Pseudohalogen Chemistry. III.[1] Orientation of Heterolytic Addition of Thiocyanogen Chloride to Some Unsymmetrical Alkenes

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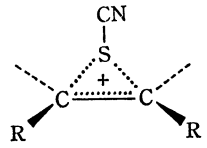
Thiocyanogen chloride reacts with various unsymmetrical alkenes, cycloalkenes, and α-arylalkenes in the presence of a radical inhibitor in acetic acid in the dark at 25 °C to yield α-chloro-β-thiocyanates, α-acetoxy-β-thiocyanates, α-hydroxy-β-thiocyanates, vinylic thiocyanates or allylic isothiocyanates in various combinations. The additions to the α-arylalkenes are regiospecific, yielding the Markownikov-orientated products, but the regiospecificity of the additions to the aliphatic alkenes depends on the structure of the alkene. The orientation of addition is discussed in terms of open carbonium ions, *e.g.* **17**, for the α-arylalkenes and cyano-sulfonium ions, *e.g.* **18**, for the aliphatic alkenes.

In Parts I[2] and II,[1] it was shown that thiocyanogen chloride, ClSCN, reacts readiily at 25 °C with symmetrical alkenes, cycloalkenes and α-arylalkenes, *e.g.* *cis*- and *trans*-2-butene, *trans*-Δ^2-octalin, *cis*- and *trans*-stilbene, and acenaphthylene, in the presence of a radical inhibitor in acetic acid in the dark, to yield α-chloro-β-thiocyanates and α-acetoxy-β-thiocyanates. A heterolytic mechanism involving a two-step, kinetically controlled addition was postulated. For the aliphatic alkenes, the formation of a symmetrical cyanosulfonium ion, *e.g.* **1**, was proposed to account for the *trans*-stereospecific additions observed;[2] for the α-arylalkenes, the formation of an open carbonium ion, *e.g.* **2**, which exists as an ion-pair, and steric control of reaction by the thiocyanato group of the carbonium ion were proposed to account for the observed *trans*- stereoselectivity.[1]



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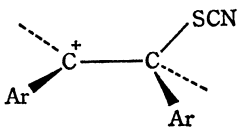

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Here we describe the orientation of addition of thiocyanogen chloride under heterolytic conditions in acetic acid to some unsymmetrical alkenes, cycloalkenes, and α-arylalkenes.

Results

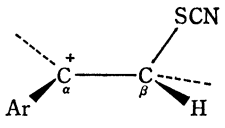
The alkenes investigated, reaction times, products, and yields are recorded in the Table 1. Constitutionally different products of the reactions were readily separated by column chromatography on silica gel, but regioisomers and stereoisomers were not completely resolved, as indicated by TLC and by IR and ^{1}H NMR spectroscopy. Structural assignments were made as before[1,2] using published IR and NMR data,[1-6] and isomer ratios were determined from the integral traces of appropriate absorption bands in the ^{1}H NMR spectra of the mixtures (see Experimental section for details).

Control experiments showed that the products listed in the Table 1 were stable under the conditions used in the reactions. No reaction occurred with *trans*-cinnamic acid, *trans*-crotonic acid, methyl *trans*-cinnamate, methyl acrylate, vinyl chloride, vinylidene chloride, trichloroethylene or vinyl bromide during 48—164 h. No isomerisation of the alkenes was observed.

Discussion

The heterolytic addition of thiocyanogen chloride, which is polarised in the manner Cl(δ−)–SCN(δ+)[7], to an unsymmetrical alkene RCH=CH_2 (R=alkyl or aryl) may yield the Markownikov-orientated adduct RCHClCH_2SCN and/or the regioisomer RCH(SCN)-CH_2Cl.

