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ALLENES—41[1]

THE ADDITION OF THIOLS TO ALLENYL- AND PHENYLPROPYNYL-NITRILE AND THE FORMATION OF THIAZOLINES AND BENZOTHIAZOLES

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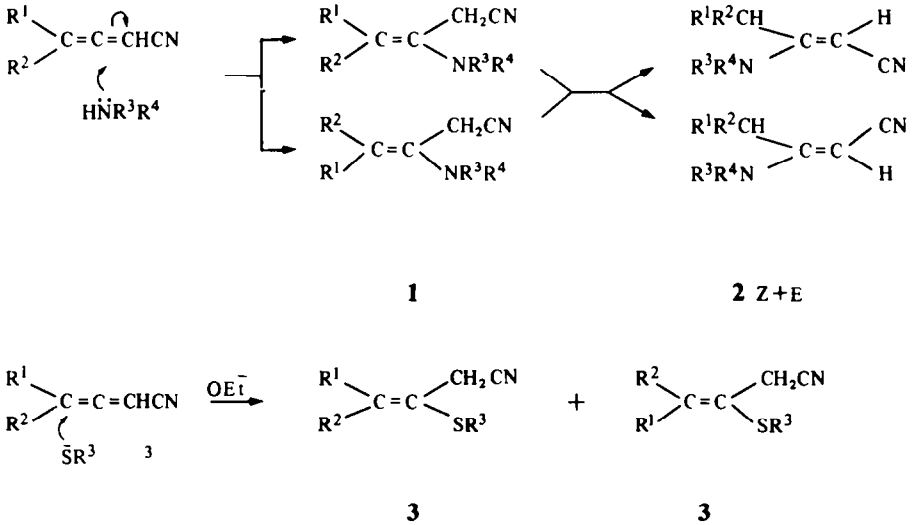
Abstract—Thiols add to allenylnitriles to give unconjugated nitriles which may be isomerised to conjugated enesulphide nitriles either at high temperature (200°) or with base. Phenylpropynenitrile gives conjugated adducts directly. Heating the conjugated adducts from aminoethanethiols at > 200° results in 5-exotrig ring closure and elimination of acetonitrile to give thiazolines and benzothiazoles.

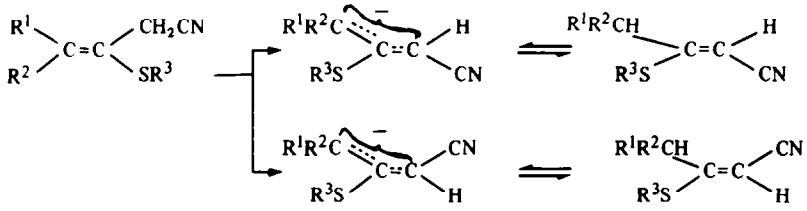
We have recently reported[2] that primary and secondary amines add to allenylnitriles and phenylpropynenitrile spontaneously and exothermically to give first unconjugated and then conjugated enaminenitrile adducts **1** and **2**. Conversion of **1** into **2** is usually fast at moderate temperatures and goes to completion (> 99%). Under the same conditions the weakly nucleophilic thiols RSH do not react either at room temperature or even at elevated temperature or under reflux, when in the event many allenylnitriles dimerise to dimethylenecyclobutanes.[3] However, in the presence of catalytic amounts of base in refluxing dichloromethane, thiols add to allenyl nitriles in 5–10 min, the sulphide anion now generated being a strong nucleophile. The products are exclusively unconjugated adducts, the 3-(alkylthio)- 3-enenitriles **3**. A mixture of *E* and *Z* isomers is obtained where R^1 and R^2 are different substituents.

No conjugated adducts [the 3-(alkylthio)-2-enenitriles] were detected at this stage. Only on heating **3** for 72 h at 200° are equilibrium mixtures of approximately 90% conjugated and 10% unconjugated enesulphide nitriles obtained. However, on heating the unconjugated adduct **3** in ethanol with base (sodium ethoxide, 0.33 molar equivalent) it rearranges fast to the E and Z forms of the conjugated adduct **4** and the equilibrium mixture (90:10) is obtained in 1 hr. Under the same basic conditions the reaction of allenyl nitriles with thiols gave 90% conjugated *E* and *Z* 3(alkylthio)-2-enentriles **4**. 3-Phenylpropynenitrile gave *E* and *Z* isomers of the conjugated 3-phenyl-3-alkylthioprop-2-enenitriles (4, $R^1R^2CH = Ph$) under similar conditions.

