

## Pseudohalogen Chemistry. Part I.<sup>1</sup> Heterolytic Addition of Thiocyanogen Chloride to Some Symmetrical Alkenes and Cycloalkenes

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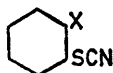
Thiocyanogen chloride reacts rapidly with ethylene, *cis*- and *trans*-but-2-ene, cyclohexene, and *trans*- $\Delta^2$ -octalin in the presence of a radical inhibitor in acetic acid in the dark to yield  $\alpha$ -chloro- $\beta$ -thiocyanates and  $\alpha$ -acetoxy- $\beta$ -thiocyanates. The reaction is *trans* stereospecific. A heterolytic mechanism, involving a two-step, kinetically controlled addition and the formation of a cyano-sulphonium ion intermediate [e.g. (VIII)] is suggested.

THIOCYANOGEN CHLORIDE, CISCN, is exclusively a thiocyanating agent in substitution processes, and is considerably more reactive than the parent pseudohalogen, thiocyanogen, (SCN)<sub>2</sub>. Depending on such experimental factors as the nature of the solvent, illumination, and the presence of radical initiators or inhibitors, these thiocyanation reactions can proceed by either a heterolytic or a homolytic mechanism. Under heterolytic conditions, thiocyanation of aromatic compounds occurs in the nucleus owing to electrophilic attack by the pseudohalogen halide, polarised in the manner Cl( $\delta^-$ )-SCN( $\delta^+$ ); under homolytic conditions, thiocyanation of aralkyl hydrocarbons occurs at the  $\alpha$ -carbon atom of the side-chain by a radical-chain reaction involving chlorine atoms as the hydrogen-abstraction agent.<sup>2</sup>

In their preliminary investigations of the chemistry of thiocyanogen chloride, Angus and Bacon<sup>3</sup> observed that the pseudohalogen halide reacted rapidly with ethylene and cyclohexene in chloroform or toluene giving products which were presumed to be the  $\alpha$ -chloro- $\beta$ -thiocyanates (I; X = Cl) and (II; X = Cl) respectively.



(I)



(II)

McGhie *et al.*<sup>4</sup> later showed that thiocyanogen chloride reacts readily with the *cis*- and *trans*-isomers of octadec-6-enoic, octadec-9-enoic, and docos-13-enoic acids. The products were not identified but were converted into the corresponding epithio-acids by treatment with alcoholic alkali. The *cis*-isomer of each pair of unsaturated acids gave the *cis*-epithio-acid, and the *trans*-isomer gave the *trans*-epithio-acid. The results were interpreted in terms of a *trans*-addition of thiocyanogen chloride, but, since the configurations of the epithio-acids were assigned by analogy of their melting points with those of the corresponding epoxy-acids, and the yields of epithio-acids were only 42–60%, the stereochemistry of the reaction cannot be claimed to have been rigorously determined. Furthermore, since none of the reactions was carried out under strictly heterolytic or homolytic con-

† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

<sup>1</sup> Preliminary communication, R. G. Guy and I. Pearson *Chem. and Ind.*, 1967, 1255.

<sup>2</sup> (a) R. G. R. Bacon and R. G. Guy, *J. Chem. Soc.*, 1960, 318; (b) 1961, 2428; (c) R. G. R. Bacon, R. G. Guy, and R. S. Irwin, *ibid.*, p. 2436.

ditions, firm conclusions cannot be drawn about the reaction mechanism.

We have now investigated the reaction of thiocyanogen chloride with alkenes under both heterolytic and homolytic conditions.<sup>1</sup> Here we describe the reaction with some symmetrical alkenes and cycloalkenes under conditions previously shown to be favourable to heterolytic fission of thiocyanogen chloride (anhydrous acetic acid solvent, darkness, room temperature, and added radical inhibitor).

### RESULTS

Reactions with ethylene, *cis*-but-2-ene, *trans*-but-2-ene, *trans*- $\Delta^2$ -octalin, and cyclohexene were complete in a few minutes in each case. Examination of each reaction product by t.l.c. showed the presence of two components in unequal amounts. These were readily isolated by column chromatography, and were identified by their i.r. and <sup>1</sup>H n.m.r. spectra and/or by synthesis. All the compounds showed the characteristic sharp absorption of thiocyanates<sup>5</sup> near 2165 cm<sup>-1</sup>. The chemical shifts ( $\tau$ ) of the protons in comparable CH(OAc), CHCl, and CH(SCN) groups increase in the order given, and usually allowed a first-order interpretation.