α-Arylalkenes. The data for the α-arylalkenes examined show that the addition reaction is regiospecific, yielding the Markownikov-orientated products **3**—**6** and **8** exclusively. Other data, *e.g.* the *trans*-stereoselectivity of the addition to indene (see products **4** and **5**), and the low chlorothiocyanate : acetoxythiocyanate ratios observed for the additions to styrene and indene (see Table 1) resemble those obtained for the corresponding additions to symmetrical α-arylalkenes.[1] Consequently, a similar mechanism is postulated, *i.e.* a two-step, kinetically controlled, electrophilic reaction in which the first step is the formation, as an ion-pair, of the more stable of the two possible open thiocyanato-carbonium ions, *e.g.* **17**, due to the stabilising effect of the α-aryl group. Nucleophilic attack on **17** by chloride ions or acetic acid solvent molecules, and steric control of reaction by the thiocyanato group, leads to the observed α-chloro-β-thiocyanates and α-acetoxy-β-thiocyanates which, in the case of 1,1-diphenylethylene and triphenylethylene, are readily hydrolysed to the corresponding α-hydroxy-β-thiocyanates **6** and **8** during the aqueous work-up procedure. Concomitant loss of a β-proton from **17** leads to the observed substitution products, *i.e.*, the vinyl thiocyanates **7** and **9** (*cf.* the formation of vinyl sulfides in the corresponding additions of 2,4-dinitrobenzenesulfenyl chloride to α-arylalkenes).[15] This substitution reaction becomes progressively more important as the number of stabilising aryl groups on the vinylic product increases (*cf.* the products from styrene, 1,1-diphenylethylene and triphenylethylene).



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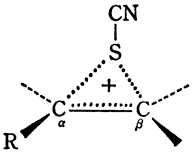

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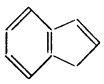
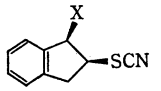
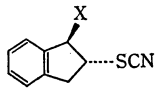
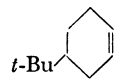
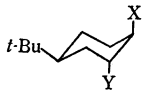
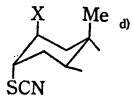
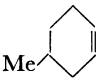
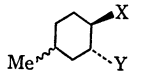
TABLE 1. HETEROLYTIC ADDITION OF THIOCYANOGEN CHLORIDE TO UNSYMMETRICAL ALKENES IN ACETIC ACID AT 25 °C

Alkene	Time[a] (min)	Products		Yield (%)	Cl/OAc[b]
$PhCH=CH_2$	2	$PhCHXCH_2SCN$	**3** {**a**; X=Cl / **b**; X=OAc	41 / 50	0.82
	5		**4** {**a**; X=Cl / **b**; X=OAc	7 / 6	0.31
			**5** {**a**; X=Cl / **b**; X=OAc	15 / 64	
$Ph_2C=CH_2$	2	$Ph_2C(OH)CH_2SCN$	**6**	77	c)
		$Ph_2C=CHSCN$	**7**	10	
$Ph_2C=CHPh$	20	$Ph_2C(OH)CH(SCN)Ph$	**8**	14	c)
		$Ph_2C=CPhSCN$	**9**	75	
$MeCH=CH_2$	10	$MeCHXCH_2Y$	**10** {**a**; X=Cl, Y=SCN / **b**; X=SCN, Y=Cl / **c**; X=OAc, Y=SCN	54 / 27 / 18	4.5
n-$BuCH=CH_2$	2	*n*-$BuCHXCH_2Y$	**11** {**a**; X=Cl, Y=SCN / **b**; X=SCN, Y=Cl / **c**; X=OAc, Y=SCN	49 / 28 / 15	5.1
	2		**12** {**a**; X=SCN, Y=Cl / **b**; X=Cl, Y=SCN / **c**; X=SCN, Y=OAc / **d**; X=OAc, Y=SCN	38 / 38 / 12 / 12	3.2
5α-cholest-2-ene	5		**13** {**a**; X=Cl / **b**; X=OAc	82 / 11	7.5
	2		**14** {**a**; X=SCN, Y=Cl / **b**; X=Cl, Y=SCN / **c**; X=SCN, Y=OAc / **d**; X=OAc, Y=SCN	34 / 34 / 13 / 13	2.6
$Et_2C=CH_2$	2	Et_2CXCH_2SCN	**15** {**a**; X=Cl / **b**; X=OAc	23 / 43	0.54
		$MeCH(NCS)C(Et)=CH_2$	**16**	22	

a) Time for 100% reaction as indicated by titration. b) Chlorothiocyanate: acetoxythiocyanate ratio. c) Could not be determined due to hydrolysis (see text). d) Partial structure only.