If a second nucleophile is present such as the amino-group in 2-aminoethanethiol, the conjugated adduct **5** in refluxing ethanol undergoes 5-exotrig ring



Scheme 1.



4

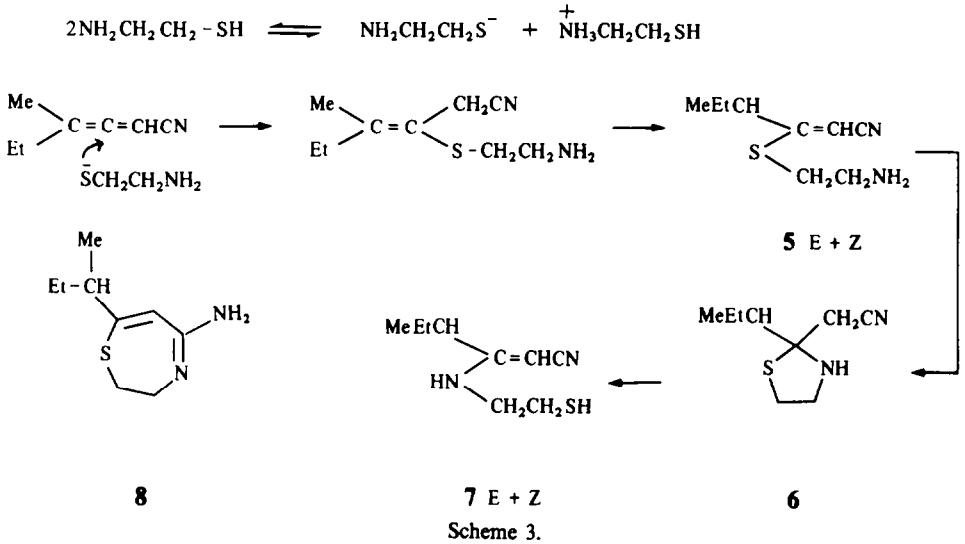
Scheme 2.

closure[4] by a second Michael addition to give the unstable thiazolidine **6** but opens again by C-S fission to give mainly the N-adduct **7**.

We have no evidence that the alternative 7-exodig attack at the carbon of the nitrile ever takes place and no thiazepine **8** was isolated or detected. It is not necessary to use a base (such as ethoxide) with aminothiols as sufficient sulphide anion is present at equilibrium for addition to take place and subsequent rearrangement to the conjugated S-adduct **5**.

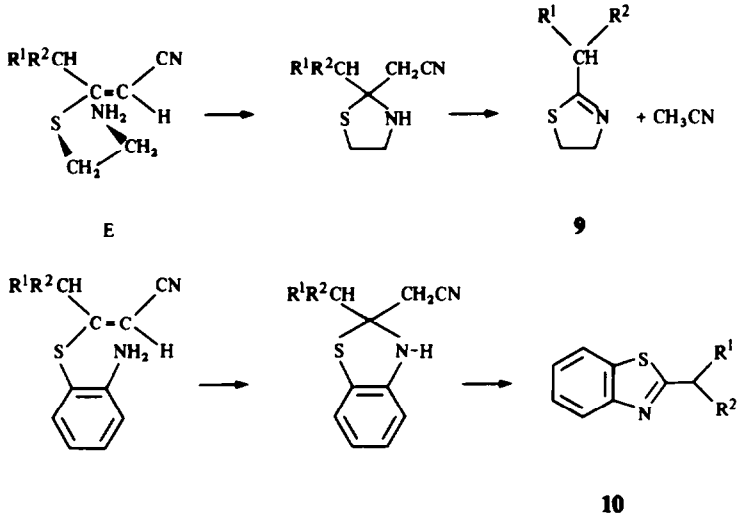
If the conjugated adducts are heated at temperatures above 200° the thiazolidines **6**, which are first formed, eliminate acetonitrile and thiazolines **9** are isolated in about 70% yield. 2-Aminothiophenol similarly gives benzothiazoles **10** in about 80% yield. The anion of acetonitrile is a good leaving group and the elimination goes smoothly and in consistent yield.[5]

Both *E* and *Z* forms can undergo 5 exotrig ring closure to give the same thiazolidine although the *E*



8 **7** E + Z **6**

Scheme 3.



E **9**

10

Scheme 4.

form, which offers slightly less steric hindrance to the attack of the nucleophile in the Michael position, would be expected to react faster. However, at 250° the two isomers are likely to be in equilibrium which is continuously displaced by 5-exotrig ring closure of the *E* form and thiazoline formation. Hence 70–80% of heterocycles are formed.

