Pseudohalogen Chemistry. Part II.[1] Heterolytic Addition of Thiocyanogen Chloride to Some Symmetrical α-Arylalkenes

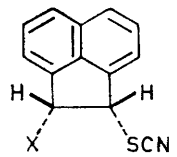
By **Robert G. Guy** * and **Ian Pearson**, Department of Chemical Sciences, The Hatfield Polytechnic, P.O. Box 109, Hatfield, Hertfordshire

Thiocyanogen chloride reacts with *cis*- and *trans*-stilbene and acenaphthylene in the presence of a radical inhibitor in acetic acid in the dark at 25° to yield α-chloro-β-thiocyanates and α-acetoxy-β-thiocyanates. The rate of addition to *trans*-stilbene in acetic acid, methylene chloride, chloroform, and benzene decreases with decreasing solvating power of the solvents. The reactions are *trans*-stereoselective. A heterolytic mechanism, involving a two-step, kinetically controlled addition and the formation of an open carbonium ion is suggested. The stereochemistry is discussed in terms of ion-pairs and steric control of reaction by the thiocyanato-group of the carbonium ion.

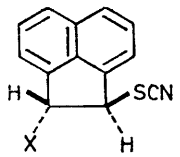
In Part I [1] it was shown that thiocyanogen chloride, ClSCN, reacts rapidly at 25° with symmetrical alkenes and cycloalkenes, *e.g.* ethylene, *cis*- and *trans*-but-2-ene, cyclohexene, and *trans*-Δ^2-octalin, in the presence of a radical inhibitor in acetic acid in the dark, to yield α-chloro-β-thiocyanates and α-acetoxy-β-thiocyanates by a stereospecific *trans*-addition. A heterolytic mechanism, involving a two-step, kinetically controlled addition and the formation of a cyanosulphonium ion intermediate, was proposed. Here we describe the reaction of thiocyanogen chloride with some symmetrical aryl-substituted alkenes under the same conditions. The effect of solvent on the reaction with *trans*-stilbene is also described.

RESULTS

Reaction with acenaphthylene in acetic acid was complete in a few minutes. The product was readily separated by column chromatography into (*a*) a mixture of *cis*- and *trans*-1-chloro-2-thiocyanatoacenaphthene (1 and 2 respectively; X = Cl) (61% yield) in the ratio of 21 : 79, and (*b*) a mixture of *cis*- and *trans*-1-acetoxy-2-thiocyanatoacenaphthene (1 and 2 respectively; X = OAc) (35%) in the ratio of 12 : 88.



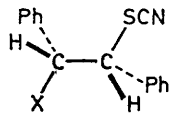
(1)



(2)

The structures were determined from the spectra of the mixtures. Each mixture showed, in its i.r. spectrum, the characteristic absorption band of the thiocyanato-group, and, in its n.m.r. spectrum, the two pairs of doublets expected for the methine protons of a mixture of (1) and (2). The doublet pairs with the larger splittings were assigned to the *cis*-isomers, and those with the smaller splittings to the *trans*-isomers.[2] The isomer ratios were determined from the integral traces of these doublets.

Reaction with each of the stilbenes was measurable by normal titration techniques, with the *cis*-isomer being more reactive than the *trans*-isomer (see Table). The product from *trans*-stilbene was separated as above into (*a*) a mixture of *threo*- and *erythro*-1-chloro-1,2-diphenyl-2-thiocyanatoethane (3 and 4 respectively; X = Cl) (52% yield), and (*b*) a mixture of *threo*- and *erythro*-1-acetoxy-1,2-diphenyl-2-thiocyanatoethane (3 and 4 respectively; X = OAc) (43% yield).



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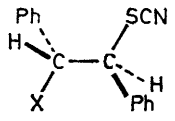


(4)

Fractional crystallisation of each mixture afforded the pure *erythro*-isomer in each case, identification being made by comparison with authentic samples of the *erythro*-chloride (4; X = Cl) and the *erythro*-acetate- (4; X = OAc) which were prepared from *trans*-stilbene oxide and thiocyanic acid by the stereospecific method described earlier.[1] Isomer ratios were determined from the integral traces of the methine doublets in the n.m.r. spectra of the mixtures, and are presented in the Table.