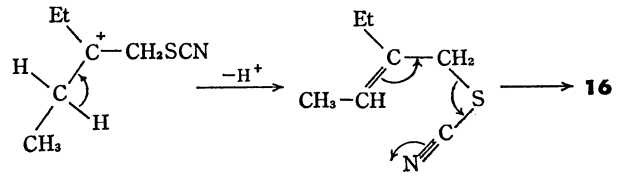
Aliphatic Alkenes. The data for the aliphatic alkenes examined show that the regiospecificity of the addition reaction varies with the structure of the alkene and the nature of the nucleophile (see products **10**—**15**). Since other data, *e.g.* the stereospecific *trans*-addition to 4-*t*-butylcyclohexene, 4-methylcyclohexene, and 5α-cholest-2-ene (see products **12**—**14**), and the high chlorothiocyanate : acetoxythiocyanate ratios observed for these alkenes (see Table 1) resemble those obtained for the corresponding additions to symmetrical alkenes and cycloalkenes,[2] a similar mechanism, but with an unsymmetrical cyano-sulfonium ion intermediate, *e.g.* **18**, is postulated.

For the terminal alkenes, propene and 1-hexene, the electron-donating alkyl substituent in **18** (R= Me, *n*-Bu) allows a greater share of the positive charge to be available at C_α than at C_β, thus permitting preferential nucleophilic attack by chloride ion at C_α and formation of the Markownikov-orientated products **10a** and **11a**. Similar non-regiospecificity and isomer ratios have been observed in the corresponding additions of bromine chloride, iodine chloride, and 2,4-dinitrobenzenesulfenyl chloride.[15] The exclusive formation of the Markownikov-orientated acetoxythiocyanates **10c** and **11c** in these cases may be due to acetic acid being a weaker nucleophile than chloride ion, and thus more selective in its attack. Similar effects have been noted in additions of sulfenyl halides to alkenes.[8]

In the cases of 4-*t*-butyl- and 4-methyl-cyclohexene, the equatorial *t*-butyl and methyl groups are too remote from the reaction centre (a) to affect the ease with which the episulfonium bridge is formed on either side of the ring, and (b) to make the bridge significantly asymmetric. Consequently diaxial ring-opening, in the manner described for Δ^2-octalin and cyclohexene,[2] can occur with equal ease at C_α and C_β leading in each case to equal amounts of regioisomers (see products **12** and **14**). Similar results have been obtained in the heterolytic addition of bromine chloride to these alkenes.[9] For 5α-cholest-2-ene, steric shielding of the β-side of the molecule by the axial C_{10} methyl group leads to exclusive formation of the 2α, 3α-sulfonium ion which, on diaxial ring opening at C_2, leads to the observed 2β-chloro-3α-thiocyanate (**13a**) and 2β-acetoxy-3α-thiocyanate (**13b**). Similar regiospecificity and stereospecificity have been noted in the heterolytic addition of iodine azide[10] and iodine isocyanate[11] to this alkene.

The disubstituted terminal alkene, 2-ethylbut-1-ene,

differs from the previous alkenes in giving (a) the Markownikov-orientated adducts **15a** and **15b** exclusively (*cf.* the exclusive Markownikov addition of iodine isocyanate to 2-methylpropene)[11] and (b) the unsaturated isothiocyanate **16**. Furthermore, the chlorothiocyanate : acetoxythiocyanate ratio (see Table 1) is in the range shown by the α-arylalkenes rather than that shown by the aliphatic alkenes. It is suggested that this alkene reacts *via* the open carbonium ion **19** rather than a cyano-sulfonium ion, due to the second ethyl group conferring stability comparable to that of a single phenyl group. Concomitant proton loss from an ethyl group of the carbonium ion (*cf.* the α-arylalkenes), followed by allylic rearrangement,[12] readily accounts for the formation of the isothiocyanate **16** as shown below.



