# Dimerisation of 3-Aryl-2-cyanothioacrylamides. A [2ₛ + 4ₛ] Cycloaddition to give Substituted 3,4-Dihydro-2H-thiopyrans

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A thermal dimerisation of the Diels–Alder type is reported for certain 3-aryl-2-cyanothioacrylamides giving rise to novel derivatives of 3,4-dihydro-2H-thiopyran. The regioselectivity and stereoselectivity of this thermal heterodiene cycloaddition reaction are rationalised in terms of frontier orbital interactions. N.m.r. and i.r. data are reported for 21 thioacrylamides in monomeric and/or dimeric form.

THE formation of a sulphur heterocycle by a thermally or photochemically promoted cycloaddition reaction involving a thiocarbonyl group is known for only a few

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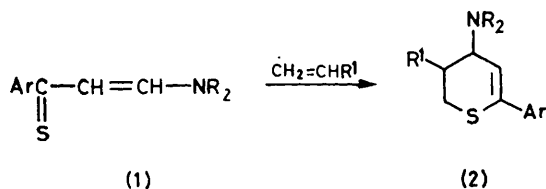
types of compound. Photocycloaddition of thio-benzophenone to olefins [1,2] can give either a thietan

(3)

(4)
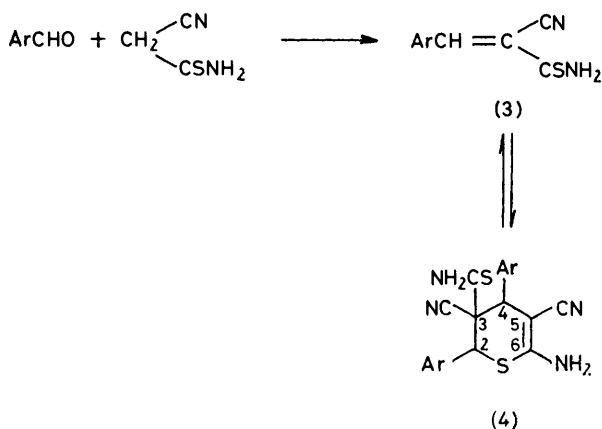
SCHEME

a; Ph	l; 2-BrC₆H₄
b; 4-MeC₆H₄	m; 2,4-Cl₂C₆H₃
c; 4-MeOC₆H₄	n; 2,6-Cl₂C₆H₃
d; 4-Me₂NC₆H₄	o; 3,5-Cl₂C₆H₃
e; 4-Et₂NC₆H₄	p; 2-Thienyl
f; 4-MeNHC₆H₄	q; 5-Me-2-thienyl
g; 4-FC₆H₄	r; 5-Cl-2-thienyl
h; 4-ClC₆H₄	s; 2-Furyl
i; 4-BrC₆H₄	t; 5-Me-2-furyl
j; 4-NO₂C₆H₄	u; 3-pyridyl
k; 2-ClC₆H₄	

(a [2 + 2] process) or a 1,4-dithian (a [2 + 2 + 2] process) and thermal cycloaddition of a variety of thioketones to dienes gives 5,6-dihydro-2H-thiopyrans (a

[2 + 4] process).[1,2] In all these cases the thioketone contributes only two atoms to the new ring. In contrast the aminovinyl-thioketones (1) undergo cycloaddition reactions with typical dienophiles. Quiniou and his co-workers [3-7] have shown that (1), acting as a hetero-diene, can give thiophens by [4 + 1] cycloaddition to α-bromo-ketones and 3,4-dihydro-2H-thiopyrans (2) by [4 + 2] cycloaddition to acrylonitrile, acrylamide, and keten. Subsequent elimination of an amine, R₂NH, gave a 2H-thiopyran. Compounds (1) are of a rather restricted type and we now report a similar reaction which indicates that cycloaddition to the moiety C=C–C=S to form a thiopyran may be a process of much wider scope.

