Synthesis of 2-Alkoxycarbonyl Enamino Thioaldehydes and Selenaldehydes (as Pentacarbonyltungsten(0) Complexes). Improved Synthesis of Simple and 2-Cyano Enamino Thioaldehydes and some Chemical Reactions of these Compounds

Motomu Muraoka,* Tatsuo Yamamoto, and Kazuo Enomoto
Department of Chemistry, Faculty of Science, Josai University, Keyaki-Dai, Sakado, Saitama 350-02, Japan
Tatsuo Takeshima
Department of Chemistry, Faculty of Science, Chiba University, Yayoi-Cho, Chiba City 260, Japan

A series of stable 2-alkoxycarbonyl enamino thioaldehydes (**2a**—**g**) were synthesized by solvolysis of the Vilsmeier salts (**1**) with aqueous or methanolic sodium hydrogen sulphide.

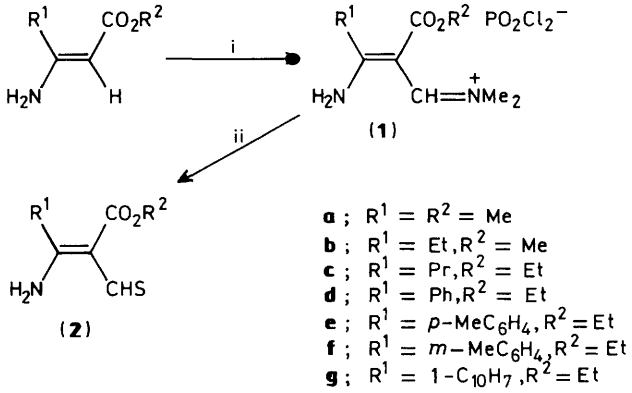
Three 2-alkoxycarbonyl enamino selenaldehydes were obtained as the pentacarbonyltungsten(0) complexes (**7a**—**c**). The 2-cyano and simple enamino thioaldehydes (**3a**—**m**) and (**6a**—**j**) (including some new homologues obtained by an improved synthetic method) are described. Some reactions of 2-cyano and 2-alkoxycarbonyl enamino thioaldehydes were examined *e.g.* oxidation with MCPBA to give the isothiazoles (**8**). The symmetrically tetrasubstituted pyridines (**9**) were produced by bimolecular cyclisation under acidic conditions: hydrolysis in acidic 95% aq. EtOH gave the enamino aldehydes (**11**) and aroylacetonitriles (**12**) together with (**9**). The imines (**13**) were formed in good yield on reaction with primary amines.

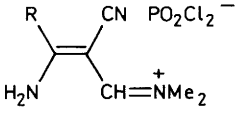
The synthesis of stable thioaldehydes has been of interest since Woodward first synthesized a thioformyldipyrrylmethane derivative[1] during the synthesis of chlorophyll-a. The stable thioaldehydes so far reported are apparently limited to those stabilised by conjugation through a hetero atom at an appropriate position. Simple thioaldehydes which are not stabilised by such conjugation are known to exist only at low temperature; the only two exceptions known are 2,4,6-tri-t-butylthiobenzaldehyde[2a] and tris(trimethylsilyl)ethanethial[2b] in which the thioformyl group is protected sterically by the neighbouring bulky t-butyl or trimethylsilyl groups.

Several reports[3] have appeared describing the generation of simple but unstable thioaldehydes and their trapping reactions with dienes or β-pinene to form Diels–Alder type or ene reaction adducts. Vedejs and co-workers first observed and characterised thiopivaldehyde[4] as a simple monomeric aliphatic thioaldehyde.

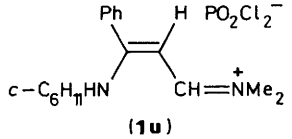
We previously found that the 3-amino-2-cyano- and 3-alkylamino-2-cyano-α,β-unsaturated thioaldehydes (**3**) were synthesized by treatment of enamino nitriles with dithioformate anion in the presence of sodium t-pentanolate.[5] These enamino thioaldehydes remain very stable for several months, even at room temperature. Several types of heterocyclic thioaldehyde[6] reported by Reid and co-workers are particularly stable.

An electron-releasing group present at the β-position stabilises α,β-unsaturated thioaldehydes.[7] The introduction of an electron-withdrawing group at the α-position of these thioaldehydes greatly enhanced their stability. Thus, compared with the 2-alkoxycarbonyl and 2-cyano enamino thioaldehydes (**2**) and (**3**), the simple enamino thioaldehydes (**6**),[8] are less stable and decompose gradually on storage at room temperature. The 2-alkoxycarbonyl enamino thioaldehydes (**2a**—**g**) are the most stable of these three types of thioaldehyde.





