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Bromothiocyanation of Alkenes

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Treatment of alkenes with ' thiocyanogen bromide ' prepared from equimolar amounts of bromine and thallium(I) thiocyanate in wet chloroform, gives moderate to high yields of *vic*-bromothiocyanates. The addition proceeds by an ionic mechanism involving nucleophilic attack of a bromide ion on an *S*-cyanothiiranium cation. Unlike *vic*-iodothiocyanates, the *vic*-bromothiocyanates are not readily isomerized to the corresponding *vic*-halogenoisothiocyanates.

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In earlier work [1] we showed that reaction of iodine and potassium thiocyanate with alkenes in polar solvents gave *vic*-iodothiocyanates in high yield. The products could be isomerized readily by Lewis acids into the more stable *vic*-iodoisothiocyanates; the latter were used to advantage for the preparation of thiazolidin-2-ones and 2-amino-2-thiazolines [2] and more recently for the preparation of 2-alkyl- or 2-aryl-2-thiazolines.[3] Work by Raby *et al.*[4] and Maxwell *et al.*[5] suggests that ' thiocyanogen bromide ' should add to alkenes as NCS^+Br^- to give *vic*-halogenothiocyanates with the opposite regiochemistry to that of the *vic*-iodoisothiocyanates formed by iodine and potassium thiocyanate. Such *vic*-bromothiocyanates would therefore have potential after isomerization to the corresponding *vic*-bromoisothiocyanates, for the preparation of heterocycles regioisomeric with those obtained from *vic*-iodoisothiocyanates.

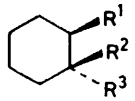
Raby *et al.*[4] prepared thiocyanogen bromide [equations (1) and (2)] which they presumed was in equilibrium with bromine and thiocyanogen.† Addition of

$$Br_2 + Pb(SCN)_2 \longrightarrow (SCN)_2 + PbBr_2 \quad (1)$$

$$Br_2 + (SCN)_2 \rightleftharpoons 2BrSCN \quad (2)$$

oct-1-ene gave two products which were not separated, but on the basis of g.l.c. analysis and a combustion analysis of the mixture, were identified as 2-bromo-1-thiocyanato-octane (1) and 1,2-dibromo-octane (2). However, the bromothiocyanate may have been the regioisomeric adduct (3). The present work reports a method for the preparation of *vic*-bromothiocyanates which does not involve the prior formation of thermally unstable thiocyanogen.

Initial attempts to prepare *vic*-bromothiocyanates by a method analogous to that which led to high yields of *vic*-iodothiocyanates,[1] *viz.* with equimolar amounts of bromine and potassium thiocyanate, were unsuccessful, reaction with cyclohexene affording *trans*-1,2-dibromocyclohexane (4) as the predominant product.‡ Likewise, treatment of cyclohexene with bromine and thallium(I) thiocyanate in dry chloroform gave the *vic*-dibromide (4) as the major product but when the reaction was carried out in wet chloroform the major product



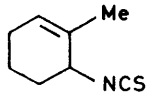
$C_6H_{13}CH(R^1)CH_2R^2$

(1) R^1 = Br, R^2 = SCN
(2) R^1 = Br, R^2 = Br
(3) R^1 = SCN, R^2 = Br

(4) R^1 = R^3 = Br, R^2 = H
(5) R^1 = R^3 = SCN, R^2 = H
(6) R^1 = NCS, R^2 = H, R^3 = SCN
(7) R^1 = Br, R^2 = H, R^3 = SCN
(8) R^1 = I, R^2 = H, R^3 = SCN
(9) R^1 = SCN, R^2 = Me, R^3 = NCS
(10) R^1 = R^3 = SCN, R^2 = Me
(11) R^1 = SCN, R^2 = Me, R^3 = Br

$PhCH(R^1)CH_2R^2$

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



(17)

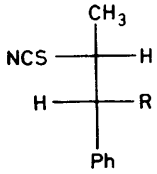
$CH_3(CH_2)_3CH(R^1)CH_2R^2$

(18) R^1 = Br, R^2 = SCN
(19) R^1 = SCN, R^2 = Br
(20) R^1 = R^2 = SCN
(21) R^1 = SCN, R^2 = NCS
(22) R^1 = NCS, R^2 = SCN

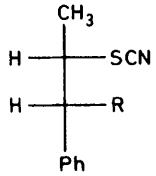
$PhC(NCS)Me_2$
(23)

