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ADDITION OF THIOCYANOGEN TO ALKYNES

R. G. Guy*, S. Cousins, D. M. Farmer, A. D. Henderson and C. L. Wilson

School of Natural Sciences, The Hatfield Polytechnic, P.O. Box 109, Hatfield, Hertfordshire, AL10 9AB, England
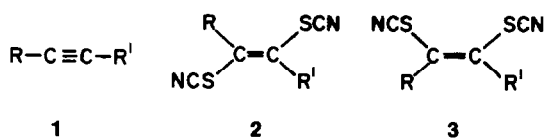
Abstract—Thiocyanogen does not react with simple alkynes under heterolytic conditions in benzene at 20–25°. Under homolytic conditions, addition occurs readily giving mixtures of $E-$ and $Z-$ dithiocyanatoalkenes with high $E:Z$ ratios; prolonged treatment with excess reagent also leads to mixtures of the dithiocyanatoalkenes but usually with lower $E:Z$ ratios. A radical-chain mechanism, involving preferential *anti*-addition of thiocyanogen in an initial kinetically-controlled reaction and subsequent thermodynamically-controlled isomerisation of the adducts, is proposed. The influence of substituents on the reaction rates and product ratios is discussed in terms of their steric effects.

In earlier papers we have shown that thiocyanogen, $(SCN)_2$, behaves as a pseudohalogen towards alkenes.[1,2] Thus, under heterolytic conditions, it acts as a weak electrophile, adding slowly to form α,β-dithiocyanates and the corresponding α-isothiocyanato-β-thiocyanates;[2] under homolytic conditions it reacts rapidly via a radical-chain mechanism involving the thiocyanato radical, and gives α,β-dithiocyanates and/or allylic isothiocyanates.[1]

Several groups of workers[3–8] have reported that thiocyanogen also reacts with alkynes giving 1:1 adducts. However, no systematic study of experimental conditions, product isolation, structure determination, or the mechanism(s) of the reaction was described. Here we describe the reactions of thiocyanogen with some simple alkynes under the controlled heterolytic and homolytic conditions used in our studies of alkenes.[1,2]

$$R-C\equiv C-R^1$$

1   **2**   **3**

a: R = H, R^1 = H
b: R = Bu^n, R^1 = H
c: R = Bu^t, R^1 = H
d: R = Ph, R^1 = H
e: R = Ph, R^1 = Me
f: R = Et, R^1 = Et
g: R = Ph, R^1 = Ph
h: R = SiMe$_3$, R^1 = SiMe$_3$

Under heterolytic conditions (darkness, a nitrogen atmosphere and added radical inhibitor), no reaction occurred between the alkynes 1a–h and thiocyanogen in benzene solution over a period of 48 hr at 20–25°. Alkynes are thus less reactive than the corresponding alkenes towards electrophilic attack by thiocyanogen;[2] similar results have been observed in the corresponding additions of the halogens,[9] and attributed to differences in (a) the ionisation potentials of the π-electrons of alkenes and alkynes, and (b) the stabilities of the corresponding cationic intermediates.

Under homolytic conditions (UV light and a N$_2$ atmosphere), equimolar amounts of thiocyanogen and

the alkynes 1a–g in benzene reacted readily at 20–25°, and gave mixtures of the corresponding E- and Z-dithiocyanatoalkenes, 2a–g and 3a–g respectively, the structures of which were assigned on the basis of microanalytical, IR, ^{1}H NMR, and X-ray data. Yields were high, with the $E-$ isomer 2 predominating in each case (Table 1). Ethyne, 1a, additionally gave compound 4 in low yield. No addition occurred to the alkyne 1h over a period of 8 hr.
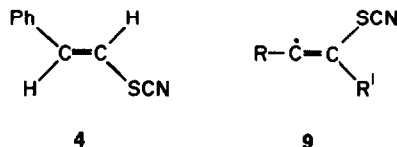
Prolonged irradiation of the alkynes 1a–g with a 1-molar excess of thiocyanogen also produced mixtures of the adducts 2a–g and 3a–g in high yield, but none of the corresponding 1:2 adducts. No change in the $E:Z$ product ratio was observed for alkynes 1f and 1g, but, for each of the alkynes 1a–e, the $E:Z$ ratio decreased with reaction time and reached the equilibrium values shown in Table 1; these values were also obtained on prolonged irradiation of the product mixtures from the 1:1 reactions in the presence of a trace of thiocyanogen. No propargylic or allenic thiocyanate or isothiocyanate was detected in any of the reactions.