Product ratios from addition of thiocyanogen chloride to stilbenes

Stilbene	Solvent	Relative reaction rate	Isomer ratio (3; X = Cl) : (4; X = Cl)	Isomer ratio (3; X = OAc) : (4; X = OAc)
cis	AcOH	40	75 : 25	88 : 12
trans	AcOH	13	46 : 54	10 : 90
trans	CH_2Cl_2	10	28 : 72	
trans	$CHCl_3$	4	8 : 92	
trans	C_6H_6	1	37 : 63	

The product from *cis*-stilbene was similarly separated into (*a*) a mixture of the chlorides (3 and 4; X = Cl) (51% yield), and (*b*) a mixture of the acetates (3 and 4; X = OAc) (38% yield). Fractional crystallisation of these mixtures gave respectively a 1-chloro-1,2-diphenyl-2-thiocyanatoethane and a 1-acetoxy-1,2-diphenyl-2-thiocyanatoethane which were not identical with the corresponding *erythro*-compounds described above. These compounds were therefore assigned the diastereoisomeric *threo*-configuration (3; X = Cl or OAc). Isomer ratios were determined as above and are presented in the Table.

Control experiments on compounds (3 and 4; X = Cl or OAc) showed that, under the conditions used in the addition reaction, they were unaffected by acetic acid or by added chloride ions.

trans-Stilbene reacted with thiocyanogen chloride in methylene chloride, chloroform, and benzene at the relative rates shown in the Table, and yielded, in each case, a mixture of the chloro-thiocyanates (3 and 4; X = Cl) (52, 60, and 42% yield respectively) in the ratios given in

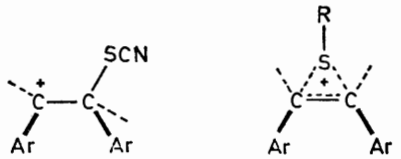
[1] Part I, R. G. Guy and I. Pearson, *J.C.S. Perkin I*, 1973, 281.
[2] M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, 1963, **85**, 2246.

the Table. Control experiments showed that the products were stable in these solvents.

No reaction occurred with *trans*-4,4′-dinitrostilbene or with tetraphenylethylene during 140 h. No isomerisation of the alkenes was observed.

DISCUSSION

The products obtained, *i.e.* α-chloro-β-thiocyanates and α-acetoxy-β-thiocyanates, are those expected on the basis of a two-step, kinetically controlled heterolytic reaction in which the first step is the addition of the



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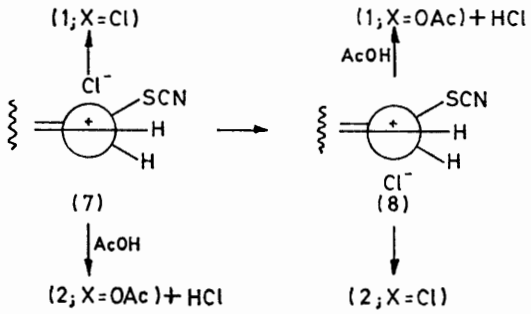
thiocyanato-cation, ^{+}SCN, and the second is nucleophilic attack by chloride ion or, in acetic acid, the



SCHEME 1

solvent. However, the lack of stereospecificity indicates an open carbonium ion intermediate, *e.g.* (5), stabilised by the $+M$ effect of the α-aryl group, rather than a cyanosulphonium ion intermediate, *e.g.* (6; R = CN), of the type postulated to account for the *trans*-stereospecific addition to aliphatic alkenes.[1]

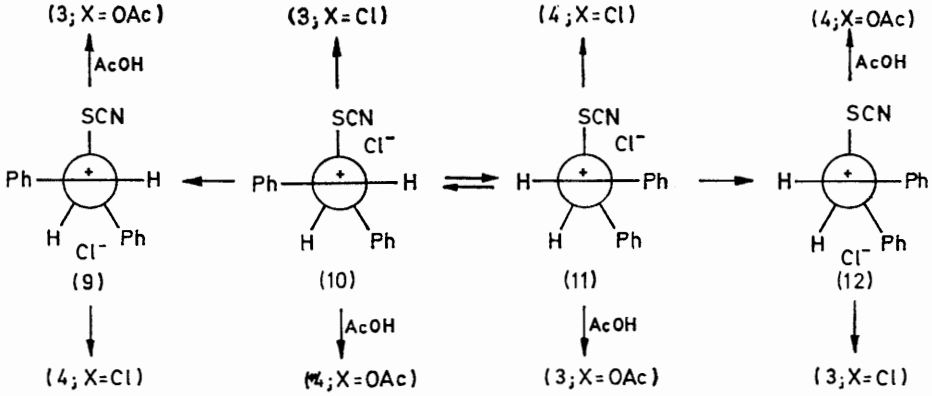
[3] R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, 1965, **87**, 5172; M. C. Cabaleiro and M. D. Johnson, *J. Chem. Soc.* (*B*), 1967, 565.