$PhC(Me)(R^1)CH_2R^2$

(24) R^1 = NCS, R^2 = SCN
(25) R^1 = R^2 = SCN
(26) R^1 = R^2 = NCS
(27) R^1 = Br, R^2 = SCN



(28) R = NCS
(29) R = SCN
(30) R = Br



(31) R = SCN
(32) R = Br

† Seel and Müller [6] have claimed the isolation of thiocyanogen bromide as a red, volatile, dissociable, and highly reactive crystalline solid from the reaction of silver thiocyanate and bromine in sulphur dioxide at −50 °C. I.r. studies support the equilibrium (2).[7]

‡ Attempts to prepare the bromothiocyanate (7) by solvolysis of the dibromide (4) with potassium thiocyanate or of the dithiocyanate (5) with potassium bromide using Adogen 464 as a phase-transfer catalyst were unsuccessful (*cf.* ref. 8).

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was now *trans*-1-bromo-2-thiocyanatocyclohexane (7) (50%); minor products were the *vic*-dibromide (4), the *vic*-dithiocyanate (5),[9] and *trans*-1-isothiocyanato-2-thiocyanatocyclohexane (6). Optimum conditions (see Experimental section) for *vic*-bromothiocyanate formation appeared to be those wherein a two or three to one mol. ratio of 'thiocyanogen bromide' to cyclohexene was used and the reaction was carried out in wet chloroform * or wet carbon tetrachloride at room temperature for 24 h.

trans-1-Bromo-2-thiocyanatocyclohexane (7) was also formed when the less toxic lead(II) thiocyanate[4,5] was substituted for thallium(I) thiocyanate but even after 36 h the yield was only 20%. The structures of the products were determined from spectroscopic data (see Experimental section) and in the case of the bromothiocyanate (7), from microanalytical data.

The regiochemistry of addition of 'thiocyanogen bromide' was investigated by reactions with styrene and 1-methylcyclohexene. The former substrate yielded 1-bromo-1-phenyl-2-thiocyanatoethane (12) (44%) in addition to the known derivatives (13) (12%) and (14) (18%).[10] The structure of the bromothiocyanate was established as (12) rather than as that of the regioisomer (15) from its spectral parameters. Thus, the presence of a CH_2SCN grouping was shown from the ^1H n.m.r. spectrum which exhibited an AB_2 pattern consisting of a one-proton multiplet centred at δ 5.09 and a two-proton multiplet centred at δ 3.66, the latter corresponding to a similar two-proton multiplet at δ 3.67 in the spectrum of 1-phenyl-1,2-dithiocyanatoethane (14). The methine proton in the spectrum of the latter compound appeared at δ 4.66. In the ^{13}C n.m.r. spectrum of (12) assignment of a signal at δ 41.4 to C-2 followed from its triplet multiplicity in the SFORD spectrum. A signal at δ 49.9 assigned to C-1 was in the range expected for CHBr,[11] and the spectrum was distinct from that of the iodo-analogue (16)[1] of (15). The mass spectrum of (12) showed an ion at *m/z* 169 and 171 corresponding to the loss of the fragment $CH_2SCN^{\bullet}$ from the molecular ion.

On the premise that formation of the compounds (13) and (14) should be repressed by the inclusion of excess bromide ions the reaction of 'thiocyanogen bromide' with styrene was repeated with the addition of potassium bromide. This led to a marked increase in the yield of 1-bromo-1-phenyl-2-thiocyanatoethane (12) to 77%, an absence of the isothiocyanato-thiocyanate (13), and the formation of only a trace of the dithiocyanate (14). However, addition of potassium bromide to the reaction of 'thiocyanogen bromide' with cyclohexene resulted in a lowered yield (40%) of the desired bromothiocyanate (7).

The reaction of bromine and thallium(I) thiocyanate with 1-methylcyclohexene afforded 3-isothiocyanato-2-methylcyclohexene (17), 1-isothiocyanato-*c*-2-thiocyanato-*r*-1-methylcyclohexane (9), 1,*c*-2-dithiocyanato-*r*-1-methylcyclohexane (10), and 1-bromo-*c*-2-thiocyanato-*r*-1-methylcyclohexane (11) in yields of 29, 17, 21, and 30%, respectively. Reaction in the presence of potassium bromide resulted in depression of the yields of isolated products. The regiochemistry of the bromothiocyanate (11) was again assigned from its spectral parameters. In the ^1H n.m.r. spectrum a one-proton multiplet centred at δ 3.81 was assigned to a proton geminal to a thiocyanate group by comparison with the lowfield signals in the spectra of the bromothiocyanate (7) and the dithiocyanate (10). Although this multiplet was at lower field than the corresponding signal in the spectrum of (10) (δ 3.48) it was not in the region (δ 3.90—4.30) where a CHBr signal would be expected. Also, the methyl signal of the dithiocyanate (10) is centred at δ 1.60 whereas that of the bromo-thiocyanate (11) is at δ 1.96, which indicates that the bromine atom is geminal to the methyl group. The half-height width (14 Hz) of the signal due to the proton geminal to the thiocyanate group indicates that it is axial and hence the thiocyanate group is equatorial. It is assumed that the bromine atom is also in an equatorial position as a result of overall *anti*-addition. Chemical shifts and signal multiplicities in the ^{13}C n.m.r. spectrum were consistent with the structural assignment.