EXPERIMENTAL

IR spectra were determined with Perkin–Elmer 257 and 337 spectrophotometers. UV spectra were obtained for ethanolic solutions with a Pye-Unicam 1800, Perkin–Elmer 137 and Beckman 25 spectrophotometers. NMR spectra were determined with a Varian T60 and Perkin–Elmer R12A spectrophotometers for solutions in deuteriochloroform, with tetramethyl silane as internal standard. The allenic nitriles were prepared as previously described.[2]

3-(*Ethylthio*)-4-*methylhex*-3-*enenitrile*. 4-Methylhexa-2, 3-dienenitrile (3.2g, 0.03 mol) in dichloromethane (20 ml) was added dropwise with shaking to a mixture of ethanethiol (2.3 g, 0.03 mol) and freshly prepared sodium ethoxide (0.1 g) in dichloromethane (50 ml). The reaction mixture was refluxed for 10 min, excess sodium ethoxide filtered off and the solvent removed to give the crude product in quantitative yield. Distillation gave 3(ethylthio)-4-methylhex-3-enenitrile (5.5 g, 95%), b.p. 120–121° at 4 mm Hg. Data for this compound (1) and four other enesulphide nitriles (**2–5**) which were prepared similarly are given in Tables 1 and 2.

3-(2-*Aminophenylthio*)-4-*methylhex*-3-*enenitrile*. (a) 2-Aminothiophenol (6.25 g, 0.05 mol) was added slowly to 4-methly-hexa-2, 3-dienenitrile (5.35 g, 0.05 mol) at room temperature. No exothermic reaction was observed. The reaction was monitored by IR spectroscopy and found to be complete after 36 h as shown by the disappearance of the allenic band (1950 cm^{-1}) and the S-H band (2530 cm^{-1}). Purification by column chromotography gave 3-(2-aminophenylthio)-4-methyl-hex-3-enenitrile (11.1 g, 96%). Data for this compound **7** and one other compound which was prepared similarly **6** are given in Tables 1 and 2. (b) 2-Aminothiophenol (3.13 g, 0.025 mol), sodium ethoxide (0.1 g) and 4-methylhexa-2, 3-dienenitrile (2.68 g, 0.025 mol) in dichloromethane (50 ml) were refluxed for 15 min. Working up gave 3-(2-aminophenyl-thio-4-methylhex-3-enenitrile (5.4 g, 93%).

3-*Propylthio*)-4-*methylhex*-2-*enenitrile*. (a) 3-(propylthio)-4-methylhex-3-enenitrile (1.81 g, 0.01 mol) was heated at 200°, the reaction being monitored by NMR. After 72 h, the product was isolated and shown to be 90% 3-(propylthio)-4-methylhex-2-enenitrile. Attempts to separate the two isomers by column chromatography were unsuccessful.

(b) 3-(Propylthio)-4-methylhex-3-enenitrile (3.62 g, 0.02 mol) and sodium ethoxide (0.5 g) were dissolved in ethanol (100 ml) and refluxed for 1 hr, the ethanol was distilled off, the residue dissolved in ether and washed with water and evaporated to give 3-(propylthio)-4-methylhex-2-enenitrile in quantitative yield (see compound **1**, tables 3 and 4). The crude material contains 5–10% of 3-(propylthio)-4-methylhex-3-enenitrile.

(c) 4-Methylhexa-2,3-dienenitrile (5.35 g, 0.05 mol), propyl-thiol (3.8 g, 0.05 mol) and sodium ethoxide (0.5 g) were dissolved in ethanol (100 ml) and refluxed for 1 h. Working up and fractional distillation gave 3-(propylthio)-4-methylhex-2-enenitrile (8.5 g, 93%). Data for this compound **1** and eight other 2-enenitriles are summarised in Tables 3 and 4.