Base-catalysed condensation of an aromatic aldehyde with cyanothioacetamide should give the corresponding 3-aryl-2-cyanothioacrylamide (3) and several reports [8,9] claim to obtain examples of (3) by this route. We required the thioamides (3) as part of our investigation into the potential of arylmethylenemalononitriles, ArCH=C(CN)₂, and related compounds for use as cytotoxic and neuropharmacological agents, and have attempted their synthesis by this route (Scheme).†

RESULTS

The products obtained had the correct elemental composition and where appropriate had melting temperatures in agreement with literature values. The thioacrylamide structure (3) was in accord with the n.m.r. spectrum [in (CD₃)₂SO] (Table 1) for compounds derived from heterocyclic aldehydes and 2- and 4-substituted benzaldehydes. Typically the aromatic proton signals appeared between δ 6.7 and 8.9, the olefinic proton at 8.1, and the amide protons as two broad peaks around 9.2 and 10.0.

However for reactions (Scheme) with Ar = Ph, 4-BrC₆H₄, 4-ClC₆H₄, and 4-NO₂C₆H₄ the products had more complex spectra. In addition to aromatic peaks (8 H) in the usual region and the two broad amide peaks at δ 9.1 and 9.9 there was a slightly broad peak (2 H) at ca. 6.9, a sharp singlet (1 H) at 5.3, and a further singlet at 4.8 whose linewidth varied from 7 to 25 Hz in the various compounds. Notably, the usual olefinic peak was absent but did appear as a small peak in the case of Ar = 4-BrC₆H₄, suggesting a mixture of the thioacrylamide (3i) and another compound.

¹ A. Ohno, *Internat. J. Sulphur Chem. (B),* 1971, **6**, 183.

² H. Gotthard *Chem. Ber.,* 1972, **105**, 2008.

³ J. P. Pradère and H. Quiniou, *Ann. Chim. (Italy),* 1973, **63**, 563.

⁴ J. C. Meslin, Y. T. N'Guessan, H. Quiniou, and F. Tonnard, *Tetrahedron,* 1975, **31**, 2679.

⁵ J. C. Meslin and H. Quiniou, *Tetrahedron,* 1975, **31**, 3055.

⁶ J. P. Pradère, Y. T. N'Guessan, H. Quiniou, and F. Tonnard, *Tetrahedron,* 1975, **31**, 3059.

⁷ J. C. Meslin, J. P. Pradère, and H. Quiniou, *Bull. Soc. chim. France,* 1976, 1195.

⁸ B. Tornetta, G. Scapini, F. Guerrera, and A. Bernardini, *Boll. Seduta Accad. Gioenia Sci. Nat. Catania,* 1970, **10**, 353 (*Chem. Abs.,* 1973, **78**, 620).

⁹ V. Grinstein and L. Serina, *Latvijas P.S.R. Zinatnu Akad. Vestes, Kim. Ser.,* 1963, **4**, 469 (*Chem. Abs.,* 1964, **60**, 5391).

From the condensation of 4-fluorobenzaldehyde with cyanothioacetamide two crystalline materials were isolated by fractional crystallisation. The higher-melting form (red prisms) was the thioacrylamide (3g). The lower-melting yellow derivative had the same spectral characteristics as the other anomalous products described above and these compounds are assigned the structure (4) (2,4-diaryl derivatives of 6-amino-3,5-dicyano-3,4-dihydro-2H-thiopyran-3-thiocarboxamide), resulting from a Diels–Alder self-condensation of the corresponding thioacrylamide (3), on the basis of the following evidence.

In the n.m.r. spectrum of the 4-chloro-derivative (4h) in $(CD_3)_2SO-CD_3CO_2H$ (1 : 1) the peak at δ 6.9 corresponded to two exchangeable protons. The spectrum of the 4-nitro-derivative (4j) showed peaks corresponding to two different 4-substituted phenyl groups and similar assignments could be made (Table 2) for the less well resolved aromatic regions

TABLE 1
Proton chemical shifts [a] (δ values) for
3-aryl-2-cyanothioacrylamides (3)

