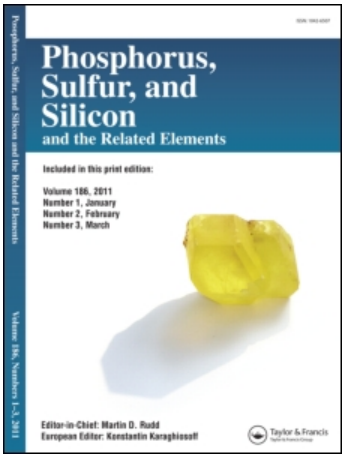

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PSEUDOHALOGEN CHEMISTRY—X STERIC EFFECTS IN THE HOMOLYTIC ADDITION OF THIOCYANOGEN TO ALKENES

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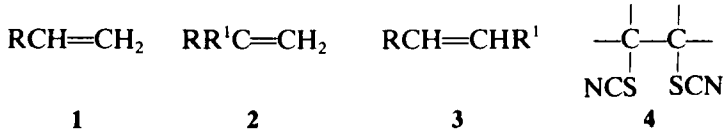
Homolytic addition of thiocyanogen to alkenes with at least three methyl groups or two phenyl groups on the double bond gives vicinal dithiocyanates and/or thiocyanato-isothiocyanates. The addition to (E)- and (Z)- PhCH=CHPh is non-stereospecific, but the thiocyanato-isothiocyanates derived from unsymmetrical alkenes are formed regiospecifically with the isothiocyanato group being attached to the more heavily substituted C atom. A radical-chain mechanism, involving competing kinetically-controlled chain transfer at the S atom and sterically-controlled chain transfer at the N atom of the thiocyanogen molecule, is proposed.

Key words: Steric effects; homolytic addition; thiocyanogen; alkenes

INTRODUCTION

In Part VI[1] we reported that homolytic addition of thiocyanogen, $(SCN)_2$, to the series of alkenes **1** (R = Me, Ph), **2** ($R = R^1 = Me$; R = Me, R^1 = Ph) and **3** ($R = R^1 = Me$; R = Me, R^1 = Ph) occurred rapidly by a radical chain mechanism and gave the corresponding vicinal dithiocyanates **4** exclusively in 71–99% yield. As part of our investigation of the scope of this reaction we have examined the effect of further methyl and phenyl groups on the alkene double bond, and have found significant differences in reaction rates, yields and products.



1 **2** **3** **4**

RESULTS AND DISCUSSION

UV irradiation of equimolar amounts of thiocyanogen and the alkenes **5–10** in benzene under nitrogen at 20–25°C led to the reaction times, products **11–21**, and yields recorded in Table I; no reaction occurred with the alkene $Ph_2C{=}CPh_2$ over a period of 3 hours.

The most striking features of these photo-thiocyanations are (a) the increase in reaction time and decrease in yield as the degree of substitution on the alkene increases, (b) the significant or even exclusive formation of the vicinal thio-

TABLE I

Thiocyanation of alkenes in benzene under nitrogen at 20–25°C

Alkene		Time (min)	Products		Yield (%) Photolytic method	Yield (%) Heterolytic method
$Me_2C{=}CHMe$	(5)	10	$Me_2C(SCN)CH(SCN)Me$	(11)	79	11
			$Me_2C(NCS)CH(SCN)Me$	(12)	13	7
$Me_2C{=}CMe_2$	(6)	11	$Me_2C(SCN)C(SCN)Me_2$	(13)	18	15
			$Me_2C(NCS)C(SCN)Me_2$	(14)	78	31
(E)-PhCH=CHPh	(7)	125	*meso*-PhCH(SCN)CH(SCN)Ph	(15)	70	0
			(±)-PhCH(SCN)CH(SCN)Ph	(16)	3	0
			erythro-PhCH(NCS)CH(SCN)Ph	(17)	14	0
			threo-PhCH(NCS)CH(SCN)Ph	(18)	4	0
(Z)-PhCH=CHPh	(8)	120	(15)		71	0
			(16)		3	0
			(17)		12	0
			(18)		4	0
$Ph_2C{=}CH_2$	(9)	150	$Ph_2C{=}CHSCN$[a]	(19)	3	15
			$Ph_2C(NCS)CH_2SCN$	(20)	54	31
$Ph_2C{=}CHPh$	(10)	180	$Ph_2C(NCS)CH(SCN)Ph$	(21)	11	0