3-(2-*Aminophenylthio*)-4-*methylhex*-2-*enenitrile*. Freshly redistilled 4-methylhexa-2, 3-dienenitrile (3.21 g, 0.03 mol), 2-aminothiophenol (3.75 g, 0.03 mol) and sodium ethoxide

Table 1. Synthesis of 1-cyanomethylvinyl sulphides

$$R^1\text{-}C=C\text{-}CH_2CN$$
$$\quad\;|\quad\;|$$
$$\quad R^2 \; SR^3$$

	NITRILE R^1	R^2	THIOL R^3	b.p.mmHg	Yield (%)	U.V. λ_{max} (nm)	ε	I.R. C≡N	C=C	FOUND C	H	N	REQUIRED C	H	N
1.	Me	Et	Et	120–121/4.0	95	206	8,900	253	3,500	2 240	1615	63.8	8.8	8.1	64.0	8.9	8.3
2.	Me	Et	Pr^i	100–102/2.0	90	208	6,400	251	3,000	2 240	1620	65.5	9.2	7.6	65.6	9.5	7.7
3.	Me	Et	Ph	123–124/0.5	91	206	9,900	246	5,800	2 250	1630	71.1	7.1	6.4	71.9	6.9	6.5
4.	Et	Et	Et	102–104/1.0	92	208	7,100	255	3,100	2 240	1615	64.4	9.3	7.5	65.6	9.5	7.7
5.	Et	Et	Bu^n	108–109/1.0	94	208	8,300	255	3,600	2 240	1620	68.5	10.2	6.8	68.2	10.0	6.6
6.	Me	Me	$PhNH_2$		95[1]	206	25,800	240[2]	11,900	2 240	1580[3]	66.3	6.3	12.6	66.1	6.4	12.8
7.	Me	Et	$PhNH_2$		94[1]	206	26,300	240[2]	10,500	2 240	1580[3]	67.1	6.8	12.3	67.2	6.9	12.1

1) Purified by column chromatography 2) Also λmax 265nm (ε 23 700) 3) Also νmax 3450, 3350 (NH_2)

Table 2. NMR data of

$$R^1\text{-}C(R^2S\text{-}R^3)=C\text{-}CH_2CN$$

	Nitrile R^1	R^2	Thiol R^3	
1.	Me	Et	Et	8.90(3H,t, $C\underline{H}_3$ CH_2CCH_3), 8.83(3H,t, $SCH_2C\underline{H}_3$), 8.07(3H,d,$CH_3CH_2CC\underline{H}_3$), 7.53(4H,m,$CH_3C\underline{H}_2$ and $CH_3C\underline{H}_2$,s, 6.58(2H,s,-$C\underline{H}_2CN$).
2.	Me	Et	Pr^i	8.95(9H,m, $C\underline{H}_3CH_2CCH_3$,$(C\underline{H}_3)_2CHS$), 8.03(3H,d, $CH_3CH_2CC\underline{H}_3$), 7.22(3H,m, $CH_3C\underline{H}_2CCH_3$, $(CH_3)_2CHS$, 6.55(2H,s,-$C\underline{H}_2CN$).
3.	Me	Et	Ph	8.92(3H,t, $C\underline{H}_2CH_2CCH_3$), 7.98(3H,d,$CH_3CH_2CC\underline{H}_3$), 7.87-7.30(2H,m,$CH_3C\underline{H}_2CCH_3$) 6.73(2H,s, $C\underline{H}_2CN$), 2.68 (5H,m, aromatic).
4.	Et	Et	Et	8.83(9H,m,(9H,m, $(CH_3CH_2)_2$ $C\underline{H}_3CH_2S$) 7.52(2H,q, $(CH_3C\underline{H}_2)_2C$) 6.57(2H,s, $C\underline{H}_2CN$).
6.	Me	Me	$PhNH_2$	8.60(6H,s, $(C\underline{H}_3)_2C$=) 7.06(2H,s,$C\underline{H}_2CN$), 5.82(2H,s, $N\underline{H}_2$, disappears on deuteration), 3.75-3.35(2H,m, aromatic), 3.15-2.60(2H,m, aromatic).
7.	Me	Et	$PhNH_2$	9.00(3H,t, $C\underline{H}_3CH_2CCH_3$), 8.18(1H,s, $C\underline{H}_3C$=, (E)), 7.96(2H,s,$C\underline{H}_3C$=, (Z)) 7.95-7.72(1.33H,q, $CH_3C\underline{H}_2$, (E), 7.63-7.40(0.67H,q, $CH_3C\underline{H}_2$, (Z)), 6.96(2H,s, $C\underline{H}_2CN$), 5.86(2H,s, $N\underline{H}_2$, disappears on deuteration), 7.50-7.16(2H,m, aromatic), 2.90-2.56 (2H,m, aromatic).