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Reactivity of Thiocyanogen Chloride. The presence of one electron-withdrawing group deactivates the double bond sufficiently to prevent addition of thiocyanogen chloride to these alkenes. This pseudohalogen chloride is therefore comparable in reactivity to the arenesulfenyl chlorides (ArSCl), but less reactive than iodine chloride and bromine chloride.[15]

Experimental

Alkenes. 4-*t*-Butylcyclohexene (bp 64—65 °C/15 mmHg, n_D^{25} 1.4567) was prepared by dehydration of 4-*t*-butylcyclohexanol with potassium hydrogensulfate. 5α-Cholest-2-ene (mp 74—75 °C) was prepared as described.[13] The other alkenes used were commercial samples purified until their physical constants agreed with those recorded in the literature.

General Procedure. This has been described in Parts I[2] and II.[1]

Propene. Propene gave (a) a mixture of 2-chloro-1-thiocyanatopropane (**10a**) and 1-chloro-2-thiocyanatopropane (**10b**) as a colourless liquid; bp 35—37 °C/0.1 mmHg; n_D^{22} 1.5010; ν 2165(SCN)cm^{-1}; τ (in CCl_4) 5.74 (sext, *J* 6.5 Hz, CHCl), 6.08 to 6.63 (m, CHSCN and CH_2Cl), 6.75 (d, *J* 6.5 Hz, CH_2SCN), 8.30 (d, *J* 6.5 Hz, CH_3CHCl), 8.40 (d, *J* 6.5 Hz, CH_3CHSCN) (Found: C, 35.2; H, 4.7; N, 10.25%. Calcd for C_4H_6ClNS: C, 35.45; H, 4.45; N, 10.35%), and (b) 2-*acetoxy*-1-*thiocyanatopropane* (**10c**) as a colourless liquid; bp 56—57 °C/0.1 mmHg; n_D^{22} 1.4700; ν 2165(SCN), 1740 (C=O) cm^{-1}; τ (in CCl_4) 4.86 (1H, p of d, *J* 6.5 and 4.5 Hz, CHOAc), 6.87 (1H, d, *J* 4.5 Hz, one H of CH_2SCN), 6.90 (1H, d, *J* 6.5 Hz, second H of CH_2SCN), 7.93 (3H, s, $OCOCH_3$), 8.61 (3H, d, *J* 6.5 Hz, CH_3) (Found: C, 45.15; H, 5.8; N, 8.9%. $C_6H_9NO_2S$ requires C, 45.3; H, 5.7; N, 8.8%). The isomer ratio for the mixture of chlorothiocyanates was determined from the integral traces of the CHX and CH_2X (X=Cl, SCN) proton signals.

1-Hexene. 1-Hexene gave (a) a mixture of 2-chloro-1-thiocyanatohexane (**11a**) and 1-chloro-2-thiocyanatohexane (**11b**) as a colourless liquid; bp 65—67 °C/0.05 mmHg n_D^{25} 1.4891; ν 2165(SCN)cm^{-1}; τ (in $CDCl_3$) 5.84 (p, *J* 6 Hz, CHCl), 6.08 to 6.55 (m, CHSCN and CH_2Cl), 6.69 (d, *J* 6 Hz, CH_2SCN), 7.80 to 9.30 (m, C_4H_9) (Found: C, 47.6; H, 7.0; Cl, 19.85; N, 7.9%. Calcd for $C_7H_{12}ClNS$: C, 47.3; H, 6.8; Cl, 19.95; N, 7.9%), and (b) 2-*acetoxy*-1-*thiocyanatohexane* (**11c**) as a colourless liquid; bp 76 °C/0.05 mmHg; n_D^{25} 1.4684; ν 2165 (SCN), 1740 (C=O)cm^{-1}; τ (in $CDCl_3$) 4.85 (1H, q of d, *J* 6.5 and 4.5 Hz, CHOAc), 6.78 (1H, d, *J* 4.5 Hz, one H of CH_2SCN), 6.85 (1H, d, *J* 6.5 Hz, second H of CH_2SCN), 7.89 (3H, s, $OCOCH_3$), 7.95 to 9.30 (9H, m, C_4H_9) (Found: C, 53.3; H, 7.45; N, 7.3; S, 15.8%. $C_9H_{15}NO_2S$ requires C, 53.7; H, 7.5; N, 6.95; S, 15.95%). The isomer ratio for the mixture of chlorothiocyanates was determined as described for propene.