Ethylene gave 1-chloro-2-thiocyanatoethane (I; X = Cl) (64% yield), identical with the product described by Angus and Bacon,<sup>3</sup> and 1-acetoxy-2-thiocyanatoethane (I; X = OAc) (6% yield). The structures of the compounds follow from the i.r. and n.m.r. data which are deposited with the N.L.L. as Supplementary Publication No. 20600 (3 pp.).†

*cis*-But-2-ene gave a 2-chloro-3-thiocyanatobutane (81% yield), and a 2-acetoxy-3-thiocyanatobutane (15% yield). The configurations of these products could not be deduced from their n.m.r. spectra. However, the compounds were each shown to have the *threo*-configuration by their identity (physical constants and spectra) with the authentic *threo*-compounds (III) and (IV) prepared by the stereospecific synthesis outlined below in Scheme 1, in which the key step is the stereospecific *trans*-opening of the epoxide ring of *cis*-2,3-epoxybutane by thiocyanic acid.<sup>6</sup>

*trans*-But-2-ene also gave a 2-chloro-3-thiocyanatobutane (89% yield) and a 2-acetoxy-3-thiocyanatobutane (8% yield). These compounds were not identical (*cf.* n.m.r. spectra) with the corresponding *threo*-compounds described above, and were, therefore, assigned the diastereoisomeric *erythro*-configuration (V; X = Cl or OAc).

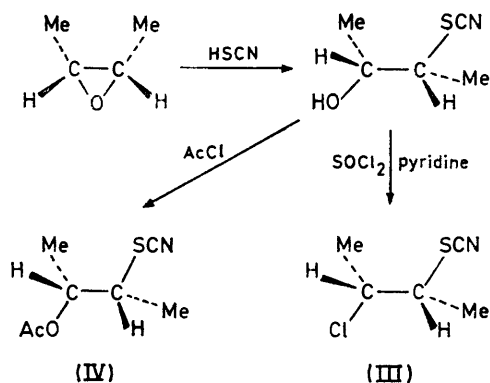
<sup>3</sup> A. B. Angus and R. G. R. Bacon, *J. Chem. Soc.*, 1958, 774.

<sup>4</sup> J. F. McGhie, W. A. Ross, F. J. Julietti, and B. E. Grimwood, *J. Chem. Soc.*, 1962, 4638.

<sup>5</sup> L. S. Luskin, G. E. Gantert, and W. E. Craig, *J. Amer. Chem. Soc.*, 1956, 78, 4965; N. S. Ham and J. B. Willis, *Spectrochim. Acta*, 1960, 16, 279, 393.

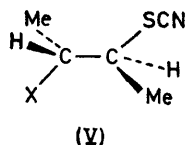
<sup>6</sup> E. E. van Tamelen, *J. Amer. Chem. Soc.*, 1951, 73, 3444.

Careful t.l.c., i.r., and  $^1\text{H}$  n.m.r. analysis of the crude reaction product from each alkene revealed no detectable amounts of the other diastereoisomers.

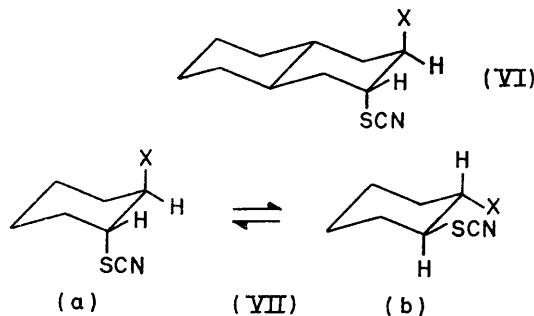


SCHEME 1

*trans*- $\Delta^2$ -Octalin gave *2ax*-chloro-*3ax*-thiocyanato-*trans*-decalin (VI; X = Cl) (69% yield), and *2ax*-acetoxy-*3ax*-thiocyanato-*trans*-decalin (VI; X = OAc) (25% yield). These configurations follow from the small band-widths and



splittings of the  $\text{CH}\cdot\text{SCN}$  and  $\text{CH}\cdot\text{X}$  (X = Cl or OAc) protons which indicate that each of these protons is in an equatorial position, coupled approximately equally to two adjacent equatorial protons and one adjacent axial proton. No isomers of (VI; X = Cl or OAc) were detected in the crude reaction product using t.l.c., i.r., and n.m.r. analysis.