Compound	H(3)	NH	Aromatic H
(3b) [b]	8.10	9.55, 10.05	7.40 [H(3')], 7.88 [H(2')]
(3e) [c]	8.10	9.07, 9.64	6.80 [H(3')], 7.90 [H(2')]
(3f) [d]	8.12	9.4, 9.9	7.85 [H(3')], 8.01 [H(2')]
(3g)	8.15	9.6, 10.1	8.1 [H(2')], 7.5 [H(3')]
(3k)	8.36	9.76, 10.29	6.5—7.6 [H(3'), H(4'), H(5')], 8.07 [H(6')]
(3l)	8.26	9.8, 10.03	7.4—8.0 [H(3'), H(4'), H(5'), H(6')]
(3m)	8.22	9.8, 10.1	7.85 [H(3')], 7.65 [H(5')], 8.02 [H(6')]
(3n)	9.14	9.8, 10.2	7.6 [H(3'), H(4'), H(5')]
(3o)	8.06	9.65, 10.17	7.86 [H(5')], 7.94 [H(6')], 8.15 [H(2')]
(3p)	8.43	9.43, 9.98	7.35 [H(4')], 7.92 [H(3')], 8.13 [H(5')]
(3q) [e]	8.35	9.25, 9.85	7.04 [H(4')], 7.73 [H(3')]
(3r)	8.30	9.40, 9.94	7.35 [H(4')], 7.76 [H(3')]
(3s)	8.05	9.37, 9.97	6.83 [H(4')], 7.45 [H(3')], 8.10 [H(5')]
(3t) [f]	8.00	9.25, 9.85	6.53 [H(4')], 7.39 [H(3')]
(3u)	8.10	9.60, 10.14	7.58 [H(5')], 8.37 [H(4')], 8.72 [H(6')], 8.96 [H(2')]
(3a) [g]	8.10	9.61, 10.10	7.6 [H(3'), H(4')], 7.9 [H(2')]
(3h) [g]	8.10	9.35, 9.85	7.55 [H(3')], 7.90 [H(2')]
(3i) [g]	8.05	9.65, 10.10	7.85 [H(2'), H(3')]
(3j) [g]	8.10	9.8, 10.3	8.15 [H(2')], 8.40 [H(3')]

[a] In $(CD_3)_2SO$.　[b] δ (Me) 2.39.　[c] δ (Me) 1.15, δ (CH$_2$) 3.47.　[d] δ (Me) 2.12.　[e] δ (Me) 2.63.　[f] δ (Me) 2.45.　[g] After dissociation of dimeric form at 100 °C.

TABLE 2
Proton chemical shifts [a] (δ values) for
2H-thiopyran derivatives (4)

Compound	CSNH₂	C=CNH₂	H(2),H(4) [b]	Aromatic H [c]	
				H(2')	H(3')
(4a)	9.05, 9.85	6.8	4.8, 5.3	7.55	7.35
(4g)	9.0, 9.9	6.9	4.9, 5.3	7.4, 7.48	7.4, 7.52
(4h)	9.0, 9.9	6.9	4.8, 5.3	7.35, 7.5	7.5, 7.6
(4i)	9.0, 9.9	6.8	4.8, 5.3	7.23, 7.26	7.47, 7.65
(4j)	9.1, 10.11	7.1	5.0, 5.6	7.7, 7.85	8.3

[a] In $(CD_3)_2SO$.　[b] Individual assignments to H(2) and H(4) are not possible.　[c] Two distinct sets of ortho- and meta-protons are distinguishable, but these cannot be assigned to a specific phenyl group.

of the spectra of the other compounds. The i.r. spectra of (4) had an extra band in the NH region (3 400—3 500 cm⁻¹) and a broadened CN band. Mass-spectral studies showed no species of greater mass than the parent ion of the monomeric

compound, presumably indicating dissociation at the probe temperature.

Convincing evidence for the correctness of structure (4) was provided by the n.m.r. spectra [in $(CD_3)_2SO$] of (3) and (4) at higher temperatures. At 100 °C all the compounds prepared by Scheme 1 had the spectral characteristics of monomeric thioacrylamides. At lower temperatures the spectra indicated a mixture of monomeric and dimeric forms for those cases which were initially pure dimeric form (4) and even at 29 °C the thiopyrans (4) slowly dissociated to an equilibrium mixture of (3) and (4). The dissociation was completely reversible and could be achieved starting from either the thioacrylamide (3) or the thiopyran (4). For the system with Ar = Ph the equilibrium constant at 22 °C was 0.244 mol l⁻¹ (from the n.m.r. spectrum), corresponding to ΔG_{295} 3.46 kJ mol⁻¹. These results are entirely in accord with a reversible Diels–Alder heterodiene cycloaddition.