4-t-Butylcyclohexene. 4-*t*-Butylcyclohexene gave (a) a mixture of 2*ax*-chloro-1*ax*-thiocyanate-4*eq*-*t*-butylcyclohexane (**12a**) and 1*ax*-chloro-2*ax*-thiocyanato-4*eq*-*t*-butylcyclohexane (**12b**) as a pale yellow liquid; bp 78—79 °C/0.05 mmHg; n_D^{25} 1.5132; ν 2165(SCN)cm^{-1}; τ (in $CDCl_3$ at 100 MHz) 5.44 and 5.77 (each 1H, distorted q, band-width 9Hz, *J*~3 Hz, CHCl), 5.96 and 6.10 (each 1H, distorted q, band-width 9 Hz, *J*~3 Hz, CHSCN), 7.50 to 9.00 (14 H, m, CH_2 and $CHBu^t$), 9.10 (18H, s, C_3H_9) (Found: C, 57.3; H, 7.7; Cl, 15.0; N, 5.9%. Calcd for $C_{11}H_{18}ClNS$: C, 57.0; H, 7.85; Cl, 15.3; N, 6.05%), and (b) a mixture of 2*ax*-acetoxy-1*ax*-thiocyanato-4*eq*-*t*-butylcyclohexane (**12c**) and 1*ax*-acetoxy-2*ax*-thiocyanato-4*eq*-*t*-butylcyclohexane (**12d**) as a colourless liquid; bp 96 °C/0.05 mmHg n_D^{25} 1.4195; ν 2165 (SCN), 1740 (C=O)cm^{-1}; τ (in $CDCl_3$ at 100 MHz) 4.87 and 5.00 (each 1H, distorted q, band-width 10 Hz, *J*~3 Hz, CHOAc), 6.12 and 6.25 (each 1H, distorted q, band-width 10 Hz, *J*~3 Hz, CHSCN), 7.50 to 9.00 (14H, m, CH_2 and $CHBu^t$), 9.10 (18H, s, C_3H_9) (Found: C, 60.9; H, 8.25; N, 5.6; S, 12.65%. Calcd for $C_{13}H_{21}NO_2S$: C, 61.15; H, 8.3; N, 5.5; S, 12.55%). The isomer ratio for each mixture was determined from the integral traces of the CHX (X=SCN, Cl or OAc) proton signals.

5α-Cholest-2-ene. 5α-Cholest-2-ene gave (a) 2β-*chloro*-3α-*thiocyanato*-5α-*cholestane* (**13a**) as colourless needles; mp 90—92 °C after crystallization from methanol; ν 2165(SCN) cm^{-1}; τ (in $CDCl_3$ at 100 MHZ) 5.49 (1H, distorted q, band-width 9 Hz, *J*~3 Hz, CHCl) 5.95 (1H, distorted q, band-width 9 Hz, *J*~3 Hz, CHSCN), 7.50 to 9.20 (44H, m, residual H) (Found: C, 72.2; H, 10.3; N, 3.25%. $C_{28}H_{46}ClNS$ requires C, 72.45; H, 10.0; N, 3.0%), and (b) 2β-acetoxy-3α-thiocyanato-5α-cholrestane (**13b**) as colourless needles, mp 110—112 °C after crystallization from methanol, identical in physical and spectral properties with the compound described by Takeda *et al.*[4] (Found: C, 73.6; H, 10.25; N, 2.8%. Calcd for $C_{30}H_{49}NO_2S$: C, 73.9; H, 10.15; N, 2.85%).