Cyclohexene gave *trans*-1-chloro-2-thiocyanatocyclohexane (VII; X = Cl) (77% yield), identical with the product described by Angus and Bacon,<sup>3</sup> and *trans*-1-acetoxy-2-thiocyanatocyclohexane (VII; X = OAc) (15% yield). The configuration and conformation of these compounds follow from the large band-widths and splitting patterns of the  $\text{CH}\cdot\text{SCN}$  and  $\text{CHX}$  (X = Cl or OAc) protons which indicate that each of these protons is predominantly in an axial position, coupled strongly to two adjacent axial protons and weakly to one adjacent equatorial proton. The products were identical in all respects with authentic samples of (VII; X = Cl or OAc) synthesised from 1,2-epoxycyclohexane by the method outlined in Scheme 1. No isomers of (VII; X = Cl or OAc) were detected in the crude reaction product, using i.r., n.m.r., and t.l.c. analysis.

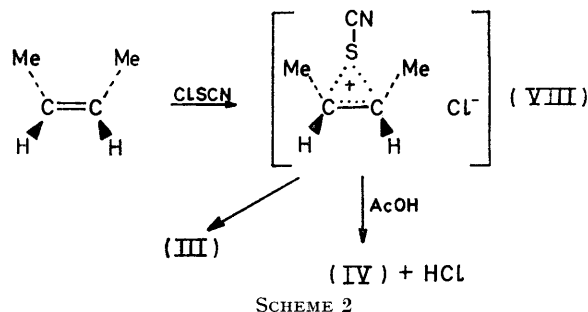
Control experiments on all these compounds showed that, under the conditions used in the addition reaction, no displacement of chloride by acetate ion, or of acetate by chloride ion, occurred.

No reaction occurred with alkenes of the type *cis*- and *trans*- $\text{RCH}\cdot\text{CHR}$  (R = Cl, CO<sub>2</sub>H, or CO<sub>2</sub>Me) or with tetrachloroethylene during 48–126 h. No isomerisation of the alkenes was observed.

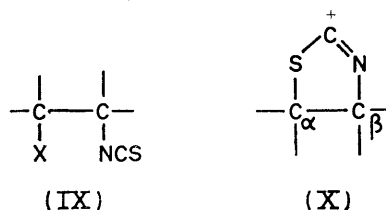
## DISCUSSION

These data show that the reaction of thiocyanogen chloride with symmetrical alkenes exhibits the following characteristics: (a) addition is rapid in the presence of electron-donating alkyl groups on the C=C bond and is prevented by similarly-situated electron-withdrawing groups; (b) the products of the reaction are  $\alpha$ -chloro- $\beta$ -thiocyanates and  $\alpha$ -acetoxy- $\beta$ -thiocyanates; (c) these are primary products; and (d) the addition is stereospecific *trans*.

These results are readily accounted for by a two-step heterolytic mechanism, involving (a) initial electrophilic attack on the alkene by the sulphur atom of the thiocyanogen chloride molecule with the formation of a cyano-sulphonium ion, and (b) the subsequent *trans*-opening of the ring by either of the available nucleophiles (chloride ion and acetic acid solvent). A mechanism of this type with the sulphonium-ion intermediate shown as an ion pair (VIII), as is appropriate for weakly dissociating solvents such as acetic acid,<sup>7</sup> and illustrated with *cis*-but-2-ene, is shown in Scheme 2.



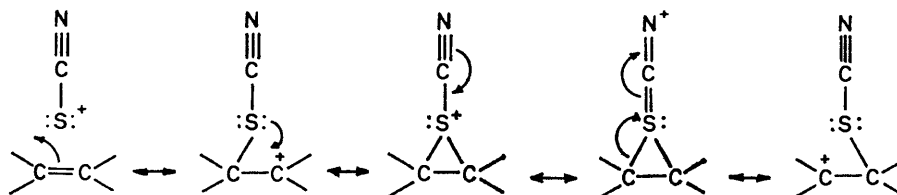
Electrophilic attack by the S atom of the thiocyanogen chloride molecule is consistent with the polarisation  $\text{Cl}(\delta^-)\text{-SCN}(\delta^+)$  previously established for aromatic substitution reactions under heterolytic conditions, and accounts for the formation of thiocyanato-compounds, *via* kinetic control of reaction, rather than the thermodynamically more stable isothiocyanato-isomers [*e.g.* (IX; X = Cl or OAc)].



<sup>7</sup> R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, 1965, **87**, 5172.