Reaction of 'thiocyanogen bromide' with hex-1-ene gave 2-bromo-1-thiocyanatohexane (18) (44%), 1-bromo-2-thiocyanatohexane (19) (9%), 1,2-dithiocyanatohexane (20) (10%), and a mixture of 1-isothiocyanato-2-thiocyanatohexane (21) and 2-isothiocyanato-1-thiocyanatohexane (22) (8%). Their dermatitic properties coupled with traces of persistent impurities precluded obtaining correct elemental analyses for compounds (18) and (19) but their structures were assigned on the basis of the i.r., ^1H n.m.r., ^{13}C n.m.r., and mass spectra (see Experimental section). Addition of potassium bromide to the reaction produced no significant change in the yields of the products.

Reaction of 'thiocyanogen bromide' with 2-phenylpropene gave 2-isothiocyanato-2-phenylpropane[2] (23), 2-isothiocyanato-2-phenyl-1-thiocyanatopropane (24), 2-phenyl-1,2-dithiocyanatopropane (25), and 1,2-diisothiocyanato-2-phenylpropane (26) in yields of 15, 24, 24, and 7%, respectively. The first three compounds were identified by comparison with authentic samples. Unlike the reactions with other alkenes, an acidic gas, presumably thiocyanic acid, was evolved during the reaction and the yields were not consistent. No bromothiocyanate adducts were detected, possibly because the bromine in the expected addition product (27) is both benzylic and tertiary and therefore would be expected to be very labile. Thus, the expected product may have been too unstable to survive either the reaction conditions or the work-up procedure. Addition of potassium bromide to the reaction with 2-phenylpropene resulted in formation of the compounds (23)—(26) in yields of 35, 23, 25, and 5%, respectively. Formation of these

* We have recently shown that water is also necessary for the formation of *vic*-iodothiocyanates from iodine and potassium thiocyanate. In this case water is supplied from the water of crystallization present in commercial samples of potassium thiocyanate.

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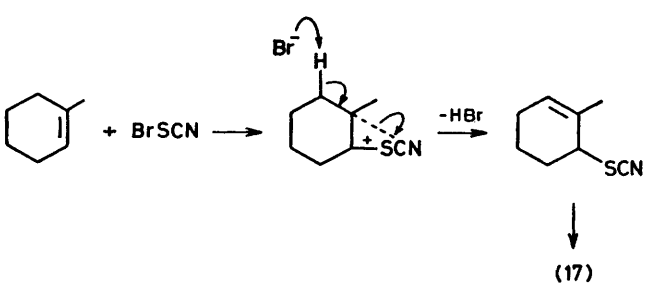
compounds probably reflects the partitioning of a tertiary carbocationic intermediate among several pathways.

Four fractions were obtained in yields of 11, 20, 11, and 8% respectively, from the reaction of (*E*)-1-phenylpropene with ' thiocyanogen bromide '. The first two were identified as *threo*-1-isothiocyanato-1-phenyl-2-thiocyanatopropane (28) and a mixture of *threo*- and *erythro*-1,2-dithiocyanato-1-phenylpropane (29) and (31) by comparison with authentic samples.[1] The other two were shown to be *threo*-1-bromo-1-phenyl-2-thiocyanatopropane (30) and *erythro*-1-bromo-1-phenyl-2-thiocyanatopropane (32), respectively. Both these compounds analysed for $C_{10}H_{10}BrNS$, and although neither gave rise to a molecular ion, bromine could be detected in some fragment ions of their mass spectra. The i.r. spectrum of each compound showed characteristic thiocyanate absorption and their structures were established by ^{1}H n.m.r. and mass spectroscopy. Each mass spectrum included the fragment ion $C_7H_6Br^+$ resulting from the loss of a $CH_3\dot{C}HSCN$ radical, thereby confirming the regiochemistry of the additions. In the ^{1}H n.m.r. spectra, the chemical shifts of the protons geminal to the bromine and thiocyanate groups were similar to those of the bromothiocyanate (12). Coupling constants of 6.5 and 9 Hz for the one-proton methine doublets allowed assignment of the stereochemistry of the *threo*- and *erythro*-adducts as (30) and (32), respectively. Addition of potassium bromide to the reaction mixture altered the ratio of the products (30) and (32) from 1.4 : 1 to 5.5 : 1.