4   **9**

These results may be rationalised by two radical-chain mechanisms, derived from that proposed for the corresponding addition of thiocyanogen to alkenes,[1] and differing from each other only in the nature of the intermediate vinyl radical.

For the aliphatic alkynes, the proposed mechanism (Scheme 1) involves (a) attack of the photochemically-generated thiocyanato radical on the alkyne 1 to give rapidly-equilibrating[10,11] thiocyanatovinyl radicals 5 and 6, (b) kinetically-controlled attack[1] by thiocyanogen on 5 and 6, during which the steric and dipolar repulsions between the incoming pseudohalogen and the thiocyanato group lead to preferential *anti*-addition on 5 and formation of the E-dithiocyanate 2, (c) subsequent thermodynamically-controlled isomerisation[1] of the dithiocyanatoalkenes 2 and 3 through reversible addition
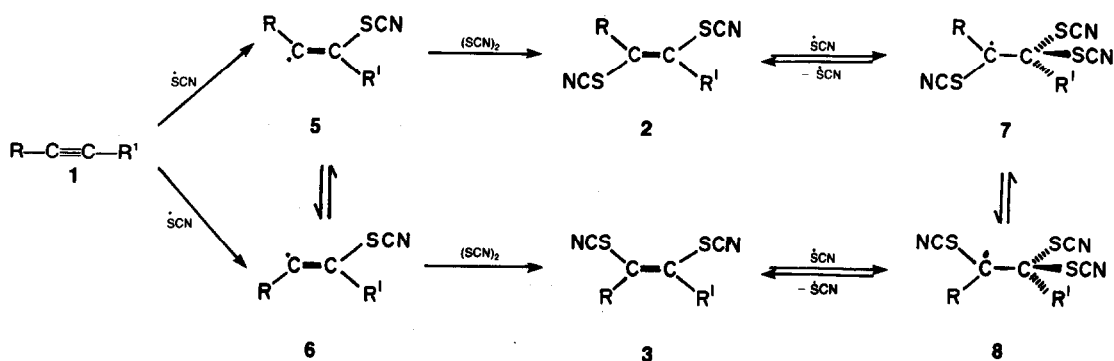
Scheme 1.

of thiocyanato radicals and equilibration of the thiocyanatoalkyl radicals 7 and 8, Formation of the 1:2 adducts is prevented by the steric and electronic effects[1] of the substituents in 7 and 8, and the absence of propargylic and allenic substitution products is consistent with the lower reactivity of propargylic H atoms than allylic ones towards radical halogenation.[12]

For phenyl alkynes, a similar mechanism, but with the linear[11] phenylvinyl radical 9 (R = phenyl) as the intermediate, accounts for the observed results.

In the 1:1 reactions, the observed reaction rates and $E:Z$ ratios (Table 1) may be correlated with the steric effects of R and R^1 on the reactivity of 5 and 6 in the chain-transfer step (b) in Scheme 1. Thus, the least sterically-hindered alkynes 1a, b, d, and e lead to fast addition and consequently little or no isomerisation of the kinetically-controlled product mixture, whereas the sterically-hindered alkynes 1c, f and g lead to slower addition and hence considerable (1c) or complete (1f and

g) isomerisation during the reaction. In the extreme case, alkyne 1h, with two bulky trimethylsilyl groups, does not react at all.