The effect of a 3α- and a 2β-thiocyanato group on the chemical shift of a 2α- and a 3β-CHCl proton respectively was calculated using a chemical shift value of τ 5.55 for the equatorial 2α- and 3β-CHCl protons,[14] and shift values of −0.03 and −0.13 τ for the 3α- and the 2β-thiocyanato groups respectively.[5]

4-Methylcyclohexene. 4-Methylcyclohexene gave (a) a mixture of 4-methyl-*trans*-1-chloro-2-thiocyanatocyclohexane (**14b**) and 4-methyl-*trans*-2-chloro-1-thiocyanatocyclohexane (**14a**) as a colourless liquid; bp 60—62 °C/0.05 mmHg; n_D^{20} 1.5224; ν 2165(SCN)cm^{-1}; τ (in $CDCl_3$ at 100 MHz) 5.45 to 5.90 (1H, 10-line m, band-width 40 Hz, overlapping CHCl), 6.10 to 6.50 (1H, 9-line m, band-width 37 Hz, overlapping CHSCN), 7.50 to 9.10 (10 H, m, residual H) (Found: C, 50.6; H, 6.55; N, 7.35%. Calcd for $C_8H_{12}ClNS$: C, 50.65; H, 6.4; N, 7.4%), and (b) a mixture of 4-methyl-

trans-1-acetoxy-2-thiocyanatocyclohexane (**14d**) and 4-methyl-*trans*-2-acetoxy-1-thiocyanatocyclohexane (**14c**) as a colourless liquid; bp 76—78 °C/0.05 mmHg; n_D^{20} 1.4960; ν 2165(SCN), 1740 (C=O) cm^{-1}; τ (in $CDCl_3$ at 100 MHz) 4.80 to 5.30 (1H, 13-line m, band-width 44 Hz, overlapping CHOAc), 6.25 to 6.65 (1H, 14-line m, band-width 35 Hz, overlapping CHSCN), 7.50 to 9.20 (10H, m, residual H) (Found: C, 56.65; H, 7.25; N, 6.35%. Calcd for $C_{10}H_{15}NO_2S$: C, 56.35; H, 7.1; N, 6.55%). Due to overlapping, the isomer ratio for each mixture could not be determined from the integral traces of the CHX (X=SCN, Cl or OAc) proton signals; the symmetry of these signals, however, indicated that the positional isomers were present in equal amounts in both cases.

2-Ethylbut-1-ene. 2-Ethylbut-1-ene gave, in order of elution from the column, (a) *2-ethyl-3-isothiocyanatobut-1-ene* (**16**) as a colourless liquid; bp 30 °C/0.1 mmHg; n_D^{21} 1.5112; ν 3100 (=C–H), 2200 to 1980(NCS), 1640(C=C) cm^{-1}; τ (in CCl_4), 4.91 and 5.08 (each 1H, d, J 1.5 Hz, vinyl H), 5.72 (1H, q, J 7 Hz, CHNCS), 7.87 (2H, q, J 7 Hz, CH_2), 8.51 (3H, d, J 7 Hz, CH_3CHNCS), 8.87 (3H, t, J 7 Hz, CH_3CH_2) (Found: C, 59.7; H, 8.0; N, 9.55; S, 22.25%. $C_7H_{11}NS$ requires C, 59.55; H, 7.85; N, 9.9; S, 22.65%), (b) *2-chloro-2-ethyl-1-thiocyanatobutane* (**15a**) as a colourless liquid; bp 50 °C/0.1 mmHg; n_D^{21} 1.4990; ν 2165(SCN) cm^{-1}; τ (in CCl_4) 6.61 (2H, s, CH_2SCN), 8.19 (4H, q, J 7 Hz, CH_2), 8.94 (6H, t, J 7 Hz, CH_3) (Found: C, 47,3; H, 6.8; N, 7.65%. $C_7H_{12}ClNS$ requires C, 47.3; H, 6.8; N, 7.9%), and (c) *2-acetoxy-2-ethyl-1-thiocyanatobutane* (**15b**) as a colourless liquid; bp 64 °C/0.1 mmHg; n_D^{23} 1.4775; ν 2165 (SCN), 1740 (C=O) cm^{-1}; τ (in CCl_4) 6.50 (2H, s, CH_2SCN), 8.01 (3H, s, $OCOCH_3$), 8.08 (4H, q, J 7 Hz, CH_2), 9.12 (6H, t, J 7 Hz, CH_3) (Found:,C, 53.9; H, 7.25; N, 6.8%. $C_9H_{15}NO_2S$ requires C, 53.7; H, 7.5; N, 6.95%).