The intermediate (VIII) is written as a sulphur-bridged species rather than a thiocyanato-bridged one (X) since the latter, on ring-opening at C<sub>α</sub> would lead to the isothiocyanato-isomers (IX; X = Cl or OAc) as well as the observed thiocyanato-compounds. Similar sulphur-bridged ions have been postulated by Kharasch<sup>8</sup> and other workers<sup>9</sup> to account for the stereospecific *trans*-addition of the closely related aryl- and alkyl-sulphenyl chlorides (RSCl) to alkenes of the type discussed above.

The stability of the sulphonium ion (VIII) is attributed to delocalisation of the positive charge by the sulphur atom, and perhaps the thiocyanato-group as a whole, *e.g.*



Supporting evidence for the ability of the thiocyanato-group to act as an electron-donor system, in spite of its strong  $-I$  effect (*cf.* the halogens) comes from the observation<sup>10</sup> that nitration of thiocyanatobenzene yields 4-nitrothiocyanatobenzene exclusively.

The *trans*-opening of the ring accounts for the formation of the *erythro*- and *threo*-products from *trans*- and *cis*-but-2-ene respectively. The formation of the thermodynamically unfavourable diaxial products from the conformationally rigid  $\Delta^2$ -octalin indicates that the ring-opening is both diaxial and kinetically controlled. This follows from the proposition<sup>11</sup> that diaxial ring-opening *via* a chair-shaped transition state leads to a diaxial product, whereas diaxial ring-opening *via* the alternative, more energetic, boat-shaped transition state leads to a flexible twist-boat product which, on ring inversion, is converted into the thermodynamically stable diequatorial product. The formation of the diequatorial products in the case of the conformationally mobile cyclohexene is attributed to inversion of the initially formed diaxial products, although the alternative mechanism described above cannot be ruled out.

These reactions of thiocyanogen chloride emphasise further its close resemblance<sup>2,12</sup> to aryl- and alkyl-sulphenyl halides, the halogens and the interhalogens.<sup>13</sup>

#### EXPERIMENTAL

**Alkenes.**—Ethylene, *cis*-but-2-ene, and *trans*-but-2-ene (Research Grade; Cambrian Chemicals Ltd.) were of 99.9, 99.82, and 99.26% purity respectively. Cyclohexene, *cis*- and *trans*-dichloroethylene, tetrachloroethylene, maleic

<sup>8</sup> N. Kharasch in 'Organic Sulfur Compounds,' Pergamon Press, Oxford, 1961, vol. 1, p. 375.

<sup>9</sup> G. H. Schmid and V. M. Csizmadia, *Canad. J. Chem.*, 1966, **44**, 1338; W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, 1966, **88**, 2866.

<sup>10</sup> F. Challenger and A. D. Collins, *J. Chem. Soc.*, 1924, 1377; F. Challenger and A. T. Peters, *ibid.*, 1928, 1364; F. Challenger, C. Higginbottom, and A. Huntington, *ibid.*, 1930, 26; F. G. Bordwell and P. J. Boutan, *J. Amer. Chem. Soc.*, 1956, **78**, 854.

acid, fumaric acid, dimethyl maleate, and dimethyl fumarate were commercial samples purified until their physical constants agreed with those recorded in the literature. *trans*- $\Delta^2$ -Octalin (b.p. 65°/12 mmHg,  $n_D^{25}$  1.4800) was prepared by dehydration of *trans*- $\beta$ -decahydronaphthol with potassium hydrogen sulphate, and purified as described by Johnson *et al.*<sup>14</sup>

**General Procedure.**—Solutions (500 ml; 0.2–0.5M) of thiocyanogen chloride in acetic acid were prepared from lead thiocyanate and chlorine in an opaque flask as described elsewhere.<sup>2a</sup> The lead chloride was not removed, and 2,6-di-*t*-butyl-*p*-cresol (0.20 g, 0.00045 mol) was added as a radical inhibitor. The peroxide-free alkene was added in acetic acid (25 ml) in a ratio of 9 : 10 if a liquid or a solid,

or *via* a sintered-glass disc if a gas, to the reagent held in a thermostat bath at 25°. The disappearance of thiocyanogen chloride was followed by iodometric titration of aliquot parts of the reaction mixture. At the end of the reaction, lead chloride was filtered off and the product was isolated by dilution of the solution with ice-cold water (3 l) followed by extraction with an organic solvent, washing with water to remove acetic acid, drying, and removal of solvent under reduced pressure. Allowance was made for material removed during titration.

