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Pseudohalogen Chemistry. V.[1] Homolytic Addition of Thiocyanogen Chloride to Some Haloalkenes on Irradiation with UV Light

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Synopsis. When irradiated with UV light, thiocyanogen chloride reacts with haloalkenes containing 1—4 halo substituents yielding α-chloro-β-thiocyanato compounds. Addition to unsymmetrical alkenes is regioselectively anti-Markownikov. A radical-chain mechanism, involving S_H2 displacement on the sulfur atom of thiocyanogen chloride and chlorine atoms as the adding/chain-carrying species, is proposed.

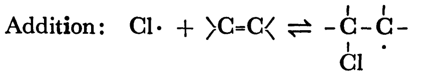
In earlier papers it was shown that, under heterolytic conditions in acetic acid, thiocyanogen chloride ($\overset{\delta-}{\text{Cl}}\text{–}\overset{\delta+}{\text{S}}\text{CN}$) behaves as an electrophile towards aliphatic alkenes[2] and α-arylalkenes[3] yielding α-chloro-β-thiocyanato compounds and the corresponding α-acetoxy-β-thiocyanato compounds; in the case of unsymmetrical alkenes preferential or exclusive Markownikov addition is observed.[4] Here we describe the homolytic reaction of thiocyanogen chloride with some alkenes previously shown to be unreactive under heterolytic conditions.[2–4]

Results and Discussion

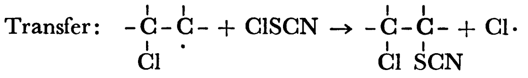
UV irradiation of equimolar amounts of thiocyanogen chloride and *cis*-dichloroethylene under conditions previously shown to lead to homolytic substitution reactions with aralkyl hydrocarbons[5] (acetic acid or carbon tetrachloride solvent, an aerial atmosphere, ambient temperatures) resulted in slow reactions. Faster reactions were achieved, especially in acetic acid, by increasing the intensity of the radiation and, more strikingly, by using a nitrogen atmosphere (see Table 1).

Under these conditions, vinyl bromide, *cis*-dichloroethylene, *trans*-dichloroethylene, 1,1-dichloroethylene, trichloroethylene, and tetrachloroethylene all yielded α-chloro-β-thiocyanato compounds exclusively (see products **1**—**8** in Table 1); unsymmetrical alkenes yielded both regioisomers, with the anti-Markownikov isomer predominating in each case (see products **2**—**7** in Table 1). Reaction times and yields are recorded in Table 1. Neither tetraphenylethylene nor *trans*-1,2-dithiocyanatoethylene added thiocyanogen chloride, but, in the latter case, the recovered alkene consisted of the equilibrium mixture of *cis*- and *trans*-isomers. No telomers or crossed products, *i. e.* dichlorides or dithiocyanates, were observed.

$$\text{Initiation: ClSCN} \xrightarrow{h\nu} \text{Cl}\cdot + \cdot\text{SCN} \qquad (1)$$



$$\text{Addition: Cl}\cdot + \rangle\text{C=C}\langle \rightleftharpoons -\underset{\text{Cl}}{\overset{|}{\text{C}}}-\overset{|}{\text{C}}^{\cdot}- \qquad (2)$$



$$\text{Transfer: } -\underset{\text{Cl}}{\overset{|}{\text{C}}}-\overset{|}{\text{C}}^{\cdot}- + \text{ClSCN} \rightarrow -\underset{\text{Cl}}{\overset{|}{\text{C}}}-\underset{\text{SCN}}{\overset{|}{\text{C}}}- + \text{Cl}\cdot \qquad (3)$$

Photochemical induction of the reaction and its inhibition by aerial oxygen point towards a radical chain reaction, albeit of low chain length as indicated by the effect of the radiation intensity and the relatively long reaction times. The chemical results are consistent with the chain reaction shown in Eqs. 1—3 in which a chlorine atom, formed photochemically from thiocyanogen chloride[5] (Eq. 1), is the adding and chain-carrying species. Reversible addition of the chlorine atom to the alkene (Eq. 2), well-established in radical additions of molecular chlorine,[6] accounts for the observed isomerisation of *trans*-dithiocyanatoethylene. The transfer step (Eq. 3) involves S_H2 displacement on the electron-deficient sulfur atom of thiocyanogen chloride by the donor[7] chloroalkyl radical and the generation of a chlorine atom to carry on the chain; this accounts for (a) the exclusive formation of chlorothiocyanato compounds rather than the corresponding, thermodynamically more stable, chloroisothiocyanato compounds, (b) the preferential anti-Markownikov orientation of addition to unsymmetrical alkenes (*via* the more stable of the two possible chloroalkyl radicals), and (c) the lower rates of reaction as the donor characteristics of the chloroalkyl radical are reduced by the electronic and steric effects of further halo, thiocyanato and phenyl substituents.[7]

In contrast, homolytic additions of all other RSCl compounds examined so far have involved either exclusive displacement on the chlorine atom with RS· radicals as the adding/chain-carrying agent (*e. g.* Cl_3CSCl,[8] $\text{Cl}_3\text{CSO}_2\text{Cl}$,[9] F_5SCl[10]), or concurrent displacements on the chlorine and sulfur atoms with RS· and Cl· radicals respectively as competing adding/chain-carrying agents (*e.g.* F_3CSCl[11]). These differences, also noted in the homolytic substitution reactions of these compounds,[12] are consistent with the steric barrier to displacement at the sulfur atom increasing in the order $\text{NCSCl} < \text{F}_3\text{CSCl} < \text{Cl}_3\text{CSCl}$, $\text{Cl}_3\text{CSO}_2\text{Cl}$, F_5SCl.