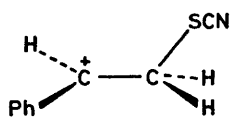
No reaction occurred when 1,3-diphenylprop-1-en-3-one was treated with ' thiocyanogen bromide '. This result was not unexpected since Guy and Pearson [12] have shown that thicyanogen chloride does not add to αβ-unsaturated carbonyl compounds, while Weber *et al.*[13] have shown that iodine(I) thiocyanate and thiocyanogen give only low yields of adducts with 1,3-diarylprop-1-en-3-ones.

Although a radical pathway cannot be entirely ruled out, it would appear that addition of ' thiocyanogen bromide ' to alkenes occurs by an ionic process initiated by electrophilic attack of a thiocyanate cation or its equivalent followed by nucleophilic attack of a bromide ion. Thus, the reactions were carried out in the absence of light and in the presence of the radical inhibitor, oxygen, and the reaction with styrene was slower than that with cyclohexene, a result in keeping with brominations involving polar intermediates [14] but opposite to that for radical processes involving thiocyanogen.[9] Moreover, in the latter reaction with cyclohexene a significant amount of allylic substitution was reported.[9] In contrast, in the present work, an allylic isothiocyanate, *viz.* (17), was isolated only from reaction with the trisubstituted alkene, 1-methylcyclohexene. It is assumed to arise *via* an ionic addition–elimination sequence (Scheme 1). The isomerization of allylic thiocyanates to allylic isothiocyanates is known to proceed rapidly.[15] All additions of ' thiocyanogen bromide ' to the alkenes examined were highly regioselective except for that to hex-1-ene where both the 1-thiocyanato- and 1-bromo-adducts (18) and (19) were produced in a 4 : 1 ratio.



SCHEME 1

The nature of the intermediate formed by initial electrophilic attack is likely to depend on the structure of the substrate. With cyclohexene, the stereospecific *anti*-addition suggests the intermediacy of a symmetrically bridged *S*-cyanothiiranium cation similar to that suggested by Guy and Pearson [16] for the addition of thiocyanogen chloride to alkenes. The high regioselectivity of addition to styrene indicates the intermediacy of either an open carbocation (33) or an unsymmetrically bridged *S*-cyanothiiranium ion (34),[10b]



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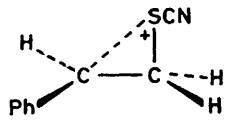

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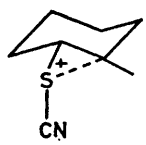

(35)

each of which would be stabilized by the phenyl ring. An unsymmetrically bridged S-cyanothiiranium ion (35) would account for both the orientation of addition to 1-methylcyclohexene and stereochemistry of the product as well as the direction of elimination leading to (17), while an equilibrating mixture of bridged cations (Scheme 2) best explains the formation of both bromothiocyanate regioisomers (18) and (19) from hex-1-ene. An open carbocation would be the expected intermediate in the case of 1-phenylpropene but the formation of the *threo*-isomer (30) as well as the *erythro*-isomer (32) suggests that the nucleophile is bound to the *S*-cyanothiiranium ion,[12,16] necessitating much of its approach to the carbocationic centre from the same side as the electrophile. However, the possibility that an equilibrium exists between the *threo*- and *erythro*-isomers, in which the former is the thermodynamically more stable adduct, has not been ruled out.

As indicated above, addition of potassium bromide to the bromothiocyanation reactions resulted in an increase

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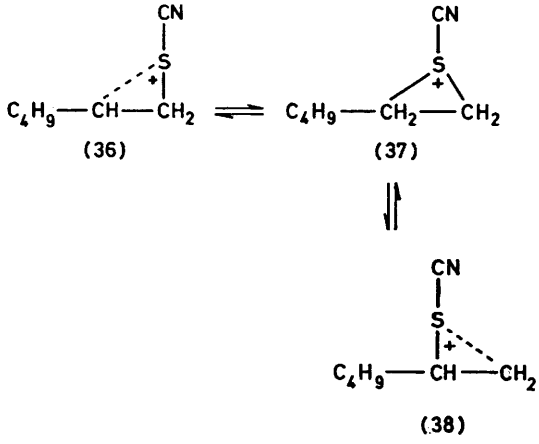
in the yields of the adducts with α-arylalkenes, little change with aliphatic acyclic alkenes, and a slight decrease in yield with cyclic alkenes. The greater effect when an open carbocation is involved suggests that addition of bromide ion results in a higher concentration of ' thiocyanogen bromide ' at the expense of thiocyanogen. However, it is not clear why addition of bromide ions increases the yield of adducts with α-arylalkenes but not with aliphatic alkenes.