Table 3. Synthesis of 2-cyanovinyl sulphides

R^1-CH(-R^2)-C(-SR^3)=CHCN

NITRILE R^1R^2	THIOL R^3	b.p. 760mmHg	Yield (%)	λmax(nm)[1]	ε	λmax(nm)[1]	ε	C≡N	C=C	FOUND C	FOUND H	FOUND N	REQUIRED C	REQUIRED H	REQUIRED N
8 Me Et	Pr^n	260-262	93	210	6 000	285	18 000	2 205	1 575	63.9	8.7	8.0	64.0	8.9	8.3
9 Me Et	C_3H_5[2]		99[3]	208	6 500	285	19 000	2 210	1 575[4]	66.4	8.0	7.5	66.3	8.3	7.7
10 Et Et	Pr^n	271-272	94	210	6 800	285	19 000	2 215	1 585	67.3	9.5	7.1	67.0	9.7	7.1
11 Et Et	Bu^n	280-181	93	209	6 700	286	20 200	2 210	1 580	68.4	9.9	6.7	68.2	10.0	6.6
12 Bu H	Pr^i	264-265	87	208	6 800	272	20 100	2 220	1 585	65.8	8.8	7.6	65.6	9.3	7.7
13 Ph	Pr^i	244-246	90	208	18 800	264	13 400	2 215	1 575	71.3	5.9	6.9	70.9	6.4	6.9
14 Ph	Et	243-245	90	207	18 700	260	14 200	2 190	1 555	70.2	6.1	7.0	69.8	5.8	7.4
15 Ph	Pr^n	246-248	91	207	18 200	260	13 200	2 190	1 555	71.0	6.5	6.8	70.9	6.4	6.9
16 Ph	Bu^n	276-277	90	207	18 500	259	12 600	2 190	1 555	71.8	6.9	6.3	71.9	6.9	6.5
17 Ph	$PhNH_2$	Oil[5]	90	208	28 000	240	13 300[6]	2 215[7]	1 625	71.2	4.9	11.0	71.4	4.8	11.1
18 Me Me	$PhNH_2$	86[8]	93	206	23 900	249	11 200[9]	2 210[10]	1 605	65.9	6.2	12.6	66.1	6.4	12.8
19 Me Et	$PhNH_2$	90[8]	94	207	24 800	250	12 600[11]	2 210[10]	1 610	67.0	6.6	12.0	67.2	6.9	12.1
20 Et Et	$PhNH_2$	98[8]	92	207	25 100	250	13 000[12]	2 210[10]	1 610	68.1	7.4	11.3	68.3	7.3	11.4

1) Ethanolic solutions 2) $CH_2CH=CH_2$ 3) Crude yield 4) Also peak at 1610 cm^{-1} ($CH=CH_2$) 5) Purified by column chromatography 6) Also λmax 290 nm (ε 10 000) 7) Also νmax 3460, 3350cm^{-1} (NH_2) 8) Melting point of recrystallized product. 9) Also λmax 270nm (ε 9 800) 10) Also νmax 3460, 3360cm^{-1} (NH_2) 11) Also λmax 270 nm (ε 10 600) 12) Also λmax 270nm (ε 11·000)