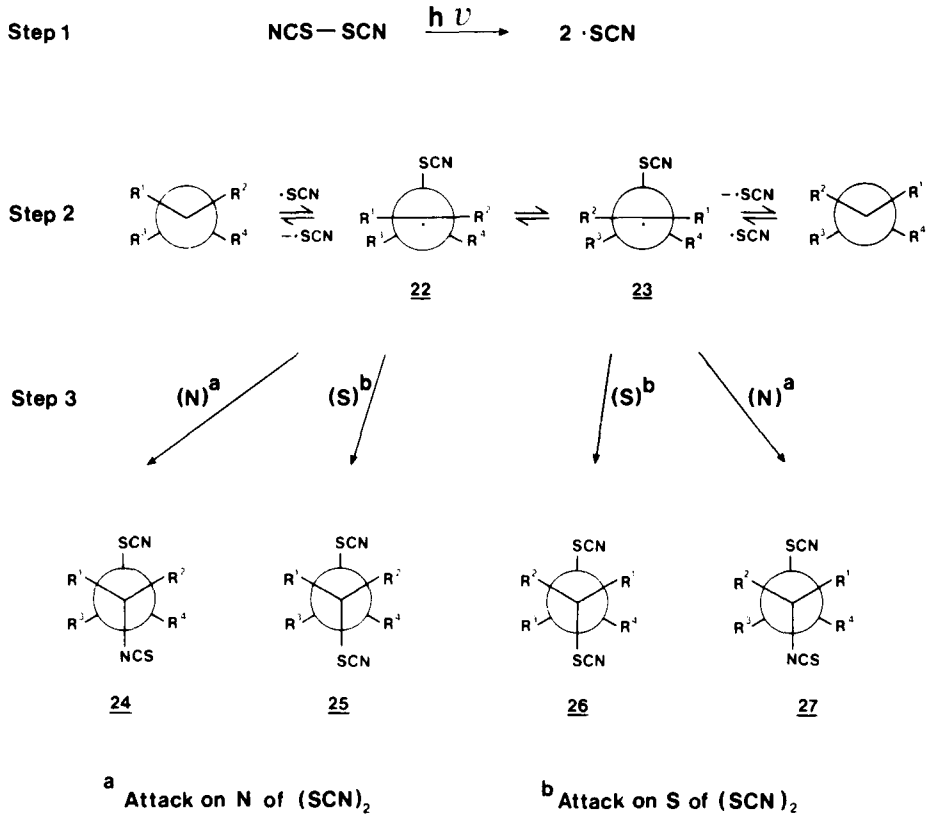
[a] Formed from $Ph_2C(SCN)CH_2SCN$ during chromatographic separation (see Experimental).

cyanato-isothiocyanates **12**, **14**, **17**, **18**, **20** and **21**, (c) the regiospecific formation of the thiocyanato-isothiocyanates **12**, **20** and **21**, with the isothiocyanato group being attached to the more heavily substituted C atom, and (d) the non-stereospecific formation of virtually identical mixtures of adducts **15–18** by (E)- and (Z)-stilbene, with the *meso*-isomer predominating.

Control experiments under heterolytic conditions showed that concurrent heterolytic addition[2] can account for some, but not all, of the thiocyanato-isothiocyanate formation (and not in the observed photothiocyanation ratios) in the cases of alkenes **5**, **6**, and **9**, and for none of it in the cases of alkenes **7**, **8** and **10** (see Table I). Control experiments also showed that the vicinal dithiocyanates were not isomerised to the corresponding thiocyanato-isothiocyanates under the reaction or work-up conditions; (Z)-PhCH=CHPh, however, was rapidly isomerised to (E)-PhCH=CHPh under the reaction conditions.

These results may be rationalised by two competing radical-chain mechanisms which differ only in the regioselectivity of the intermediate thiocyanatoalkyl radical in the chain-transfer step (Scheme 1).