SCHEME 2

It is possible that the special property of moist thallium(I) thiocyanate involves the formation of a complex between the thallium(I) ion and the ' thiocyanogen bromide ' [equation (3)] which either stabilises

$$TlBr + NCS{-}Br \longrightarrow [BrTl^{\delta+} \ldots {}^{\delta-}Br{-}NCS^{\delta+}] \quad (3)$$

the reagent or polarizes it to facilitate its reaction with the olefinic bond [17] with a consequential displacement of the equilibrium reaction (2) to the right. Since bromine has been reported to oxidize thallium(I) to thallium(III) salts [18] the latter cannot be excluded as possible reactants, but the high regioselectivity of the addition and electropotential data would indicate that this is not the case.

Attempts to isomerize the bromothiocyanates to bromoisothiocyanates by treatment with boron trifluoride [1] or thermally in the solvents benzene, sulpholan, dimethylformamide, or acetonitrile [15] were unsuccessful. Attempts to replace the bromo-substituent by iodine by treatment with sodium iodide in dry acetone did not produce iodothiocyanates. Thus, 1-bromo-2-thiocyanatocyclohexane (7) was unaffected while 1-bromo-1-phenyl-2-thiocyanatoethane (12) afforded iodine and styrene. Treatment of the *vic*-bromothiocyanate (7) with methanolic potassium hydroxide gave a rapid and quantitative conversion into 7-thiabicyclo[4.1.0]heptane.[2]

EXPERIMENTAL

General experimental details are given in ref. 1.

General Procedure for Formation of Bromothiocyanates.—Equimolar amounts of thallium(I) thiocyanate and bromine in chloroform containing water (20 mg per 20 ml) were stirred at room temperature in the dark for *ca.* 30 min. During this period the bromine colour disappeared and a reddish-brown precipitate was formed. A solution of the alkene in chloroform was added and the mixture was stirred for 24 h unless otherwise stated. The mixture was filtered to remove a yellow precipitate and the filtrate was washed successively with saturated aqueous sodium disulphite, water, and saturated aqueous sodium chloride. Solvent was removed from the dried solution under reduced pressure to give the crude product which was purified by p.l.c. (hexane–ether, 19 : 1).

Reactions with Cyclohexene.—(a) Products from the reaction with thallium(I) thiocyanate (0.3—1.5 g) and bromine (0.06—0.3 ml) are shown in Table 1.

TABLE 1

Mol. ratio ' BrSCN ' : cyclohexene	Yield (%) (7)	(4)	(5)	(6)
1 : 1	20	2	6	2
2 : 1	51	7	15	
3 : 1	50		10	5
3 : 1 [a]	50	3	5	3
2 : 1 [b]	40		10	Trace

[a] In CCl_4–H_2O. [b] Plus 2 mol equiv. KBr.

(b) Reaction of bromine (0.1 ml, 1.9 mmol) and potassium thiocyanate (0.18 g, 1.9 mmol) in chloroform (20 ml) with cyclohexene (0.15 g, 1.8 mmol) in chloroform (3 ml) gave a yellow oil (0.37 g) which after p.l.c. afforded *trans*-1,2-dibromocyclohexane (4) (0.28 g, 63%), δ 1.00—3.00 (m, CH_2) and 4.52 (m, CHBr), and traces of three other products, one of which was *trans*-1,2-dithiocyanatocyclohexane (5).

Use of a 2 : 2 : 1 ratio of reactants in chloroform–water gave a similar result.

(c) Reaction of bromine (0.38 ml, 7.8 mmol) and lead(II) thiocyanate (1.27 g, 3.9 mmol) in chloroform–water with cyclohexene (0.30 g, 3.7 mmol) in chloroform (5 ml) for 3 h gave a yellow oil (0.40 g) which contained *trans*-1,2-dibromocyclohexane (4) (44%).