In the 1:2 reactions, the widely different thermodynamically-controlled $E:Z$ ratios (Table 1) may be correlated with the steric effects of R and R^1 on the relative stabilities of the products 2 and 3. Thus, in the series R–C≡C–R^1 (R^1=H), the $E:Z$ ratios fall in the order R=H > Bu^n > Ph > Bu^t due to the increasing tendency of the R group, with its increasing steric requirements,[13] to adopt the Z-configuration 3, in which it is *cis* to the H atom, rather than the E-configuration 2, in which it is *cis* to the bulkier SCN group.[14] In the series R–C≡C–R^1 (R^1=Ph), the $E:Z$ ratios fall in the order R=Ph > Me > H, and in the series R–C≡C–R^1 (R=R^1=H, Et, Ph) the $E:Z$ ratios fall in the order Ph > Et > H; this is consistent with the decreasing tendency of the R and R^1 groups to adopt a *trans* arrangement, and hence the E-configuration 2, as they decrease in size.

Table 1. Photothiocyanation of alkynes in benzene under nitrogen at 20–25°C

| Alkyne (1)		Molar ratio	Time	Products (2 and 3)	
R	R^1	[1 : (SCN)$_2$]	(h)	Yield (%)	$E:Z$ Ratio
				(2 + 3)	(2 : 3)
H	H	1:1	1	90[a]	95:5
		1:2	24	91[b]	80:20
Bu^n	H	1:1	0.4	93	95:5
		1:2	24	95	76:24
Bu^t	H	1:1	1.25	87	60:40
		1:2	24	94	10:90
Ph	H	1:1	0.05	98	94:6
		1:2	24	98	35:65
Ph	Me	1:1	0.1	90	89:11
		1:2	24	92	70:30
Et	Et	1:1	1.5	97	90:10
		1:2	24	98	90:10
Ph	Ph	1:1	1.5	90	94:6
		1:2	24	94	95:5

[a] Additional product: compound 4 (8%).   [b] Additional product: compound 4 (6%).

Table 2. Thiocyanation of phenylethyne in benzene

Reaction Conditions	Time (h)	Products (2d and 3d)	
		Yield (%) (2d + 3d)	E:Z Ratio (2d : 3d)
N$_2$, diffuse daylight, ~20°C	0.25	98	94:6
N$_2$, darkness, ~20°C	168	74	85:15
N$_2$, darkness, 80°C	1	63	86:14
N$_2$, darkness, 0.1% BP[a], 80°C	1	68	83:17
N$_2$, darkness, 0.1% AIBN[b], 80°C	1	78	84:16
air, darkness, ~20°C	0.5	97	95.5

[a] BP = Benzoyl peroxide.   [b] AIBN = Azoisobutyronitrile.

The formation of compound 4 is attributed to competing attack of the very reactive radical 5 (R=R^1=H) on the benzene solvent, and subsequent abstraction of the allylic H atom from 10 by a thiocyanato radical (Scheme 2). Since this is not a chain process, the yield of 4 is low.

10
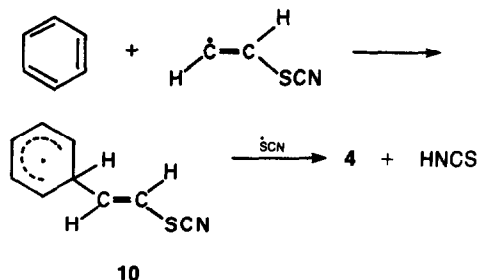
Scheme 2.

Experiments with equimolar amounts of thiocyanogen and phenylethyne (1d) showed that this homolytic reaction could also be initiated under nitrogen (a) by diffuse daylight, and (b) in darkness by heat or radical initiators; atmospheric oxygen at ambient temperatures was also an efficient initiator, in contrast to its inhibiting effect on the corresponding reactions of alkenes.[1] The dithiocyanato products 2d and 3d were formed in E:Z ratios consistent with those observed in the UV-initiated reactions, but yields were sometimes lower due to polymerisation of the reagent as a result of longer reaction times or higher temperatures (Table 2).