Table 4. NMR data of 2-cyanovinyl sulphides

R^1-CH(R^2)-C(SR^3)=CHCN

	R^1	R^2	R^3	
8.	Me	Et	Pr	9.10(3H,t, $C\underline{H}_3CH_2$), 8.90(3H,d, $CH_3CH_2CC\underline{H}_3$), 8.75(3H,t,$C\underline{H}_3CH_2CH_2$), 8.70-8.00(4H,m,$CH_2\underline{CH}_2$) 7.50-7.20(2H,m,$CH_3C\underline{H}_2CH$), 7.00-6.30(1H,m,$CH_3CH_2C\underline{H}$), 5.20(0.16H,s,=C$\underline{H}$CN) , 4.70(0.84H,s, =C$\underline{H}$CN)
11.	Et	Et	Bu	9.10(6H,t,$(C\underline{H}_3CH_2)_2$),9.00(3H,t,$C\underline{H}_3(CH_2)_3$),8.60-8.25(4H,m, $(CH_3C\underline{H}_2)_2$), 7.50-7.20(4H,m, $C\underline{H}_2C\underline{H}_2CH_3$), 7.15-7.00(2H,t, $C\underline{H}_2(CH_2)_2CH_3$, 6.95-6.55(1H,m,$(CH_3CH_2)_2C\underline{H}$), 5.20(0.70H,s, =C$\underline{H}$CN), 4.70(0.3H,s, =C$\underline{H}$CN)
12.	Bu^n	H	Pr^i	9.03(3H,t,$C\underline{H}_3(CH_2)_3$), 8.83-8.27(10H,m, $CH_3(C\underline{H}_2)_2CH_2$, $SCH(C\underline{H}_3)_2$), 7.90-7.30(2H,m, $CH_3(CH_2)_2C\underline{H}_2$) 6.67(1H,m, $SC\underline{H}(CH_3)_2$), 5.12(0.75H,s,=C$\underline{H}$CN), 4.67(0.25H,s,=CHCN),
13.	Ph		Pr^i	8.75(6H,q, $SCH(C\underline{H}_3)_2$), 7.33-6.63(1H,m, $SC\underline{H}(CH_3)_2$), 4.75(0.5H,s,=C$\underline{H}$CN), 4.52 (0.5H,s,=C$\underline{H}$CN), 2.70-2.57(5H,m, aromatic).
14.	Ph		Et	8.78(3H,t, $SCH_2C\underline{H}_3$), 7.48-7.05(2H,m, $SC\underline{H}_2CH_3$), 4.88(0.33H,s,=C$\underline{H}$CN) 4.57(0.67H,s,=C$\underline{H}$CN), 2.72-2.57(5H,m, aromatic).
15.	Ph		Pr	9.03(3H,t, $S(CH_2)_2C\underline{H}_3$), 8.77-8.13(2H,m, $SCH_2C\underline{H}_2CH_3$), 7.50-7.15(2H,m, $C\underline{H}_2CH_2CH_3$), 4.87(0.33H,s,=C$\underline{H}$CN), 4.57(0.67H,s,=C$\underline{H}$CN) w.70-2.57(5H,m, aromatic).
16.	Ph		Bu	9.05(3H,t, $SCH_2(SCH_2)_2C\underline{H}_3$), 8.82-8.20(4H,m, $SCH_2(C\underline{H}_2)_2CH_3$), 7.42-7.08(2H,m, $SCH_2(CH_2)_2CH_3$), 4.87(0.5H,s,=C$\underline{H}$CN), 4.55(0.5H,s, =C$\underline{H}$CN), 2.65-2.40(5H,m, aromatic).
17.	Ph		$PhNH_2$	5.93-5.53(2H,s, $N\underline{H}_2$, disappears on deuteration), 4.53(1H,s,=C$\underline{H}$CN), 3.67-2.40 (9H,m, aromatic).
18.	Me	Me	$PhNH_2$	8.65(6H,d,$(C\underline{H}_3)_2CH$), 6.95-6.38(1H,m,$(CH_3)_2C\underline{H}$), 5.76 (2H,s,$N\underline{H}_2$, disappears on deuteration), 5.60(1H,s,=CHCN), 3.43-3.15(2H,m,aromatic), 2.80-2.60(2H,m, aromatic).
20.	Et	Et	$PhNH_2$	9.00(6H,t,$(C\underline{H}_3CH_2)_2CH$), 8.52-8.05(4H,m,$(CH_3C\underline{H}_2)_2CH$), 7.42-6.85(1H,m,$(CH_3CH_2)_2C\underline{H}$), 5.70(2H,s,$N\underline{H}_2$, disappears on deuteration), 5.50(1H,s,=C$\underline{H}$CN), 3.45-3.17(2H,m, aromatic), 2.92-2.60(2H,m, aromatic).

(0.5 g) were refluxed in ethanol (100 ml) for 1 h. Working up gave a solid which was recrystallised from hexane to give 3-(2-aminophenylthio)-4-methylhex-2-enenitrile (6.5 g, 94%), m.p. 90°. Data for this compound **19** and two similar compounds are summarised in Tables 3 and 4.

3-(2-Aminophenylthio-3-phenylprop-2-enenitrile. Freshly distilled phenylpropynenitrile[2] (2.54 g, 0.02 mol) was mixed with 2-aminothiophenol (2.5 g, 0.02 mol). A slighly exothermic reaction (the temperature reached 32°) took place to give a thick oil. Purification by column chromatography on alumina (grade H, activity 3) and elution with 40% chloroform–hexane gave 3(2-aminophenylthio)-3-phenylprop-2-enenitrile (4.8 g, 95%) ν_{max} 3460, 3350 (NH_2) 2215 (C ≡ N) and 1625 cm^{-1}(C–C). The band for S-H at ν_{max} 2520 cm^{-1} had disappeared. Other data for this compound **17** are summarised in tables 3 and 4.