A confusing aspect of the n.m.r. spectra of the thiopyrans in $(CD_3)_2SO$, was the differential broadening of the two NH peaks and the two CH peaks. As the temperature was lowered from ca. 50 to ca. 25 °C the high-field absorption of each pair became progressively broader while the other absorption in each pair remained essentially unchanged (amide peaks are of course intrinsically much broader than the methine peaks). Some dynamic process was evidently involved and the spectrum of the nitro-derivative (4j) [in $(CD_3)_2SO-(CD_3)_2CO$ (1 : 1)] at temperatures down to -25 °C showed successive broadening and splitting of the CH and NH peaks until all four resonances appeared as doublets at -25 °C. The differential effects simply reflect the different coalescence temperatures for these four protons. Further detailed study of this process is under way but we suggest that it represents a ring inversion process, probably between two pseudoboat forms (5a and b).
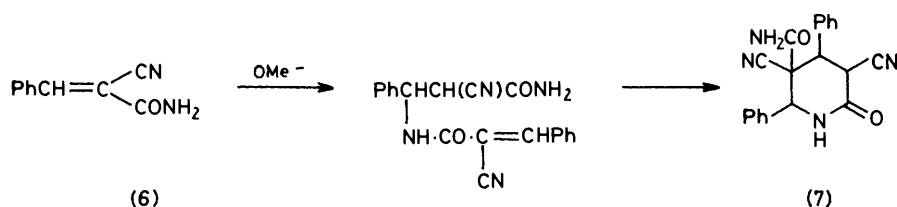

(5a)　　　　　　　　　　　　(5b)

DISCUSSION

Diels–Alder heterodiene cyclisations have been most frequently reported for the moiety $-C=C-C=O$ and many examples are noted in a recent review.[10] In contrast, cycloadditions of the analogous thiones are known only for the electron-rich heterodiene $NH_2-C=C-C=S$. The role of the amino-group in promoting cycloadditions of compounds containing this moiety has not been studied in detail. In terms of a frontier-orbital approach an electron-donating group will raise the energy of the highest-occupied molecular orbital (h.o.m.o.) of the diene, increasing the tendency to react with a suitable dieno-phile. However, the existence of this cycloaddition reaction does not preclude the possibility of a similar reaction for the unsubstituted thione. 3-Aryl-2-cyano-thioacrylamides (3) are heterodienes substituted with both an electron-donating group (NH_2) and an electron-withdrawing group (CN). To a first approximation these substituent effects on reactivity can be regarded as additive and hence in the present case cancelling and the

[10] G. Desimoni and G. Tacconi, Chem. Rev., 1975, 75, 651.

h.o.m.o. energy and diene reactivity in (3) must be lower than in the simpler enaminothiones. The present work has shown that in certain cases aryl-substituted thio-acrylamides can act as heterodienes and form cyclo-adducts. This implies that the moiety C=C–C=S is potentially reactive and it is likely that suitable modification to this group can lead to new routes to sulphur heterocycles through cycloaddition to appropriate dienophiles.

There appears to be no report of an αβ-unsaturated thioamide acting as a dienophile. In contrast, acryl-amides are known [11] to be good dienophiles as members of the general class of electron-deficient olefins. In such compounds the lowest-unoccupied molecular orbital (l.u.m.o.) energy is reduced relative to that for the unsubstituted olefin. Dimerisation has been reported [12] for 2-cyanocinnamamide (6) [the oxygen anlogue of (3)]

A further compression of these levels can be expected from conjugation [11] with a phenyl group. The energy difference between the h.o.m.o. and l.u.m.o. for (9), 11.1

TABLE 3

Frontier-orbital energies (eV) *

Compound	E (h.o.m.o.)	E (l.u.m.o.)	ΔE
(7)	−13.13	1.83	14.96
(8)	−10.46	0.64	11.10

* Unmodified values from CNDO/2 calculations.

eV, is rather high for a cycloaddition reaction. However, the corresponding orbital energy separation for acrylaldehyde,[11] which is known to dimerise, is 12.0 eV. Hence dimerisation for (9) may also be possible under severe conditions, although alternative reaction pathways are likely to compete significantly if not exclusively.