These profound effects of initiators and inhibitors may account for earlier conflicting reports on the ease of thiocyanation of alkynes,[3-8] and also suggest that due care should be exercised in the interpretation of published comparative rate data.[5]

The similarity of these results with those obtained for the homolytic addition of chlorine,[15] bromine,[16] and organic disulphides, RSSR,[17] to alkynes emphasizes further the dual pseudohalogen and disulphide nature of thiocyanogen.[18]

EXPERIMENTAL

Alkynes. 3,3-Dimethylbut-1-yne was prepared from 3,3-dimethylbutan-2-one as described.[19] The other alkynes were commercial samples purified where necessary until their physical constants agreed with those recorded in the literature.

General procedures. The heterolytic and homolytic procedures described in Parts IV[2] and VI[1] respectively were followed.

Product characterisation. The dithiocyanato structure of 2a–g and 3a–g was established by elemental analysis and by the sharp SCN absorption band which each showed in its IR spectrum[20] (see below). Configurations were assigned on the basis of (a) the Z-isomers 3 showing more numerous and, particularly for the C=C stretching vibration around 1600 cm^{-1}, more intense IR absorption bands than the corresponding E-isomers 2,[15,21,22] and (b) the ^{1}H NMR and X-ray data described below. In most cases, isomer ratios were determined from the integral traces of appropriate absorption bands in the ^{1}H NMR spectra of the mixtures; in a few cases, they were determined by chromatographic separation or fractional crystallisation of the products (see below).

IR spectra were recorded with Perkin–Elmer 237 and 337 spectrometers, and were taken for films of liquid products and for Nujol mulls of solid products. ^{1}H NMR spectra were recorded at 60 MHz in CDCl$_3$ with Perkin–Elmer R12 and Varian A60A spectrometers using SiMe$_4$ as internal standard. In the NMR data given below, s = singlet, t = triplet, and q = quartet.

Ethyne 1a gave, after column chromatography on silica gel, (a) E-2a as colourless needles; m.p 98°–99° (from benzene) (lit.[4] 97–98.5°); √2170 (SCN) and 915 (*trans* H–C=C–H) cm^{-1}; δ6.53 (s, vinyl H). (Found: S, 44.8. Calc. for C$_4$H$_2$N$_2$S$_2$: S, 45.05%); (b) Z-3a as a pale yellow liquid;[4] √2170 (SCN) and 705 (*cis* H–C=C–H) cm^{-1}; δ6.81 (s, vinyl H). (Found: S, 45.1%); and (c) E-4 identical (IR and NMR spectra) with an authentic sample.[23] As for related alkenes, the E-isomer shows the higher-field vinyl singlet.[24]

Hex-1-yne 1b gave a mixture of E- 2b [√2160 (SCN) cm^{-1}; δ6.53 (s, vinyl H)] and Z- 3b [√2160 (SCN) cm^{-1}; δ6.45 (t, J=1Hz, vinyl H)] as a pale yellow liquid. (Found: C, 48.65; H, 5.2; N, 13.95; S, 32.8. Calc. for C$_8$H$_{10}$N$_2$S$_2$: C, 48.45; H, 5.1; N, 14.15; S, 32.35%). As for related alkenes, the Z-isomer shows the larger allylic coupling.[17,22]

3,3-Dimethylbut-1-yne 1c gave a mixture of E-2c [√2160 (SCN) cm^{-1}; δ6.74 (s, vinyl H) and 1.32 (s, Bu^t)] and Z-3c [√2160 (SCN) cm^{-1}; δ6.89 (s, vinyl H) and 1.25 (s, Bu^t) as a pale yellow liquid, b.p. 161–162°/31 mm Hg. (Found: C, 48.45; H, 5.1; N, 13.7; S, 32.8. Calc. for C$_8$H$_{10}$N$_2$S$_2$: C, 48.45; H, 5.1; N, 14.15; S, 32.35%). As for related alkenes, the E-isomer shows the lower-field t-Bu singlet.[15]