In agreement with different carbonium ion intermediates, the chlorothiocyanate : acetoxythiocyanate product ratios for the two types of alkenes are distinctly different, ranging from 2·8 : 1 to 11·4 : 1 for the aliphatic alkenes,[1] but from 1·2 : 1 to 1·7 : 1 for the aryl alkenes. This is consistent with the open carbonium ion (5) being more heavily solvated than the bridged ion (6), and hence more likely to form the acetate.

Closer examination of the results shows that (*a*) the predominant products from acenaphthylene, *trans*-stilbene, and *cis*-stilbene are the *trans*-, *erythro*-, and *threo*-adducts respectively, *i.e.* the addition is *trans*-stereoselective, and (*b*) *cis*- and *trans*-stilbene give different product ratios in acetic acid, *i.e.* the two additions do not involve a common intermediate.

These results are readily accounted for by (*a*) an ion-pair mechanism, as is appropriate for the weakly dissociating solvents used,[3] and (*b*) steric control of reaction by the bulky thiocyanato-group. Thus, for acenaphthylene, the initially formed ion-pair (7) and its isomer (8), formed by chloride ion migration, and the various reaction pathways are shown in Scheme 1. The sterically favoured pathways, outlined in the lower half of the Scheme, lead to the preferred *trans*-adducts.

Similarly, the initially formed ion-pairs (10) and (11) from *trans*- and *cis*-stilbene respectively, their isomers (9) and (12), their interconversion routes (*i.e.* chloride ion migration and rotation), and the various reaction pathways are shown in Scheme 2. The observed preference of each stilbene for *trans*-addition is again consistent with the sterically favoured pathways, outlined in the lower half of the Scheme, and also shows that the ion-pairs (9)—(12) have not reached equilibrium before the associative processes occur, *i.e.* the rates of rotation are slower than the rates of chloride ion migration and ion-pair collapse.[4] The differences in



SCHEME 2

stereoselectivity in the four solvents investigated (see Table) are hardly surprising, since the stability, rate of isomerisation, and rate of product formation of each of the ion-pairs (9)—(12) will be different in each

[4] C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, 1963, **85**, 2519; S. Winstein, *ibid.*, 1965, **87**, 381.

solvent (*cf.* the heterolytic addition of bromine to the stilbenes).[5]

The observed rates of addition to the alkenes investigated are also consistent with a carbonium ion mechanism. Thus, the reactivity sequence, acenaphthylene > *cis*- and *trans*-stilbene ≫ *trans*-4,4'-dinitrostilbene = 0, is consistent with the relative stabilities of the corresponding carbonium ion intermediates, and the relative rates of addition to *trans*-stilbene in acetic acid, methylene chloride, chloroform, and benzene (see Table) decrease in the order of decreasing solvating power (Z) [6] of the solvents (Z = 332, 270, 265, and 226 kJ mol^{-1} respectively).

cis-Stilbene reacts faster than *trans*-stilbene (see Table), and, as for other electrophilic additions, *e.g.* bromination,[5] which show similar relative reactivities, this difference is attributed to the greater free energy of the *cis*-isomer. The lack of addition to tetraphenylethylene is a further illustration of the passivity of this alkene towards electrophilic reagents; this lack of reactivity has been attributed to the dual character of the phenyl groups reducing the π-electron density at the reaction centre.[7]

The involvement of bridged carbonium ions in its addition to aliphatic alkenes, but of open carbonium ions in its addition to α-arylalkenes, places thiocyanogen chloride with chlorine, bromine, and bromine chloride rather than with iodine, iodine chloride, iodine azide, iodine isocyanate, and the closely related methanesulphenyl chloride and 2,4-dinitrobenzenesulphenyl chloride, which all involve bridged carbonium ions in both types of reaction.[8] The cyanosulphonium ion (6; R = CN) is therefore less stable than the corresponding methyl- and 2,4-dinitrophenyl-sulphonium ions [6; R = Me and 2,4-$(NO_2)_2C_6H_3$ respectively]; this probably reflects the relative abilities of the groups R in (6) to delocalise further the positive charge of the sulphonium ion.

