10.7; S, 23.5. $C_{14}H_8N_2S_2$ requires C, 62.6; H, 3.0; N, 10.4; S, 23.9%), $\delta(CDCl_3)$ 5.40 (s, CHS) and 7.54—8.04 (m, ArH), m/e 268 ($M^{+\cdot}$); (v) trans-1-iodo-2-thiocyanatoacenaphthene (38) (27%), unstable oil, $\delta(CDCl_3)$ 5.50 (d, J 1.5 Hz, CHS) and 6.07 (d, J 1.5 Hz, CHI); and (vi) two unidentified compounds (traces).

Repetition of the reaction using thallium(I) thiocyanate (0.92 g, 3.75 mmol) and iodine (0.76 g, 3.0 mmol) at 0—3 °C for 48 h gave an oil (0.30 g) which was separated by p.l.c. into trans-1,2-di-isothiocyanatoacenaphthene (6%), pale yellow crystals, m.p. 112—115° (from carbon tetrachloride), $\delta(CDCl_3)$ 5.67 (s, CHN), and 7.46—7.92 (m, ArH), m/e 268 ($M^{+\cdot}$), (35) (27%), (39) (3%), (36) (3%), and two unidentified compounds (traces).

Repetition of the latter reaction in solvent B (1 : 9) gave an oil (0.32 g) which was separated by p.l.c. into compounds (35) (10%), (39) (5%), (36) (10%), and two unidentified products (traces).

(c) *Using potassium thiocyanate and iodine(I) chloride.* A cold solution of potassium thiocyanate (0.29 g) in solvent B (1 : 9) (10 ml) was added to iodine(I) chloride (0.41 g, 2.5 mmol) and the mixture was stirred at 0 °C for 2 h. Acenaphthylene (0.19 g) in chloroform (1 ml) was added over 10 min and the stirring continued at 0—3 °C for 24 h. Work-up gave an oil (0.30 g) which was separated by p.l.c. into compounds (37) (7%), (36) (5%), trans-1-chloro-2-thiocyanatoacenaphthene (12%) [$\delta(CDCl_3)$ 5.24 (d, J 1.5 Hz, CHS), 5.81 (d, J 1.5 Hz, CHCl), and 7.30—7.95 (m, ArH), m/e 247 and 245 ($M^{+\cdot}$)], (31) (5%), (36) (8%), and (38) (14%).

Addition of Iodine(I) Thiocyanate to 5α-Androst-2-ene.—(a) *Using potassium thiocyanate, iodine, and Adogen* 464. Potassium thiocyanate (0.61 g, 6.25 mmol) in water (1 ml)

was added to a mixture of 5α-androst-2-ene (0.32 g, 1.25 mmol), iodine (0.76 g, 3.0 mmol), and Adogen 464 (29 mg, 0.06 mmol) in chloroform (10 ml). The mixture was stirred at 20 °C for 92 h and worked up to give an oil (0.52 g) which was separated by p.l.c. into (i) a 2.4 : 1 mixture (2%) of 2β-chloro-3α-iodo-5α-androstane [25] (45) and 3α-chloro-2β-iodo-5β-androstane (46), δ [for (46)] 0.71 (s, 18-H$_3$), 1.20 (s, 19-H$_3$), 4.46 (m, $W_{1/2}$ 7.5 Hz, CHCl), and 4.77 (m, CHI); (ii) a 7 : 1 mixture (23%) of 3α-*iodo*-2β-*isothiocyanato*-5α-*androstane* (41) and 2β-iodo-3α-isothiocyanato-5α-androstane (42) which after recrystallization from ether afforded pure (41) as needles, m.p. 125—127° (Found: C, 54.1; H, 6.8; I, 28.7; N, 3.4. C$_{20}$H$_{30}$INS requires C, 54.2; H, 6.8; I, 28.6; N, 3.2%), δ 0.71 (s, 18-H$_3$), 1.07 (s, 19-H$_3$), 4.35 (m, $W_{1/2}$ 8 Hz, CHN), and 4.70 (m, $W_{1/2}$ 6 Hz, CHI), *m/e* 443 ($M^{+\cdot}$), δ (for 42) 0.71 (s, 18-H$_3$), 1.20 (s, 19-H$_3$), 4.35 (m, $W_{1/2}$ 8 Hz, CHN), and 4.70 (m, $W_{1/2}$ 6 Hz, CHI); (iii) a 5 : 1 mixture (34%) of 3α-*iodo*-2β-*thiocyanato*-5α-*androstane* (43) and 2β-iodo-3α-thiocyanato-5α-androstane (44) which after recrystallization from ether gave pure (43) as needles, m.p. 125—127.5° (Found: C, 54.4; H, 6.7; I, 28.4; N, 3.3. C$_{20}$H$_{30}$INS requires C, 54.2; H, 6.8; I, 28.6; N, 3.2%), δ 0.71 (s, 18-H$_3$), 0.94 (s, 19-H$_3$), 4.14 (m, $W_{1/2}$ 9.5 Hz, CHS), and 5.01 (m, $W_{1/2}$ 6 Hz, CHI), *m/e* 443 ($M^{+\cdot}$), δ [of (44)] 0.71 (s, 18-H$_3$), 1.21 (s, 19-H$_3$), 4.35 (m, $W_{1/2}$ 8 Hz, CHS), and 4.93 (m, $W_{1/2}$ 9 Hz, CHI); and (iv) starting alkene (13%).