Experimental

Alkenes. The haloalkenes and tetraphenylethylene were commercial samples purified until their physical constants agreed with those recorded in the literature. *trans*-1,2-Dithiocyanatoethylene was prepared as described.[13]

General Procedure. Reactions were carried out on an ≈0.4 M scale using the procedure described earlier[5] and the modifications recorded in the text and Table 1. Irradiation was continued until iodometric titrations showed at least 70% consumption of thiocyanogen chloride. Products were isolated as described.[5]

Identification of the Products. Adducts of the haloalkenes were identified as before by IR and NMR spectroscopy;[2–4] regioisomers were not separated, but isomer

TABLE 1. PHOTO-CHLOROTHIOCYANATION OF HALOALKENES

Alkene	Conditions[a)]			Time (h)	Product(s)	Yield (%)
	Solvent	Distance[b)]	Atmosphere			
cis-$CHCl{=}CHCl$	CCl_4	10	air	1	$CHCl_2CH(SCN)Cl$ (**1**)	5
	CCl_4	10	N_2	1	**1**	14
	CCl_4	1	N_2	1	**1**	30
	AcOH	10	air	1	**1**	7
	AcOH	10	N_2	1	**1**	17
	AcOH	1	N_2	1	**1**	60
trans-$CHCl{=}CHCl$	AcOH	1	N_2	1	**1**	58
$CH_2{=}CHBr$	AcOH	1	N_2	1	$CH_2ClCH(SCN)Br$ (**2**)	61
					$CH_2(SCN)CHClBr$ (**3**)	9
$CH_2{=}CCl_2$	AcOH	1	N_2	2.5	$CH_2ClC(SCN)Cl_2$ (**4**)	55
					$CH_2(SCN)CCl_3$ (**5**)	4
$CHCl{=}CCl_2$	AcOH	1	N_2	12	$CHCl_2C(SCN)Cl_2$ (**6**)	52
					$CHCl(SCN)CCl_3$ (**7**)	6
$CCl_2{=}CCl_2$	AcOH	1	N_2	12	$CCl_3C(SCN)Cl_2$ (**8**)	11

a) During the reactions, the temperature rose from 20 to *ca.* 40 °C. b) Distance (in cm) between UV light source and side of reaction flask.

TABLE 2. CHARACTERISATION DATA FOR α-CHLORO-β-THIOCYANATO COMPOUNDS

Product	^{1}H-NMR Spectrum[a)]	IR Spectrum (νSCN) (cm^{-1})	Bp (°C/Torr)	Formula	Analysis (%)					
					Calcd			Found		
					C	H	N	C	H	N
1	3.88, d, 3.5, $C\underline{H}Cl_2$; 4.23, d, 3.5, $C\underline{H}(SCN)Cl$	2165	115—117/15	$C_3H_2Cl_3NS$	18.9	1.05	7.35	18.65	1.1	7.15
2	4.71, t, 7, $C\underline{H}(SCN)Br$; 5.86, d, 7, $C\underline{H}_2Cl$	2164	50—53/0.1	$C_3H_3BrClNS$	17.95	1.5	7.0	17.95	1.35	6.75
3	4.60, t, 7, $C\underline{H}ClBr$; 6.21, d, 7, $C\underline{H}_2SCN$	2164								
4	5.61, s, —, $C\underline{H}_2Cl$	2165	60—63/0.2	$C_3H_2Cl_3NS$	18.9	1.05	7.35	19.0	1.0	7.0
5	5.90, s, —, $C\underline{H}_2SCN$	2165								
6	3.75, s, —, $C\underline{H}Cl_2$	2165	68—70/0.1	C_3HCl_4NS	16.0	0.45	6.25	16.3	0.6	6.55
7	3.85, s, —, $C\underline{H}Cl(SCN)$	2165								
8	—	2164	61—63/0.05	C_3Cl_5NS	13.9	0.0	5.4	14.0	0.1	5.35

a) τ(ppm in CCl_4), multiplicity (s=singlet, d=doublet, t=triplet), J(Hz), assignment.

ratios were determined from the integral traces of appropriate signals in the NMR spectra of the crude mixtures. Characterisation data are recorded in Table 2.

trans-1,2-Dithiocyanatoethylene was recovered quantitatively as the 80 : 20 equilibrium mixture[13)] of *trans*- and *cis*-isomers respectively as shown by IR and NMR spectroscopy. Tetraphenylethylene was recovered quantitatively and identified by its IR spectrum.

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