Styrene. Styrene gave (a) *1-chloro-1-phenyl-2-thiocyanatoethane* (**3a**) as a colourless liquid; bp 79 °C/0.05 mmHg; n_D^{23} 1.5802; ν 2165(SCN) cm^{-1}; τ (in $CDCl_3$) 2.61 (5H, s, aromatic H), 4.90 (1H, t, J 7.5 Hz, CHCl), 6.50 (2H, d, J 7.5 Hz, CH_2SCN) (Found: C, 54.7; H, 4.25; Cl, 17.65; N, 7.2; S, 16.1%. C_9H_8ClNS requires C, 54.7; H, 4.1; Cl, 17.95; N, 7.1; S, 16.15%), and (b) *1-acetoxy-1-phenyl-2-thiocyanatoethane* (**3b**) as a colourless liquid; bp 107 °C/0.05 mmHg; n_D^{20} 1.5412; ν 2165(SCN), 1740(C=O) cm^{-1}; τ (in $CDCl_3$) 2.63 (5H, s, aromatic H), 3.96 (1H, t, J 7 Hz, CHOAc), 6.67 (2H, d, J 7 Hz, CH_2SCN), 7.85 (3H, s, $OCOCH_3$) (Found: C, 59.5; H, 5.25; N, 6.25%. $C_{11}H_{11}NO_2S$ requires C, 59.7; H, 5.0; N, 6.35%).

1-Chloro-1-phenyl-2-thiocyanatoethane (1 g) was heated under reflux with triethylamine (1 g) in toluene (25 ml) for 12 h. After cooling triethylamine hydrochloride was filtered off, and the filtrate was washed with dilute sulfuric acid and then water. Drying ($MgSO_4$) and removal of solvent gave *trans-β-thiocyanatostyrene* (0.7 g, 86%) as a colourless liquid; bp 89 °C/0.2 mmHg, n_D^{24} 1.6178; ν 2170(SCN) cm^{-1}; τ (in $CDCl_3$) 2.70 (5H, s, aromatic H), 3.06 (1H, d, J 15 Hz, *trans*-C=CHSCN), 3.60 (1H, d, J 15 Hz, *trans*-C=CHPh) (Found: C, 67.1; H, 4.25; N, 8.75%. C_9H_7NS requires C, 67.05; H, 4.4; N, 8.7%)

Indene. Indene gave (a) a mixture of *cis*- and *trans*-1-chloro-2-thiocyanatoindane (**4a** and **5a**) as a colourless liquid; bp 105—107 °C/0.05 mmHg; n_D^{27} 1.6015; ν 2165 (SCN) cm^{-1}; τ (in CCl_4) 2.50 to 3.10 (m, aromatic H) 4.63 (d, J 5.5 Hz, *cis*-CHCl), 4.73 (d, J 4.5 Hz, *trans*-CHCl), 5.65 to 6.50 (m, *cis*- and *trans*-CHSCN and one H of *trans*-CH_2), 6.65 (d, J 7.5 Hz, *cis*-CH_2), 7.00 (d of d, J 17 Hz and 5 Hz, second H of *trans*-CH_2) (Found: C, 57.4; H, 4.05; Cl, 16.5; N, 6.65%. Calcd for $C_{10}H_8ClNS$: C, 57.25; H, 3.85; Cl, 16.9; N, 6.7%), and (b) a mixture of *cis*- and *trans*-1-acetoxy-2-thiocyanatoindane (**4b** and **5b**) as a colourless liquid; bp 123—125 °C/0.05 mmHg; n_D^{25} 1.5585; ν 2165(SCN), 1740 (C=O); τ (in CCl_4) 2.60—2.90 (m, aromatic H), 3.82 (d, J 5 Hz, coincidental *cis*- and *trans*-CHOAc), 5.65 to 6.20 (m, *cis*- and *trans*-CHSCN), 6.40 (d of d, J 15.5 Hz and 7.5 Hz, one H of *trans*-CH_2): 6.60 (d, J 7 Hz, *cis*-CH_2), 7.00 (d of d, J 15.5 Hz and 6.5 Hz, second H of *trans*-CH_2), 7.96 (s, $OCOCH_3$) (Found: C, 61.45; H, 4.9; N, 6.25%. Calcd for $C_{12}H_{11}NO_2S$: C, 61.80; H, 4.75; N, 6.0%). The isomer ratio for each mixture was determined from the integral traces of the *cis*-CH_2 and the high-field *trans*-CH_2 proton signals. The *cis*- and *trans*-CHX (X=Cl, OAc) proton signals were more clearly resolved in dimethyl sulfoxide solvent [τ 4.23 (d, J 5.5 Hz, *cis*-CHCl), 4.37 (d, J 4.5 Hz, *trans*-CHCl), 3.70 (d, J 5.5 Hz, *cis*-CHOAc), 3.75 (d, J 5 Hz, *trans*-CHOAc)].