If the cycloaddition of two molecules of (3) proceeds

(6)   (7)

but this is not a thermal pericyclic reaction. The proposed mechanism involves a base-catalysed Michael condensation followed by cyclisation to a piperidone (7) rather than the pyran analogous to (4).

Hence self-condensation of a thioacrylamide (3), showing characteristics of both diene and dienophile, is a very interesting extension to the class of thermal peri-cyclic dimerisations. It is particularly interesting because the mild experimental conditions compare favourably with those for other thermal dimerisations.[10] The h.o.m.o. and l.u.m.o. energies have been calculated * using the CNDO/2 approximation for the model compounds (8) and (9), since computing limitations ruled out

(8)   (9)
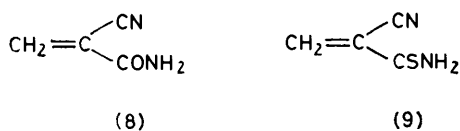
calculations on the analogous aryl-substituted amides [e.g. (3)]. The presence of a phenyl group containing an electron-withdrawing 4-substituent is evidently essential for the cycloaddition reaction to occur. But, although the correct absolute values of the frontier-orbital energies cannot be obtained with model compounds, these calculations will effectively demonstrate the difference between amides and thioamides. The calculated energy levels (Table 3) show that substituting sulphur for oxygen raises the h.o.m.o. energy and lowers the l.u.m.o. energy.

via a suprafacial–suprafacial mode, $[4_s + 2_s]$, four possible products can result [(10)—(13)] corresponding to

(10) R¹ = H, R² = Ar   (12) R¹ = H, R² = Ar

(11) R¹ = Ar, R² = H   (13) R¹ = Ar, R² = H
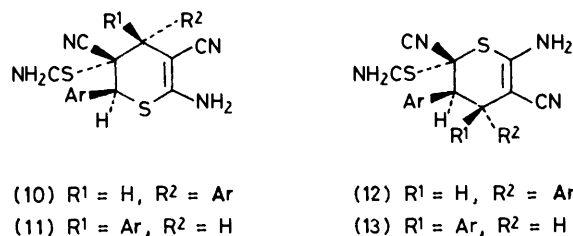
exo- and *endo*-addition for each of the two mutual orientations of the diene and dienophile. In practice the reaction is completely regiospecific since compounds (12) and (13) are not observed in any case. [These compounds would both be characterised by vicinal coupling between the thiopyran ring protons and be easily distinguished from (10) and (11).] The frontier-orbital

h.o.m.o.		l.u.m.o.
0.213	C	−0.549
0.096	C	0.256
−0.242	C	0.532
−0.860	S	−0.406

(14)

coefficients for the model compound (9) are shown in (14). The large coefficient for the sulphur atom in the

* Geometrical parameters were derived from data for acetamide, thioacetamide, and acrylonitrile.[13]

[11] I. Fleming, ' Frontier Orbitals and Organic Chemical Reactions,' Wiley, London, 1976, ch. 4.

[12] G. Dietz, W. Fiedler, and G. Faust, *Chem. Ber.*, 1967, **100**, 3127.

[13] · Interatomic Distances,' Chemical Society, London, 1958.

h.o.m.o. of the diene does suggest that the most favourable interaction will be between the sulphur atom and the β-carbon of the dienophile. Interaction energies were calculated following the perturbational treatment of Salem.[14] If only the frontier orbitals are considered then for a dimerisation the interaction energy is given by (A)

$$E_{int.} = \frac{2}{E^H - E^L}\left[\left(\sum_{mn} c_m^H c_n^L \beta_{mn}\right)^2 + \left(\sum_{mn} c_m^L c_n^H \beta_{mn}\right)^2\right] \quad (A)$$

where H = h.o.m.o., L = l.u.m.o., c is an orbital coefficient, and β is the interaction exchange integral between pairs of atoms m and n in different molecules. A value of 5.0 eV was taken for β_{CC}, corresponding to an orbital separation of 2.0 Å, and β_{CS} was assumed equal to β_{CC}. For the orientation leading to the analogues of (10) and (11) $E_{int.} = 1.54$ eV and for the reverse orientation $E_{int.} = 0.61$ eV confirming the complete regioselectivity observed in practice.