Repetition of the reaction without Adogen 464 gave starting material (37%), and iodoisothiocyanato- and iodothiocyanato-5α-androstanes (2 : 1). In the absence of water the product contained starting material (71%) and the products in the ratio 1 : 1.

(b) *Using potassium thiocyanate, iodine, and* 18-*crown*-6. A mixture of anhydrous potassium thiocyanate (73 mg, 0.75 mmol) and 18-crown-6 (40 mg, 0.15 mmol) in chloroform (10 ml) was stirred at 20 °C for 10 min. Iodine (0.15 g, 0.60 mmol) was added, followed by a solution of 5α-androst-2-ene (65 mg, 0.25 mmol) in chloroform (1 ml). The mixture was stirred for 94 h and worked up to give an oil (98 mg) containing starting material (44%), the iodothiocyanates (43) and (44) in the ratio 2 : 1, and traces of iodo-isothiocyanates.

Repetition of the reaction without 18-crown-6 gave a product containing starting material (67%) and iodoisothiocyanato- and iodothiocyanato-derivatives in the ratio 1.3 : 1.

[7/2280 *Received, 29th December,* 1977]

REFERENCES

[1] J. C. Hinshaw, *Tetrahedron Letters*, 1972, 3567.
[2] (*a*) C. Raby, *Ann. Chim.* (*France*), 1961, **6**, 481; (*b*) P. Mesnard and C. Raby, *Chim. Anal.*, 1962, **44**, 463; *Bull. Soc. chim. France*, 1964, 2569; C. Raby and P. Mesnard, *Bull. Soc. Pharm. Bordeaux*, 1967, **106**, 13; C. Raby, J. Buxeraud, and J. Claude, *Ann. Chim.* (*France*), 1976, **1**, 65 (*Chem. Abs.*, 1976, **85**, 27,990).
[3] H. P. Kaufmann and H. Grosse-Oetringhaus, *Chem. Ber.*, 1937, **70**, 911.
[4] G. Collin, U. Jahnke, G. Just, G. Lorenz, W. Pritzkow, M. Röllig, L. Winguth, P. Dietrich, C.-E. Doring, H. G. Hauthal, and A. Wiedenhoft, *J. Prakt. Chem.*, 1969, **311**, 238.
[5] L. Birckenbach, J. Goubeau, and E. Berninger, *Chem. Ber.*, 1932, **65**, 1339.
[6] (*a*) P. D. Woodgate, H. H. Lee, P. S. Rutledge, and R. C. Cambie, *Tetrahedron Letters*, 1976, 1531; (*b*) *Synthesis*, 1977, 462.
[7] R. C. Cambie, R. C. Hayward, P. S. Rutledge, T. Smith-Palmer, and P. D. Woodgate, *J.C.S. Perkin I*, 1976, 840.
[8] M. D. Monica and U. Lamanna, *Gazzetta*, 1968, **98**, 256.
[9] R. S. Ramakrishna and R. Thuraisingham, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2805.
[10] R. C. Cambie, R. C. Hayward, J. L. Roberts, and P. S. Rutledge, *J.C.S. Perkin I*, 1974, 1858.
[11] G. C. Levy and G. L. Nelson, ' Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley–Interscience, New York, 1972, p. 133; J. B. Stothers, ' Carbon-13 n.m.r. Spectroscopy,' Academic Press, New York, 1972, p. 307; G. E. Maciel and D. A. Beatty, *J. Phys. Chem.*, 1965, **69**, 3920.
[12] P. Mesnard and C. Raby, *Bull. Soc. Pharm. Bordeaux*, 1961, **100**, 73.
[13] W. B. Jennings, *Chem. Rev.*, 1975, **75**, 307.
[14] J. Feeney, D. Shaw, and P. J. S. Pauwels, *Chem. Comm.*, 1970, 554.
[15] K. Bock and C. Pedersen, *J. Magnetic Resonance*, 1977, **25**, 227.
[16] M. N. Hughes in ' Chemistry and Biochemistry of Thiocyanic Acid and its Derivatives,' ed. A. A. Newman, Academic Press, London, 1975, ch. 1; A. Fava in ' The Chemistry of Organic Sulphur Compounds,' eds. N. Kharasch and C. Y. Meyers, Pergamon Press, Oxford, 1966, vol. 2, p. 73.
[17] W. E. Rosen, L. D. Dorfman, and M. P. Linfield, *J. Org. Chem.*, 1964, **29**, 1723.
[18] R. G. Pearson, *J. Chem. Educ.*, 1968, **45**, 581, 643; T. L. Ho, *Chem. Rev.*, 1975, **75**, 1.
[19] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, ' Purification of Laboratory Chemicals,' Pergamon Press, Oxford, 1966.
[20] S. J. Patel, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3708.
[21] P. Pascal, ' Nouveau Traite de Chimie Minerale,' Masson et Cie, Paris, 1961, vol. 6, p. 1000.
[22] S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *J. Amer. Chem. Soc.*, 1948, **70**, 816.
[23] R. C. Cambie, R. C. Hayward, B. G. Lindsay, A. I. T. Phan, P. S. Rutledge, and P. D. Woodgate, *J.C.S. Perkin I*, 1976, 1961.
[24] R. Bonnett, R. G. Guy, and D. Lanigan, *Tetrahedron*, 1976, **32**, 2439.
[25] R. C. Cambie, D. Chambers, P. S. Rutledge, and P. D. Woodgate, *J.C.S. Perkin I*, 1977, 2231.