EXPERIMENTAL

Alkenes.—The alkenes used were commercial samples purified until their physical constants agreed with those recorded in the literature.

General Procedure.—The reactions in acetic acid were carried out as described in Part I.[1] Solutions of thiocyanogen chloride in chloroform, methylene chloride, and benzene were prepared by mixing equimolar solutions of thiocyanogen and chlorine as described elsewhere.[9] The reagent was used in 100% excess to allow for loss by decomposition during the (slow) reactions with *cis*- and *trans*-stilbene. Reaction rates were followed, and the products isolated and separated, as described in Part I. The relative rates quoted in the Table are inversely proportional to the respective times taken by *ca.* 0·25M solutions of thiocyanogen chloride to show 15% consumption of reagent (*i.e.* 30% reaction).

Acenaphthylene.—Acenaphthylene (0·09 mol) reacted completely with thiocyanogen chloride (0·1 mol) in acetic acid in 5 min, giving (*a*) a mixture of *cis*- and *trans*-1-chloro-2-thiocyanatoacenaphthene as a viscous oil: $\nu_{max.}$ 2165 (SCN) cm^{-1}, τ (CCl_4) 2·10—2·55 (m, aromatic H), 4·06 (d, *J* 7 Hz, *cis*-CHCl), 4·20 (d, *J* 1·5 Hz, *trans*-CHCl), 4·52 (d, *J* 7 Hz, *cis*-CHSCN), and 4·77 (1H, d, *J* 1·5 Hz, *trans*-CHSCN) (Found: C, 63·15; H, 2·9; N, 6·0. Calc. for $C_{13}H_8ClNS$: C, 63·55; H, 3·3; N, 5·7%), and (*b*) a mixture of *cis*- and *trans*-1-acetoxy-2-thiocyanatoacenaphthene as a viscous oil; $\nu_{max.}$ 2165 (SCN) and 1740 (C=O) cm^{-1}, τ 1·90—2·60 (m, aromatic H), 3·55 (d, *J* 2 Hz, *trans*-CHOAc), 3·36 (d, *J* 7 Hz, *cis*-CHOAc), 4·70 (d, *J* 7 Hz, *cis*-CHSCN), 4·97 (d, *J* 2 Hz, *trans*-CHSCN), 7·82 (s, *cis*-O_2CMe), and 7·94 (s, *trans*-O_2CMe) (Found: C, 67·4; H, 3·75; N, 5·3. Calc. for $C_{15}H_{11}NO_2S$: C, 66·9; H, 4·1; N, 5·2%). Both sets of products were vesicant and unstable, depositing a yellow amorphous solid (probably polymeric thiocyanic acid) on standing at room temperature or on attempted distillation under reduced pressure.

trans-*Stilbene.*—*trans*-Stilbene (0·1 mol) reacted completely with thiocyanogen chloride (0·2 mol) in acetic acid in 2 h, giving (*a*) a mixture of *threo*- and *erythro*-1-chloro-1,2-diphenyl-2-thiocyanatoethane which after four crystallisations from methanol gave the erythro-*isomer* as needles, m.p. 112—114°, identical in physical and spectral properties with an authentic sample prepared as described below, $\nu_{max.}$ 2165 (SCN) cm^{-1}, τ 2·60 (10H, s, aromatic H), 4·60 (1H, d, *J* 10 Hz, CHCl), and 5·20 (1H, d, *J* 10 Hz, CHSCN) (Found: C, 65·85; H, 4·55; Cl, 12·85; N, 5·2; S, 11·55. $C_{15}H_{12}ClNS$ requires C, 65·95; H, 4·4; Cl, 13·0; N, 5·15; S, 11·7%), and (*b*) a mixture of *threo*- and *erythro*-1-acetoxy-1,2-diphenyl-2-thiocyanatoethane which after three crystallisations from methanol gave the erythro-*isomer* as needles, m.p. 107—108°, identical in physical and spectral properties with an authentic sample prepared as described below, $\nu_{max.}$ 2165 (SCN) and 1740 (C=O) cm^{-1}, τ 2·67 (10H, s, aromatic H), 3·70 (1H, d, *J* 7 Hz, CHOAc), 5·23 (1H, d, *J* 7 Hz, CHSCN), 8·00 (3H, s, O_2CMe) (Found: C, 68·55; H, 5·05; N, 4·75; S, 10·9. $C_{17}H_{15}NO_2S$ requires C, 68·65; H, 5·1; N, 4·7; S, 10·75%).