The stereochemistry indicated in (10) and (11) is based on the assumption that the monomeric amide (3) has the

cis) is more likely than (11) (Ar,CN,Ar *cis*) but (10) contains a significant interaction (Ar,CSNH$_2$ *cis*). Hence although only one product is obtained the stereochemical course of the reaction cannot be determined experimentally. However, secondary overlap of the
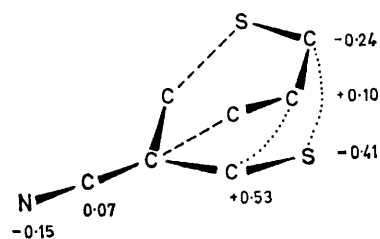
Secondary overlap of frontier orbitals ($\cdots$) stabilising the *endo*-transition state for the indicated primary overlap (– – – –)

frontier orbitals probably significantly stabilises the transition state (*endo* †) shown in the Figure. Bonding overlap exists for both the central carbon atoms in the diene with the C=S group in the dienophile. In the

TABLE 4

M.p.s, i.r. data, and analyses for 3-aryl-2-cyanothioacrylamides and 6-amino-2,4-diaryl-3,5-dicyano-3,4-dihydro-2H-thio-pyran-3-thiocarboxamides

Compound	Method of prep.†	Yield (%)	M.p. (°C)	ν_{NH} cm^{-1}	ν_{CN}	Found (%) C	H	N	Required (%) C	H	N
(4a)	a	52	148—150 ᵃ	3 420, 3 410, 3 375sh, 3 320sh	2 190, 2 180						
(3b)	a	48	185—187	3 350, 3 280	2 220	65.7	4.9	13.7	65.3	4.9	13.7
(3c)	a	50	190 ᵇ	3 400, 3 320	2 205						
(3d)	a	60	230 ᶜ	3 330, 3 285	2 215						
(3e)	a	46	157	3 340, 3 310	2 210	64.5	6.5	16.0	64.8	6.6	16.2
(3f)	c	96	253 ᵈ	3 290, 3 240, 3 150	2 250	59.1	4.5	17.2	58.8	4.5	17.1
(3g) (4g)	a	50	185 ᵉ	3 365, 3 285 3 460, 3 415, 3 310	2 220 2 190	58.6	3.6	13.6	58.3	3.4	13.6
(4h)	a, b	50, 78	180	3 400, 3 300, 3 290	2 180	53.9	2.8	12.4	53.9	3.2	12.6
(4i)	b	50	195	3 390, 3 270sh	2 200	44.8	2.7	10.6	45.0	2.6	10.5
(4j)	a	50	188 ᶠ	3 420, 3 300, 3 280sh	2 190						
(3k)	a	35	173	3 320, 3 285sh	2 220	54.0	3.4	12.5	53.9	3.2	12.6
(3l)	b	40	170	3 320, 3 290sh	2 220	45.2	2.7	10.9	45.0	2.6	10.6
(3m)	a, b	66, 78	198	3 330, 3 270, 3 180	2 230	46.9	2.4	10.9	46.2	2.6	10.9
(3n)	a	42	123	3 345, 3 250	2 225	46.2	2.2	10.8	46.2	2.6	10.9
(3o)	a	50	183—184	3 340, 3 250	2 220	46.6	2.1	10.8	46.7	2.6	10.9
(3p)	a	69	168 ᵍ	3 360, 3 260	2 200						
(3q)	a	60	218	3 360, 3 280	2 220	52.0	3.7	13.6	51.9	3.8	13.5
(3r)	a	33	212	3 360, 3 280	2 220	42.1	2.2	12.2	42.0	2.2	12.3
(3s)	a	58	158 ʰ	3 350, 3 275	2 205						
(3t)	a	46	177	3 350, 3 290	2 210	56.6	4.2	14.7	56.3	4.2	14.6
(3u)	a	50	180	3 320sh, 3 240sh	2 210	57.1	3.8	22.1	57.1	3.7	22.2

ᵃ Lit.,[15] 149—150 °C. ᵇ Lit.,[8] 190—191 °C. ᶜ Lit.,[9] 231—232 °C. ᵈ Lit.,[8] 265 °C decomp. ᵉ The two fluoro-derivatives (3g) and (4g) were separated by fractional crystallisation from EtOH. (4g) is converted into (3g) before melting. ᶠ Lit.,[9] 188—189 °C. ᵍ Lit.,[8] 169—170 °C. ʰ Lit.,[8] 156 °C.