Repetition of the reaction for 36 h with the addition of further water (1 ml) gave *trans*-1-bromo-2-thiocyanatocyclohexane (7) (0.16 g, 20%).

trans-1-*Bromo*-2-*thiocyanatocyclohexane* (7).—This was an *oil*, b.p. 103° at 0.7 mmHg (Found: C, 38.6; H, 4.6; N, 6.3. $C_7H_{10}BrNS$ requires C, 38.2; H, 4.6; N, 6.4%), $\nu_{max.}$ 2 160 cm^{-1} (SCN), δ 1.00—2.85 (m, CH_2), 3.40 (m, $W_{\frac{1}{2}}$ 20 Hz, CHS), and 4.03 (m, $W_{\frac{1}{2}}$ 15 Hz, CHBr), δ_C 24.8 (C-4*), 25.3 (C-5 *), 33.4 (C-6), 37.0 (C-3), 53.6 (C-2 †), 54.7 (C-1 †), and 110.2 (SCN), *m/z* 219 and 221 ($M^{+\cdot}$, $M^{+\cdot}$ + 2).

trans-1,2-*Dithiocyanatocyclohexane* (5).—This crystallized from carbon tetrachloride as needles, m.p. 57—58° (lit.,[9] 57—58°), δ 1.10—2.78 (m, CH_2) and 3.16 (m, CHS), *m/z* 198 ($M^{+\cdot}$).

trans-1-*Isothiocyanato*-2-*thiocyanatocyclohexane* (6).—This was an oil,[10] δ 1.10—2.85 (m, CH_2), 3.10 (t × d, *J* 9.5, 4 Hz, CHSCN), and 3.75 (d × t, *J* 9.5, 4 Hz, CHNCS).

Reactions with Styrene.—Products from the reaction with thallium(I) thiocyanate (1.0—3.95 g) and bromine (0.19—0.72 ml) are shown in Table 2.

1-*Bromo*-1-*phenyl*-2-*thiocyanatoethane* (12).—This was an *oil*, b.p. 100° at 1.5 mmHg (Found: C, 44.7; H, 3.6; N,

*, † Assignments may be reversed.

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5.9; S, 13.3; Br, 32.75. C_9H_8BrNS requires C, 44.7; H, 3.3; N, 5.8; S, 13.25; Br, 33.0%), δ 3.66 (d × t, *J* 13, 8 Hz, CH_2SCN), 5.09 (d × d, *J* 6, 13 Hz, CHBr), and 7.38 (s, ArH), δ_C 41.4 (C-2), 49.9 (C-1), 110.8 (SCN), 127.5 (*o*-C), 129.1 (*m*-C), 129.5 (*p*-C), and 137.8 (*ipso*-C), *m/z* 241 and 243 ($M^{+\cdot}$, $M^{+\cdot}$ + 2), 183 and 185 ($M^{+\cdot}$ − SCN·, $M^{+\cdot}$ + 2 − SCN·), and 169, and 171 ($M^{+\cdot}$ − CH_2SCN·, $M^{+\cdot}$ + 2 − CH_2SCN·).

TABLE 2

Mol. ratio 'BrSCN' : styrene	Yield (%) (12)	(13)	(14)
2 : 1 [a]	34	6	11 [c]
3 : 1	44	12	18
2 : 1 [b]	77		Trace

[a] Reaction for 3 h. [b] Plus 2 mol. equiv. KBr. [c] Plus starting material (9%).

1-*Isothiocyanato*-1-*phenyl*-2-*thiocyanatoethane* (13).—This was an oil, b.p. 147° at 0.15 mmHg,[10] δ($CDCl_3$) 3.28 (m, CH_2SCN), 5.10 (d × d, *J* 7.5, 5.5 Hz, CHN), and 7.40 (s, ArH), *m/z* 220 ($M^{+\cdot}$).

1-*Phenyl*-1,2-*dithiocyanatoethane* (14).—This crystallized from carbon tetrachloride as pale yellow needles, m.p. 97—98° (lit.,[10] 101—102°), δ 3.67 (m, CH_2S), 4.66 (d × d, *J* 8.5, 6.5 Hz, CHS), and 7.43 (s, ArH), *m/z* 220 ($M^{+\cdot}$).