The product was examined by t.l.c. using 20 × 10 cm glass plates spread with silica gel (250  $\mu$ m thick). After development with benzene, the plates were dried at 40° and the spots located with iodine vapour or with fluorescein spray. Quantitative separation of the components was achieved by chromatography of aliquot parts (4–7 g) on columns of silica gel (B.D.H. Laboratory Reagent, 60–120 mesh; 150 g), the purity of the eluted fractions (each 100 ml) being monitored by refractive index measurements and by i.r. spectroscopy. Typically, elution with benzene–light petroleum (b.p. 60–80°) (1 : 1) gave the  $\alpha$ -chloro- $\beta$ -thiocyanate in fractions 5–15; elution with benzene gave no product in fractions 16–24; and elution with benzene–ether (9 : 1) or chloroform gave the  $\alpha$ -acetoxy- $\beta$ -thiocyanate in fractions 25–35.

**Ethylene.** Ethylene gave (a) 1-chloro-2-thiocyanatoethane as a colourless liquid, b.p. 83–84°/11 mmHg,  $n_D^{20}$  1.5142, identical in physical and spectral properties with the compound prepared from 1,2-dichloroethane and ammonium thiocyanate, as described by Angus and Bacon,<sup>3</sup> and (b) 1-acetoxy-2-thiocyanatoethane as a colourless liquid,

<sup>11</sup> J. Valls and E. Toromanoff, *Bull. Soc. chim. France*, 1961, 758; H. J. Hageman and E. Havinga, *Rec. Trav. chim.*, 1966, **85**, 1141.

<sup>12</sup> R. G. Guy, *Mechanisms of Reactions of Sulfur Compounds*, 1968, **3**, 57; R. G. R. Bacon in 'Organic Sulfur Compounds,' Pergamon, Oxford, 1961, vol. 1, p. 306.

<sup>13</sup> P. B. D. de la Mare and R. Bolton, 'Electrophilic Additions to Unsaturated Systems,' Elsevier, London, 1966.

<sup>14</sup> W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Amer. Chem. Soc.*, 1961, **83**, 606.

b.p. 48°/0.1 mmHg,  $n_D^{22}$  1.4750 (Found: C, 41.0; H, 5.2; N, 9.4.  $C_5H_7NO_2S$  requires C, 41.4; H, 4.85; N, 9.65%).

*cis-But-2-ene*. *cis-But-2-ene* gave (a) *threo-2-chloro-3-thiocyanatobutane* as a colourless liquid, b.p. 50°/0.1 mmHg,  $n_D^{20}$  1.4974, identical in physical and spectral properties with an authentic sample prepared as described below (Found: C, 39.95; H, 5.2; N, 9.3.  $C_5H_8ClNS$  requires C, 40.15; H, 5.4; N, 9.35%), and (b) *threo-2-acetoxy-3-thiocyanatobutane* as a colourless liquid, b.p. 58–59°/0.1 mmHg,  $n_D^{20}$  1.4710, identical in physical and spectral properties with an authentic sample prepared as described below (Found: C, 48.7; H, 6.5; N, 7.8.  $C_7H_{11}NO_2S$  requires C, 48.55; H, 6.4; N, 8.1%).

For alternative syntheses of these compounds, *cis-2,3-epoxybutane* (b.p. 58–60°/756 mmHg,  $n_D^{20}$  1.3820) was prepared from 3-bromobutan-2-one as described.<sup>15</sup> Treatment of the epoxide with thiocyanic acid as described by van Tamelen<sup>6</sup> gave *threo-2-hydroxy-3-thiocyanatobutane* (49%) as a colourless oil,  $n_D^{25}$  1.4885,  $\nu_{OH}$  at 3450  $cm^{-1}$ ,  $\nu_{SCN}$  at 2165  $cm^{-1}$ , which on treatment with (a) acetyl chloride in pyridine gave *threo-2-acetoxy-3-thiocyanatobutane* (70%), and (b) thionyl chloride in dry dioxan<sup>16</sup> gave *threo-2-chloro-3-thiocyanatobutane* (64%).

*trans-But-2-ene*. *trans-But-2-ene* gave (a) *erythro-2-chloro-3-thiocyanatobutane* as a colourless liquid, b.p. 52°/0.1 mmHg,  $n_D^{20}$  1.4968 (Found: C, 39.9; H, 5.35; N, 9.25%), and (b) *erythro-2-acetoxy-3-thiocyanatobutane* as a colourless liquid, b.p. 60–61°/0.1 mmHg,  $n_D^{20}$  1.4771 (Found: C, 49.0; H, 6.55; N, 7.9%).