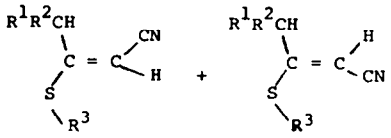
2-Phenyl-2-benzothiazole. 3-(2-Aminophenylthio)-3-phenyl-prop-2-enenitrile (3 g, 0.012 mol) was heated at 200° for 20 minutes. Acetonitrile was given off. The residue in the flask was allowed to cool to room temperature, then recrystallised from benzene to give 2-phenyl-2-benzothiazole (2.1 g, 84%). Data for this compound (25) is given in Tables 6 and 7.

2-(1-Methylpropyl-2-benzothiazole. 3-(2-Aminophenylthio)-4-methylhex-2-enenitrile (4.64 g, 0.02 mol) was heated at 250°. Acetonitrile distilled off and was followed by crude product (7.2 g). This was dissolved in ether, washed with water and redistilled to give 2-(1-methylpropyl)-2-benzothiazole (6.8 g, 82%). Data for this compound **22** and three other similar compounds **21**, **23** and **24** are given in Tables 6 and 7.

3-2-Aminoethanethio)-4-methylhex-2-enenitrile. 2-Aminoethanethiol hydrochloride (11.35 g, 0.1 mol) was dissolved in water (100 ml) and calcium carbonate added to the solution followed by a solution of 4-methylhexa-2, 3-dienenitrile (10.7 g, 0.1 mol) in ethanol (100 ml). Refluxing for 30 min. gave, on working up, slightly impure 3-(2-aminoethanethio)-4-methylhex-2-enenitrile in quantitative yield, the only contaminant being 3-(2-aminoethanethio)-4-methylhex-3-enenitrile. This compound was used in the next experiment without further purification.

2-(1-Methylpropyl)-2-thiazoline. 3-(2-Aminoethanethio)-4-methylhex-2-enenitrile (12.2 g, 0.066 mol) was heated at 250° when acetonitrile, followed by crude product distilled off. The latter was dissolved in ether, washed with water and dried ($MgSO_4$). Fractionation after removal of solvent gave 2-(1-methylpropyl)thiazoline (6.73 g, 71%), b.p. 189–190° at 760 mm Hg. Data for this compound **27** and three others are given in Tables 8 and 9.

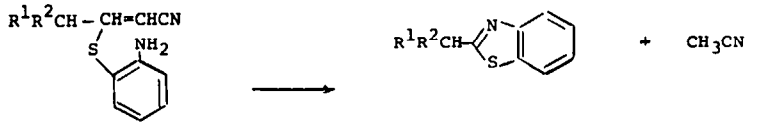
Table 5. Chemical shift (τ) of the olefinic protons and ratio of the *E* and *Z* isomers of 2-cyanovinyl sulphides



	R^1	R^2	R^3	E	Z	Ratio of E:Z
8.	Me	Et	Pr^n	4.80	5.30	1:5
11.	Et	Et	Bu^n	4.80	5.30	3:7
12.	$Me(CH_2)_3$		Pr^i	4.67	5.12	1:3
13.	Ph	Pr^i	Pr^i	4.52	4.75	1:1
14.	Ph		Et	4.57	4.88	2:1
15.	Ph		Pr^n	4.57	4.87	2:1
16.	Ph		Bu^n	4.55	4.87	1:1
	Et	Et	Et*	4.62	5.02	1:2
	Me	Et	Et*	4.67	5.18	2:3
	Me	Et	Pr^{i*}	4.62	5.15	2:3
	Me	Et	Ph*	4.65	5.62	1:2

*These compounds also contained some unconjugated adduct.

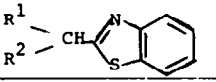
Table 6. Synthesis of benzothiazoles



	Nitrile		b.p.	Yield	U.V.						Found			Required		
	R^1	R^2	at 670mmHg	(%)	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	C	H	N	C	H	N
21.	Me	Me	260-262°	82[a]	217	21900	250	8200	285	2500	67.7	6.1	7.7	67.8	6.2	7.9
22.	Me	Et	285-286°	82[b]	218	22800	249	9100	285	2700	69.0	6.9	7.1	69.1	6.8	7.3
23.	Me	Pr	290-291°	80	220	23100	250	9500	285	3000	70.2	7.0	7.0	70.2	7.3	6.8
24.	Et	Et	289-291°	86	220	23600	250	9300	285	2900	70.2	7.1	6.5	70.2	7.3	6.8
25.	Ph		112°*	82[c]	226	19300	230	18800	300	18800	73.9	4.4	6.6	73.9	4.3	6.6

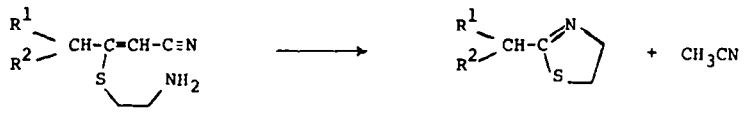
*Melting point; (a) m/e 177; (b) m/e 191; (c) m/e 211.