Phenylethyne 1d gave a mixture of E-2d [√2160 (SCN) cm^{-1}; δ6.80 (s, vinyl H)] and Z-3d [√2160 (SCN) cm^{-1}; δ6.92 (s, vinyl H)] as an oily solid. (Found: C, 55.0; H, 2.75; N, 12.85; S, 29.4%). Recrystallisation from EtOH gave 2d as colourless needles, m.p. 68–69° (lit.[4] 67–68°). As for related alkenes, the E-isomer shows the higher-field vinyl singlet.[16,22,25]

1-Phenylprop-1-yne **1e** gave a mixture of *E*-**2e** [$\sqrt{}$2170 (SCN) cm^{-1}; δ2.53 (s, Me)] and *Z*-**3e** [$\sqrt{}$2170 (SCN) cm^{-1}; δ2.21 (s, Me)] as a pale yellow liquid, b.p. 140°/0.01 mm Hg. (Found: C, 57.4; H, 3.35; N, 12.2. Calc. for $C_{11}H_8N_2S_2$: C, 56.9; H, 3.45; N, 12.05%). As for related alkenes, the *E*-isomer shows the lower-field Me singlet.[16, 22, 25]

Hex-3-yne **1f** gave a mixture *E*-**2f** [$\sqrt{}$2155 (SCN) cm^{-1}; δ2.74; (q, *J* = 7.5 Hz, CH$_2$) and 1.25 (t, *J* = 7.5 Hz, CH$_3$)] and *Z* − **3f** [$\sqrt{}$2155 (SCN) cm^{-1}; δ2.69 (q, *J*=7.5 Hz, CH$_2$) and 1.25 (t, *J*=7.5 Hz, CH$_3$) as an oily solid. (Found: C, 48.65; H, 5.25; N, 14.1; S, 32.1. Calc. for $C_8H_{10}N_2S_2$: C, 48.45; H, 5.1; N, 14.15; S, 32.5%). As for related alkenes, the *E*-isomer shows the lower-field methylene quartet.[22]

Diphenylethyne **1g** gave, after fractional crystallisation of the crude product from benzene and light petroleum (b.p. 60–80°), *E* − **2g** as colourless plates; m.p. 197–199° (lit.[4] 194–195°), $\sqrt{}$2140 (SCN) cm^{-1}. (Found: C, 65.6; H, 3.9; N, 9.65; S, 21.85. Calc. for $C_{16}H_{10}N_2S_2$: C, 65.3; H, 3.4; N, 9.5; S, 21.8%) and *Z* − **3g** as colourless needles; m.p. 122–123° (lit.[4] 123–124°); $\sqrt{}$2140 (SCN) cm^{-1}. (Found: C, 65.2; H, 3.4; N, 9.5; S, 21.8%). As for related alkenes, the *E*-isomer has the higher m.p. and the much lower solubility in organic solvents;[26] it also shows a centre of symmetry (see below).

X-Ray measurements on compound **2g** (by P. Carr and M. E. Foulkes). Single crystal oscillation and Weissenberg photographs using CuK$_\alpha$ radiation showed the system to be monoclinic, with $a = 6.03(2)$Å, $b = 6.88(2)$Å, $c = 18.08(3)$Å, $\beta = 107.0(5)°$ The spacegroup is $P2_1/c$ from the systematic absences $h0l$ when $l \neq 2n$ and $0k0$ when $k \neq 2n$. The density as measured by flotation is 1.29g cm^{-3}, corresponding to 2 molecules per unit cell.

Since the space-group $P2_1/c$ requires four asymmetric units per cell, each molecule must be centrosymmetric and thus have the *E* configuration.

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