For alternative syntheses of these compounds, *trans*-stilbene oxide was treated on a 0·01 mole scale with thiocyanic acid as described,[1] giving *erythro*-1,2-diphenyl-1-hydroxy-2-thiocyanatoethane (37%) as plates, m.p. 92—93° (from methanol), $\nu_{max.}$ 3400 (OH) and 2165 (SCN) cm^{-1}, which on treatment with (*a*) acetyl chloride in pyridine gave *erythro*-1-acetoxy-1,2-diphenyl-2-thiocyanatoethane (74% yield), and (*b*) thionyl chloride in dry dioxan gave *erythro*-1-chloro-1,2-diphenyl-2-thiocyanatoethane (77% yield).

The reactions of *trans*-stilbene (0·1 mol) with thiocyanogen chloride (0·2 mol) in methylene chloride, chloroform, and benzene were stopped after 5, 15, and 72 h respectively, when 50% consumption of reagent had occurred as shown by iodometric titration. Excess of reagent was removed by shaking with dilute sodium thiosulphate solution. After drying ($MgSO_4$), the solvent was removed under reduced pressure. The i.r. and n.m.r. spectra of each crude product showed the presence of unreacted *trans*-stilbene and a small amount of an unidentified material, probably a

[5] R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *J. Org. Chem.*, 1962, **27**, 4523; G. Hueblein, *J. prakt. Chem.*, 1966, **31**, 84.

[6] E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253.

[7] C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 1931, 2354; S. V. Anantakrishnan and C. K. Ingold, *ibid.*, 1935, 984, 1396.

[8] R. C. Fahey, in 'Topics in Stereochemistry,' eds. E. L. Eliel and N. L. Allinger, Interscience, New York, 1968, vol. 3, p. 237.

[9] R. G. R. Bacon and R. S. Irwin, *J. Chem. Soc.*, 1958, 778.

decomposition product of thiocyanogen chloride,[9] which contained an isothiocyanato-group. The stilbene was removed by chromatography on silica gel, using benzene–light petroleum (1 : 3) as eluant; the isothiocyanato-material was removed by treatment with morpholine which gave an insoluble adduct.[10]

cis-*Stilbene*.—*cis*-Stilbene (0·1 mol) reacted with thiocyanogen chloride (0·2 mol) in acetic acid in 40 min, giving (*a*) a mixture of *threo*- and *erythro*-1-chloro-1,2-diphenyl-2-thiocyanatoethane, which after six crystallisations from methanol gave the threo-*isomer* as plates, m.p. 103—104°, $\nu_{max.}$ 2165 (SCN) cm^{-1}, τ 2·70 (10H, s, aromatic H), 4·58 (1H, d, *J* 10 Hz, CHCl), and 5·00 (1H, d, *J* 10 Hz, CHSCN) (Found: C, 65·9; H, 4·65; N, 5·25%), and (*b*) a mixture of *threo*- and *erythro*-1-acetoxy-1,2-diphenyl-2-thiocyanatoethane which after four crystallisations from methanol gave the *threo*-isomer as needles, m.p. 96·5—97°, $\nu_{max.}$ 2165 (SCN) and 1740 (C=O) cm^{-1}, τ 2·74 (10H, s, aromatic H), 3·70 (1H, d, *J* 7 Hz, CHOAc), 5·16 (1H, d, *J* 7 Hz, CHSCN), and 7·8 (3H, s, O_2CMe) (Found: C, 68·65; H, 5·2; N, 4·55%).

Control Experiments.—These were carried out as described in Part I.[1]

Unreactive Alkenes.—*trans*-4,4′-Dinitrostilbene and tetraphenylethylene were recovered quantitatively from the reaction mixtures after 140 h, and identified by their m.p. and i.r. spectra.

Spectra.—I.r. spectra were recorded with a Perkin-Elmer 237 spectrometer, and were taken for liquid films of the acenaphthylene adducts and for Nujol mulls of the stilbene adducts. ^1H N.m.r. spectra were recorded as in Part I.[1]

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[10] R. G. R. Bacon, R. G. Guy, and R. S. Irwin, *J. Chem. Soc.*, 1961, 2436.