Formation of the di-thiocyanato products **25** and **26** involves (a) photolytic formation of the thiocyanato radical (step 1), (b) kinetically-controlled attack by the S atom of the thiocyanato radical on the less substituted C atom of the alkene double bond giving the rapidly equilibrating thiocyanatoalkyl radicals **22** and **23** (step 2), and (c) a kinetically-controlled S_H2 displacement by the donor radicals **22** and **23** on one of the electron-deficient S atoms of thiocyanogen in the chain transfer step 3(S).[1] As the donor characteristics[3] of radicals **22** and **23** decrease due to increasing steric effects of the various R groups (H < Me < Ph), the alternative chain transfer step 3(N), involving sterically-controlled S_H2 displacement on one of the more readily accessible terminal N atoms of thiocyanogen,



SCHEME 1

becomes correspondingly more important, thus leading to increasing formation of the thiocyanato-isothiocyanates **24** and **27**, but at a decreasing rate.

In unsymmetrical alkenes, e.g., **5**, **9** and **10**, preferential formation[4] of the more stable and less sterically hindered thiocyanatoalkyl radical in step 2 leads to regiospecific transfer of the isothiocyanato group in step 3(N) to the more heavily substituted C atom (cf. the structure of products **12**, **20** and **21**). The thiocyanatoalkyl radicals derived from (E)- and (Z)-PhCH=CHPh undergo conformational equilibration (step 2) faster than they react in the transfer steps 3(S) and 3(N), thus leading to non-stereospecific addition but identical ratios of adducts **24**–**27** from each alkene. Preferential transfer via the preponderant radical (e.g., **22**, $R^1 = R^4 = Ph$; $R^2 = R^3 = H$) leads to the observed predominance of *meso* and *erythro* adducts **24** and **25**. Similar stereochemical behaviour was noted in the corresponding reactions of (E)- and (Z)-MeCH=CHMe.[1]

Steric effects on the position of radical attack on ambident reagents have been noted in several other systems, e.g., substitution reactions of $(SCN)_2$[5] and NCSCl[6] (S *v* N attack), addition and substitution reactions of NCSCl,[7] F_3CSCl,[8] Cl_3CSCl,[9] Cl_3CSO_2Cl[10] and F_5SCl[11] (S *v* Cl attack), and addition reactions of N_2O_4[12] (N *v* O attack).

EXPERIMENTAL

Alkens. These were commercial samples purified until their physical constants agreed with those recorded in the literature.

General Procedures. The homolytic[1] and heterolytic[2] procedures described earlier were employed.

Product Characterisation. Products were identified by (a) comparison of their physical and spectral properties with those of authentic samples prepared previously by other methods,[2,13] or (b) by IR and ^{1}H NMR spectroscopy as described in earlier papers.[1,2,13] IR spectra were recorded on Perkin–Elmer 197, 237 or 337 spectrometers, using films of liquid products and Nujol mulls of solid products. ^{1}H NMR spectra were recorded at 60 MHz in $CDCl_3$ with $SiMe_4$ as internal standard on Perkin–Elmer R12A or Varian A60A spectrometers; in the NMR data given below, s = singlet, d = doublet, m = multiplet. TLC examination of the products was carried out using Kodak–Eastman silica gel with fluorescent indicator, and quantitative separation of the components was achieved by column chromatography using Merck-Kieselgel 60 as adsorbent and light petroleum/diethyl ether mixtures as eluant.

2-Methylbut-2-ene (**5**) gave 2-methyl-2,3-dithiocyanatobutane (**11**) and (b) 2-methyl-2-isothiocyanato-3-thiocyanatobutane (**12**) identical with authentic samples.[2]

2,3-Dimethylbut-2-ene (**6**) gave 2,3-dimethyl-2,3-dithiocyanatobutane (**13**) and (b) 2,3-dimethyl-2-isothiocyanato-3-thiocyanatobutane (**14**) identical with authentic samples.[2]