*Cyclohexene*. Cyclohexene gave (a) *trans-1-chloro-2-thiocyanatocyclohexane* as a colourless liquid, b.p. 82°/0.2 mmHg,  $n_D^{20}$  1.5269 (lit.,<sup>3</sup>  $n_D^{25}$  1.5255), identical in physical and spectral properties with an authentic sample prepared as described below (Found: C, 48.2; H, 5.8; Cl, 19.55; N, 7.55; S, 17.95. Calc. for  $C_6H_{10}ClNS$ : C, 47.85; H, 5.75; Cl, 20.2; N, 8.0; S, 18.25%), and (b) *trans-1-acetoxy-2-thiocyanatocyclohexane* as a colourless liquid, b.p. 102–103°/0.2 mmHg,  $n_D^{20}$  1.4971, identical in physical and spectral properties with an authentic sample prepared as described below (Found: C, 54.3; H, 6.7; N, 6.8; S, 15.9.  $C_8H_{13}NO_2S$  requires C, 54.25; H, 6.55; N, 7.05; S, 16.1%).

For alternative syntheses of these compounds, 1,2-epoxycyclohexane<sup>17</sup> was treated with thiocyanic acid as described by van Tamelen,<sup>6</sup> giving *trans-2-thiocyanatocyclohexanol*,  $n_D^{22}$  1.5300 (lit.,<sup>6</sup>  $n_D^{25}$  1.5307) which on treatment with (a) acetyl chloride in pyridine gave *trans-1-acetoxy-2-*

*thiocyanatocyclohexane* (69%) and (b) thionyl chloride in dry dioxan<sup>16</sup> gave *trans-1-chloro-2-thiocyanatocyclohexane* (73%).

*trans- $\Delta^2$ -Octalin*. *trans- $\Delta^2$ -Octalin* gave (a) *2ax-chloro-3ax-thiocyanato-trans-decalin* as a colourless liquid, b.p. 108°/0.05 mmHg,  $n_D^{25}$  1.5388 (Found: C, 57.65; H, 7.35; Cl, 15.55; N, 6.05.  $C_{11}H_{16}ClNS$  requires C, 57.5; H, 7.0; Cl, 15.45; N, 6.1%), and (b) *2ax-acetoxy-3ax-thiocyanato-trans-decalin* as colourless needles, m.p. 107–108° after crystallisation from methanol (Found: C, 61.4; H, 7.7; N, 5.2; S, 12.6.  $C_{13}H_{19}NO_2S$  requires C, 61.6; H, 7.6; N, 5.55; S, 12.6%).

*Control Experiments*.—The following experiments carried out on the products derived from cyclohexene (see above) are typical. *trans-1-Chloro-2-thiocyanatocyclohexane* (2.00 g) was dissolved in acetic acid (70 ml) and left at 25° for 2 h. The reaction solution was then treated in the usual way and gave starting material (1.85 g) as shown by the identity of refractive indices, i.r. spectra, and t.l.c. behaviour. *trans-1-Acetoxy-2-thiocyanatocyclohexane* (2.00 g, 0.0105 mol) and lithium chloride (1.00 g, 0.0235 mol) were dissolved in acetic acid (70 ml) and left at 25° for 2 h. The reaction solution was then treated in the usual way, and gave starting material (1.85 g) as shown by the identity of refractive indices, i.r. spectra, and t.l.c. behaviour.

*Unreactive Alkenes*.—Maleic acid, fumaric acid, dimethyl maleate, dimethyl fumarate, and tetrachloroethylene were recovered quantitatively from the reaction mixtures after 48 h, and identified by their i.r. spectra. *cis*-Dichloroethylene and *trans*-dichloroethylene yielded no product after 126 h, but were not recovered due to their loss by volatilisation during the isolation procedure.

*Spectra*.—I.r. spectra were recorded with a Perkin-Elmer 237 spectrometer, and were taken for liquid films unless otherwise stated. <sup>1</sup>H n.m.r. spectra were recorded with a Varian A60A spectrometer, using deuteriochloroform as solvent and tetramethylsilane as internal standard.

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[2/1436 Received, 20th June, 1972]

<sup>15</sup> S. M. Iqbal and L. N. Owen, *J. Chem. Soc.*, 1960, 1030.

<sup>16</sup> D. J. Cram, *J. Amer. Chem. Soc.*, 1953, **75**, 332.

<sup>17</sup> A. E. Osterberg, *Org. Synth.*, Coll. Vol. I, 1941, 185.