Reactions with 1-*Methylcyclohexene*.—Reaction of thallium(I) thiocyanate (1.5 g, 5.7 mmol) and bromine (0.29 ml, 5.7 mmol) in chloroform–water with 1-methylcyclohexene (0.18 g, 1.9 mmol) in chloroform (5 ml) gave a yellow oil (0.40 g). This was separated into (i) 3-isothiocyanato-2-methylcyclohexene (17) (86 mg, 29%), δ 1.30—2.30 (m, CH_2), 1.83 (s, CH_3), 4.01 (m, CHNCS), and 5.61 (m, C=CH), *m/z* 153 ($M^{+\cdot}$); (ii) 1-*bromo*-c-2-*thiocyanato*-r-1-*methylcyclohexane* (11) (0.13 g, 30%) (Found: C, 41.1; H, 5.3; N, 6.3. $C_8H_{12}BrNS$ requires C, 41.1; H, 5.2; N, 6.0%), δ 1.40—2.60 (m, CH_2), 1.97 (s, CH_3), and 3.83 (4 lines, $J_{obs.}$ 8, 4 Hz, CHSCN) δ_C 23.1 (C-4 *), 23.8 (C-5 *), 28.0 (CH_3), 30.8 (C-3), 42.7 (C-6), 60.1 (C-2), 68.4 (C-1), and 111.4 (SCN), *m/z* 233 and 235 ($M^{+\cdot}$, $M^{+\cdot}$ + 2); (iii) 1-isothiocyanato-*c*-2-thiocyanato-*r*-1-methylcyclohexane (9) (67 mg, 17%), δ 1.40—2.60 (m, CH_2), 1.60 (s, CH_3), and 3.42 (4 lines, J_{obs} 8, 4 Hz, CHSCN), *m/z* 212 ($M^{+\cdot}$); and (iv) 1,*c*-2-dithiocyanato-*r*-1-methylcyclohexane (10) (84 mg, 21%) which crystallized from methanol as plates, m.p. 59—60.5° (lit.,[19] 60°), δ 1.40—2.45 (m, CH_2), 1.58 (s, CH_3), and 3.46 (4 lines, J_{obs} 8, 4 Hz, CHSCN), *m/z* 212 ($M^{+\cdot}$).

Repetition of the reaction with the addition of potassium bromide (0.67 g, 5.6 mmol) gave compounds (17) (55 mg, 14%), (11) (84 mg, 20%), (9) (49 mg, 12%), and (10) (84 mg, 21%).

Reactions with Hex-1-*ene*.—Reaction of thallium(I) thiocyanate (2.35 g, 8.9 mmol) and bromine (0.46 ml, 8.9 mmol) in chloroform–water with hex-1-ene (0.25 g, 2.9 mmol) in chloroform (5 ml) gave a yellow oil (0.60 g). This was separated into (i) 1-bromo-2-thiocyanatohexane (19) (60 mg, 9%), b.p. 80° at 2.5 mmHg, δ 0.97 (t, CH_3), 1.17—2.33 (m, CH_2), and 3.05—3.92 (m, CH_2Br and CHSCN), δ_C 13.7 (C-6), 22.0 (C-5), 28.6 (C-4), 32.4 (C-3), 34.9 (C-2), 51.0 (C-1), and 110.1 (SCN), *m/z* 221 and 223 ($M^{+\cdot}$, $M^{+\cdot}$ + 2); (ii) 2-bromo-1-thiocyanatohexane (18) (0.26 g, 44%), b.p. 85° at 3.0 mmHg, δ 0.97 (t, CH_3), 1.17—2.33 (m, CH_2), 3.32, 3.37 (2 m, $J_{1,2}$ − 14.5, $J_{1,3}$ 6.9, $J_{2,3}$ 7.5 Hz,† CH_2SCN), and 4.08 (m, $J_{1,3}$ 6.9, $J_{2,3}$ 7.5 Hz,† CHBr), δ_C 13.8 (C-6), 21.9 (C-5), 29.2 (C-4), 36.5 (C-3), 41.7 (C-1), 52.2 (C-2), and 111.3 (SCN), *m/z* 221, and 223 ($M^{+\cdot}$, $M^{+\cdot}$ + 2) and 115 [$M^{+\cdot}$ − (HBr + CN·)]; (iii) a mixture of 1-isothiocyanato-2-thiocyanatohexane (21) and 2-isothiocyanato-1-thiocyanatohexane (22) [10] (47 mg, 8%), δ 0.70—2.35 (m, CH_2 and CH_3) and 3.04—3.50 (m, overlapping CHNCS, CHSCN, CH_2SCN, and CH_2NCS), *m/z* 200 ($M^{+\cdot}$); and (iv) 1,2-dithiocyanatohexane (20),[10] δ 0.65—2.35 (m, CH_2 and CH_3) and 3.20—3.50 (m, CHSCN and CH_2SCN), *m/z* 200 ($M^{+\cdot}$).

Repetition of the reaction with the addition of potassium bromide (2 mol. equiv.) gave compounds (19) (10%), (18), (43%), (21) and (22) (5%), and (20) (7%).