Table 7. NMR data for benzolthiazoles



	R^1	R^2	
21.	Me	Me	8.52 (6H, d, $(C\underline{H}_3)_2CH$), 6.59-6.48(1H,m, $(CH_3)_2C\underline{H}$), 2.74-2.44 (2H,m, aromatic), 2.22-1.92 (2H,m,aromatic)
22.	Me	Et	9.00 (3H,t,$C\underline{H}_3CH_2CCH_3$), 8.55 (3H,d,$C\underline{H}_3CHCH_3CH_2$), 8.40-7.70 (2H,m,$CH_3\underline{CH}_2CCH_3$), 7.17-6.58 (1H,m,$CH_3CH_2C\underline{H}CH_3$), 2.93-2.40 (2H,m,aromatic), 2.37-1.90 (2H,m,aromatic)
23.	Me	Pr	9.05 (3H,t,$C\underline{H}_3(CH_2)_2CCH$), 8.65 (3H,d,$CH_3(CH_2)_2CC\underline{H}_3$), 6.70-6.35 (1H,m,$CH_3(CH_2)_2C\underline{H}CH_3$) 2.80-2.52 (2H,m,aromatic), 2.48-1.98(2H,m,aromatic)
24.	Et	Et	9.05 (6H,t,$(C\underline{H}_3CH_2)_2CH$), 8.50-7.78 (4H,m,$(CH_3(C\underline{H}_2)_2CH$), 7.24-6.72(1H,m,$(CH_3CH_2)_2C\underline{H}$) 2.90-2.55 (2H,m,aromatic), 2.33-1.87 (2H,m,aromatic).
25.	Ph		2.87-2.33 (5H,m,aromatic), 2.25-1.77 (4H,m,aromatic).

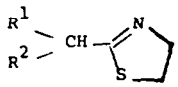
Table 8. Synthesis of thiazolines



	NITRILE R^1	R^2	b.p. at 760mmHg	Yield (%)	U. λmax	ε	V. λmax	ε	FOUND C	H	N	REQUIRED C	H	N
26.	Me	Me	180-182	67	202	3 800	230	2 200	56.0	8.7	10.7	55.8	8.5	10.9
27.	Me	Et	189-190	71*	202	4 200	232	2 300	58.5	9.3	9.5	58.7	9.1	9.8
28.	Et	Et	218-220	73	202	4 100	232	2 400	61.1	9.5	8.6	61.2	9.6	8.9
29.	Me	Pr	220-243	70	202	4 000	232	2 200	61.0	9.3	8.8	61.2	9.6	8.9

*m/e 143

Table 9. NMR data of thiazolines



	R^1	R^2	
26.	Me	Me	8.85(3H,d, $(C\underline{H}_3)_2CH$), 7.45-6.95(1H,m, $(CH_3)_2C\underline{H}$), 6.85(2H,t,$CH_2C\underline{H}_2N$), 5.85(2H,t, $SC\underline{H}_2CH_2$)
27.	Me	Et	9.12(3H,t, $C\underline{H}_3$,t, $C\underline{H}_3CH_2CHCH_3$), 8.87(3H,d,$C_2H_5CHC\underline{H}_3$), 8.60-8.25(2H,m, $CH_3C\underline{H}_2CHCH_3$) 7.60-7.15(1H,m,$CH_3CH_2C\underline{H}CH_3$), 6.82(2H,t,$CH_2C\underline{H}_2N$), 5.85(2H,t,$SC\underline{H}_2CH_2$)
28.	Et	Et	9.12(3H,t, $(C\underline{H}_3CH_2)_2CH$), 8.85-8.05(4H,m, $(CH_3C\underline{H}_2)_2CH$), 7.85-7.25(1H,m, $(CH_3CH_2)_2C\underline{H}$), 4.82(2H,t, $CH_2C\underline{H}_2N$), 5.85(2H,t,$SC\underline{H}_2CH_2$)

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[5]For preliminary publication of some of this work see Z. T. Fomum, P. D. Landor, S. R. Landor and G. B. Mpango, *Tetrahedron Letters.* 1101 (1975).