1,1-Diphenylethylene. 1,1-Diphenylethylene gave (a) 1,1-diphenyl-2-thiocyanatoethylene (**2**) as a waxy solid; ν 2165 (SCN), 1600(C=C) cm^{-1}; τ (in CCl_4) 2.40 to 2.85 (10H, m, aromatic H), 3.47 (1H, s, CHSCN). This product, on treatment with lithium aluminium hydride and then 2,4-dinitrochlorobenzene,[7] gave 1,1-*diphenyl-2-(2,4-dinitrophenylthio)ethylene* as yellow needles; mp 138—141 °C after crystallisation from acetic acid (Found: C, 63.1; H, 3.7; N, 7.45%. $C_{20}H_{14}N_2O_4S$ requires C, 63.5; H, 3.75; N, 7.4%), and (b) 1-*hydroxy*-1,1-*diphenyl*-2-*thiocyanatoethane* (**6**) as colourless needles; mp 99—100 °C after crystallisation from benzene–light petroleum; ν 2165 (SCN), 3350(OH) cm^{-1}; τ (in CCl_4) 2.62 (10H, s, aromatic H), 6.11 (2H, s, CH_2SCN), 7.12 (1H, s, OH); (Found: C, 70.8, H, 5.1; N, 5.5%. $C_{15}H_{13}NOS$ requires C, 70.6; H, 5.15; N, 5.5%).

Triphenylethylene. Triphenylethylene gave (a) *triphenylthiocyanatoethylene* (**9**) as colourless plates; mp 103—104 °C after crystallisation from carbon tetrachloride; ν 2165(SCN), 1530(C=C) cm^{-1}; τ (in $CDCl_3$) 2.60 to 2.98 (m, phenyl H) (Found: C, 80.5; H, 4.8; N, 4.4. $C_{21}N_{15}NS$ requires C, 80.5; H, 4.85; N, 4.45%), and (b) 1-*hydroxy*-1,1,2-*triphenyl*-2-*thiocyanatoethane* (**8**) as colourless needles; mp 165—168 °C after crystallisation from carbon tetrachloride; ν 2165(SCN), 3350(OH) cm^{-1}; τ (in $CDCl_3$) 2.65 to 3.05 (15H, m, aromatic H), 4.49 (1H, s, CHSCN), 7.04 (1H, s, OH) (Found: C, 76.5; H, 5.1, N, 4.1%. $C_{21}H_{17}NOS$ requires C, 76.1; H, 5.15; N, 4.25%).

Control Experiments. These were carried out as described in Part I.[2]

Unreactive Alkenes. *trans*-Cinnamic acid, *trans*-crotonic acid, and methyl *trans*-cinnamate were recovered quantitively from the reaction mixtures after 48—140 h, and identified by their IR spectra. Methyl acrylate, vinyl chloride, vinylidene chloride, trichloroethylene, and vinyl bromide yielded no product after 48—126 h, but were not recovered due to their loss by volatilisation during the isolation procedure.

Spectra. IR spectra were recorded with a Perkin-Elmer 237 spectrometer, and were taken for films of liquid products and for Nujol mulls of solid products. ^1H NMR spectra were recorded with Varian A60A and HA100 spectrometers, using tetramethylsilane as internal standard. In the NMR data given above, s=singlet, d=doublet t=triplet, q=quartet, p=pentet, sext=sextet, m=multiplet; band-widths are separations of outer lines.[3]

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