(E)-Stilbene (**7**) gave (a) the very insoluble *meso*-1,2-diphenyl-1,2-dithiocyanatoethane (**15**) which crystallised from the reaction solution as pale yellow prisms; m.p. 224–225° (lit., [14] 225–226°); ν 2160 (SCN) cm^{-1}; δ 7.32 (10H, s, aromatic H), 5.05 (2H, s, CHSCN) (Found: C, 65.0; H, 4.0; N, 9.15; S, 21.35. Calc. for $C_{16}H_{12}N_2S_2$: C, 64.85; H, 4.1; N, 9.45; S, 21.65%), (b) (±)-1,2-diphenyl-1,2-dithiocyanatoethane (**16**) as colourless prisms; m.p. 158–160° (from MeOH); ν 2160 (SCN) cm^{-1}; δ 7.33 (10H, s, aromatic H), 4.87 (2H, s, CHCSN) (Found: C, 64.95; H, 4.4; N, 9.45; S, 21.5%), and (c) a mixture of *erythro*-1,2-diphenyl-1-isothiocyanato-2-thiocyanatoethane (**17**) [ν 2165 (SCN) and 2060 (NCS) cm^{-1}; δ 7.30 (10H, s, aromatic H), 5.28 (1H, d, J 8 Hz, CHNCS), 4.68 (1H, d, J 8 Hz, CHSCN)] and *threo*-1,2-diphenyl-1-isothiocyanato-2-thiocyanatoethane (**18**) [ν 2165 (SCN) and 2060 (NCS) cm^{-1}; δ 7.30 (10H, s, aromatic H), 5.46 (1H, d, J 6.5 Hz, CHNCS), 4.64 (1H, d, J 6.5 Hz, CHSCN)] as a viscous pale yellow oil (Found: C, 64.1; H, 3.7; N, 9.45; S, 21.65%) from which **17** was obtained as colourless prisms, m.p. 115–117°, by two crystallisations from light petroleum containing a little benzene. The isomer ratio of **17**:**18** was determined from the integral traces of their CHNCS signals.

NMR spectra, and by isolation of the products as described above.

1,1-Diphenylethene (**9**) gave (a) 1,1-diphenyl-1,2-dithiocyanatoethane which was identified by the CH_2SCN singlet at δ 4.20 in the spectrum of the crude product mixture and which, during the chromatographic separation, underwent dehydrothiocyanation to 1,1-diphenyl-2-thiocyanatoethene (**19**) identical with an authentic sample,[13] and (b) 1,1-diphenyl-1-isothiocyanato-2-thiocyanatoethane (**20**) as colourless prisms; m.p. 69–71.5° (from light petroleum); ν 2150 (SCN) and 2060 (NCS) cm^{-1}; δ 7.25 (10H, s, aromatic H), 3.90 (2H, s, CH_2) (Found: C, 64.75; H, 3.95; N, 9.45. Calc. for $C_{16}H_{12}N_2S_2$: C, 64.86; H, 4.05; N, 9.45%). The structure of **20** was confirmed by heating the product with triethylamine in toluene at 100° for 1 hour; this gave **19**, identical with an authentic sample.[13]

Triphenylethene (**10**) gave 1,1,2-triphenyl-1-isothiocyanato-2-thiocyanatoethane (**21**) as colourless prisms; m.p. 125–7°; ν 2150 (SCN) and 2060 (NCS) cm^{-1}; δ 6.75–8.00 (15H, m, aromatic H), 5.65 (1 H, s, CHSCN) (Found: C, 70.95; H, 4.4; N, 7.4. Calc. for $C_{22}H_{16}N_2S_2$: C, 70.95; H, 4.3; N, 7.5%). The structure of **21** was confirmed by heating the product with triethylamine in toluene at 100° for 1 hour; this gave triphenylthiocyanatoethene, identical with an authentic sample.[13]

Control Experiments. A solution of (Z)-stilbene (1.00 g) in benzene (80 ml) was irradiated under nitrogen for 1 hour. Normal work-up procedure[1] gave starting material (1.00 g) as shown by IR and NMR spectroscopy. Under the same conditions, but in the presence of an equimolar amount of thiocyanogen, (Z)-stilbene was isomerised to (E)-stilbene before any addition products could be detected by IR and NMR spectroscopy (3 min).

2,3-Dimethyl-2,3-dithiocyanatobutane (0.50 g) in benzene (100 ml) containing thiocyanogen (2.32 g) was irradiated under nitrogen for 75 min. Normal work-up procedure[1] gave starting material (0.48 g) as shown by IR and NMR spectroscopy. Identical results were obtained when the other dithiocyanates **11**, **15** and **16** were similarly examined.

Heterolytic control experiments were carried out as described in Part IV.[2]

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