† See Experimental section.

aryl and thioamide groups *trans*.* The corresponding oxygen analogue (6) is known to exist entirely in this form.[15,16] The stereochemistry of the adduct cannot be determined from the n.m.r. spectrum since predicting the chemical shifts for the heterocyclic ring protons is impossible for such a heavily substituted system. Steric considerations might suggest that (10) (Ar,CN,H

exo-transition state only one small bonding overlap is possible with the carbon of the C≡N group. Hence the *endo*-stereochemistry (10) is the most likely form for all of the products of type (4).

EXPERIMENTAL

M.p.s were recorded on a hot-stage apparatus. I.r. spectra were determined for potassium bromide discs with a

* An X-ray structure determination is currently under way to confirm this stereochemistry.

† The terms *exo* and *endo* have no absolute significance for these compounds and are assigned arbitrarily.

[14] L. Salem, *J. Amer. Chem. Soc.*, 1968, **90**, 543.
[15] J. Zabicky, *J. Chem. Soc.*, 1961, 683.
[16] R. F. Silver, A. Kerr, P. D. Frandsen, S. J. Kelly, and H. L. Holmes, *Canad. J. Chem.*, 1967, **45**, 1001.

Perkin-Elmer 521 grating spectrometer. N.m.r. spectra were determined on a JEOL PMX60 or JEOL 4H100 spectrometer. M.p.s, i.r. data, and analytical data are in Table 4.

Cyanothioacetamide.—A saturated solution of malononitrile (10 mol) in dry ethanol containing a catalytic amount of triethylamine was prepared in a resin flask. A stream of anhydrous H_2S was bubbled through this solution with vigorous stirring. The precipitate was collected after 1 h and washed with cold ethanol. This crude product (80%) had m.p. 118—120 °C and was sufficiently pure for subsequent reactions. After recrystallisation from ethanol (charcoal), cyanothioacetamide had m.p. 121 °C (lit.,[17] 114—120 °C) (Found: C, 35.9; H, 4.1; N, 28.3. Calc. for $C_3H_4N_2S$: C, 36.0; H, 4.0; N, 28.0%).

3-Aryl-2-cyanothioacrylamides (3).—*Method* (*a*). *Knoevenagel condensation between an aromatic aldehyde and cyanothioacetamide.* A mixture of the appropriate aldehyde (0.1 mol), cyanothioacetamide (0.1 mol), and 4 drops of triethylamine in absolute ethanol (200 ml) was stirred for 30 min at 40—50 °C. The dark red solution was cooled to room temperature, and the crude 3-aryl-2-cyanothioacryl-

amide collected after 1 h and recrystallised from ethanol (hot filtration). Condensations with thiophen- and furancarbaldehydes took place at room temperature.

Method (*b*). *Knoevenagel condensation using Cope's modification.* Cyanothioacetamide (25 g, 0.25 mol) was suspended in dry benzene (80 ml) in a flask provided with a Dean–Stark water separator and triethylamine (0.5 g) was added. The aldehyde (0.25 mol) was added in small portions to the refluxing solution, followed by dry benzene (400 ml). The solution gradually turned dark red and refluxing was continued until the correct amount of water had separated. The crude product separated on cooling, and was recrystallised from ethanol (hot filtration).

Method (*c*). *Thiolysis of arylmethylenemalononitriles with* H_2S. H_2S was bubbled through a stirred suspension of the dinitrile in dry benzene (500 ml) containing triethylamine (0.2 g) for 2 h. The crude precipitate was washed (ethanol) and recrystallised from ethanol.

[17] M. A. McCall, *J. Org. Chem.*, 1962, **27**, 2433.