Reactions with 2-*Phenylpropene*.—Reaction of thallium(I) thiocyanate (1.5 g, 5.7 mmol) and bromine (0.3 ml, 5.7 mmol) in chloroform–water with 2-phenylpropene (0.22 g, 1.9 mmol) in chloroform (5 ml) gave a pale yellow oil (0.34 g). This was separated into (i) 2-phenyl-2-isothiocyanatopropane (23) [2] (50 mg, 15%), δ 1.76 (s, CH_3) and 7.37 (s, ArH); (ii) 1,2-*di-isothiocyanato*-2-*phenylpropane* (26) (33 mg, 7%), b.p. 120° at 2 mmHg (Found: C, 56.4; H, 4.3; N, 11.9. $C_{11}H_{10}N_2S_2$ requires C, 56.4; H, 4.3; N, 11.95%), δ 2.00 (s, CH_3), 3.69 (s, CH_2NCS), and 7.36 (s, ArH), *m/z* no $M^{+\cdot}$, 176 ($M^{+\cdot}$ − ·NCS), and 162 ($M^{+\cdot}$ − ·CH_2NCS); (iii) 2-isothiocyanato-2-phenyl-1-thiocyanatopropane (24) (0.11 g, 24%), b.p. 140° at 0.1 mmHg (correct ^{1}H n.m.r. spectrum [1]); and (iv) 2-phenyl-1,2-dithiocyanatopropane (25) [1] (0.10 g, 24%), which crystallized from carbon tetrachloride as needles, m.p. and mixed m.p. 51—52° (correct ^{1}H n.m.r. spectrum [1]).

Repetition of the reaction with the addition of potassium bromide (0.67 g, 5.6 mmol) gave compounds (23) (0.12 g, 35%), (26) (22 mg, 5%), (24) (0.10 g, 23%), and (25) (0.12 g, 25%).

Reactions with (E)-1-*Phenylpropene*.—Reaction of thallium(I) thiocyanate (1.5 g, 5.7 mmol) and bromine (0.3 ml, 5.7 mmol) in chloroform–water with (*E*)-1-phenylpropene (0.23 g, 1.9 mmol) in chloroform (5 ml) gave a yellow oil (0.31 g). This was separated into (i) *threo*-1-bromo-1-phenyl-2-thiocyanatopropane (30) (51 mg, 11%), b.p. 106° at 1 mmHg, δ 1.50 (d, *J* 6.5 Hz, CH_3), 3.85 (d, *J* 6.5 Hz, CHSCN), 5.08 (d, *J* 6.5 Hz, CHBr), and 7.34 (s, ArH), *m/z* no $M^{+\cdot}$, 197 and 199 ($M^{+\cdot}$ − SCN·, $M^{+\cdot}$ + 2 − SCN·), and 169 and 171 [$M^{+\cdot}$ − $CH(CH_3)SCN$, $M^{+\cdot}$ + 2 − ·$CH(CH_3)SCN$]; (ii) *erythro*-1-bromo-1-phenyl-2-thiocyanatopropane (32) (36 mg, 8%), b.p. 100° at 1 mmHg, δ 1.80 (d, *J* 6.5 Hz, CH_3), 3.61 (m, CHSCN), 4.91 (d, *J* 9 Hz, CHBr), and 7.32 (s, ArH), *m/z* no $M^{+\cdot}$, 197 and 199 ($M^{+\cdot}$ − SCN·, $M^{+\cdot}$ + 2 − SCN·), and 169 and 171 [$M^{+\cdot}$ − ·$CH(CH_3)SCN$, $M^{+\cdot}$ + 2 − ·$CH(CH_3)SCN$]; (iii) *threo*-1-isothiocyanato-1-phenyl-2-thiocyanatopropane [1] (28) (42 mg, 11%) (correct ^{1}H n.m.r. and mass spectra [1]); and (iv) a mixture of *threo*- and *erythro*-1-phenyl-1,2-dithiocyanatopropane (29) and (31) (87 mg, 20%) which crystallized from carbon tetrachloride as plates, m.p. 95—103° (lit.,[1] 90—101°) (correct ^{1}H n.m.r. and mass spectra).

Repetition of the reaction with the addition of potassium bromide (0.67 g, 5.6 mmol) gave starting material (14 mg, 6%), (30) (0.11 g, 22%), (32) (17 mg, 4%), (28) (12 mg, 3%), and (29) and (31) (46 mg, 10%).

[0/214 *Received*, 6th *February*, 1980]

* Assignments may be reversed.

† Obtained by simulation of the low-field region of the spectrum (as an ABM system) with the LAOCOON IV computer program.

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