(**1h**) R = Me
(**1k**) R = Ph
(**1n**) R = *p*-MeC$_6$H$_4$
(**1p**) R = *m*-MeC$_6$H$_4$

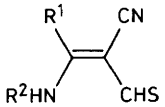


(**1u**)

Scheme 1. *Reagents:* i, DMF $POCl_3$ in DMF–THF; ii, NaHS

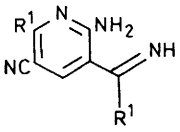
Results and Discussion

Potassium dithioformate could be used in only a limited number of cases for the thioformylation of enamino nitriles, as indicated by more detailed study on thioformylation. In some cases, by-products such as the pyridine derivatives (**4**) and (**5**) were produced by further reaction of the enamino thioaldehydes



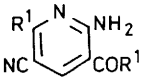
(3)

a; R^1 = Me, R^2 = H
b; R^1 = R^2 = Me
c; R^1 = Me, R^2 = Et
d; R^1 = Ph, R^2 = H
e; R^1 = Ph, R^2 = Me
f; R^1 = Ph, R^2 = Et
g; R^1 = *p*-MeC_6H_4, R^2 = H
h; R^1 = *p*-MeC_6H_4, R^2 = Me
i; R^1 = *m*-MeC_6H_4, R^2 = H
j; R^1 = *m*-MeC_6H_4, R^2 = Me
k; R^1 = *p*-$MeOC_6H_4$, R^2 = H
l; R^1 = 2-$C_{10}H_7$, R^2 = H
m; R^1 = 2-$C_{10}H_7$, R^2 = Me



(4)

a; R^1 = Me
b; R^1 = Ph
c; R^1 = *p*-$MeOC_6H_4$
d; R^1 = 2-$C_{10}H_7$



(5)

a; R^1 = Me
b; R^1 = Ph
c; R^1 = *m*-MeC_6H_4

with the starting enamino nitriles. This resulted in lesser yields of these thioaldehydes. Using this method, 3-amino-2-cyanothiocinnamaldehyde (**3d**) could not be obtained, even in a trace amount, and 3-amino-2-cyanothiocrotonaldehyde (**3a**) was formed only occasionally in low yield.

When ethyl *O*-thioformate was used instead of potassium dithioformate as the thioformylating agent, the yield of the thioaldehydes formed was not improved. The limited extent to which potassium dithioformate could be used as a thioformylating agent towards imines and several types of enamines prompted us to devise other methods for their thioformylation. The general preparation of several types of enamino thioaldehydes (**2**), (**3**), and (**6**) and enamino selenaldehyde complexes (**7**) and some of their chemical reactions such as oxidation, bimolecular cyclisation, hydrolysis, and imine formation are presented in this paper.

Treatment of an enamino ester with the Vilsmeier reagent resulted in the separation of a new Vilsmeier salt (**1**) from the reaction mixture as a very hygroscopic paste-like solid. This salt was solvolysed immediately with aqueous sodium hydrogen sulphide to obtain the corresponding 2-alkoxycarbonyl enamino thioaldehydes (**2**) as light orange crystals in high to moderate yield (Scheme 1). The thioaldehydes (**2**) were the most stable of all the thioaldehydes examined in the present study. The 2-cyano enamino thioaldehydes (**3a**—**m**) could also be produced in the same way giving essentially the same yields. The 3-amino-2-cyanothiocinnamaldehyde (**3d**) was obtained initially as light orange crystals in moderate yield. One of the simplest thioaldehydes of this series, 3-amino-2-cyanothiocrotonaldehyde (**3a**), was also formed in a 60% yield by a similar procedure. The 6 enamino thioaldehydes (**3b**—**f**) and (**3m**) were added to this series of thioaldehydes by this method. The yields of other homologous 2-cyano enamino thioaldehydes (**3**) were greatly improved by solvolysis of the corresponding new Vilsmeier salts with aqueous sodium hydrogen sulphide. Using this method, some imines and simple enamines gave the corresponding enamino thioaldehydes (**6a**—**j**) which we have previously reported, but which were generally isolated in low yields.[8] Considerably greater yields were obtained by using a freshly prepared methanolic solution instead of aqueous NaHS and prolonging the reaction time at a slightly higher temperature (see Table 1 and Experimental). In this manner, several new homologous enamino thioaldehydes, (**6a**—**b**), (**6e**—**f**), and (**6j**), were obtained. The simplest enamino thioaldehyde was 3-dimethylaminothioacrolein, whose preparation by thionation of the corresponding enamino aldehyde with P_2S_5,[7b] has been reported without specified yield.

The Vilsmeier salts (**1**) could not be isolated owing to their hygroscopicity. The only exception was the salt (**1u**), formed from α-(cyclohexylamino)styrene and the Vilsmeier reagent. This non-hygroscopic salt (**1u**) was purified by recrystallisation. When treated with methanolic NaHS for 15 min at room temperature, this salt gave thioaldehyde (**6a**) in 81% yield (overall yield, 41%). To obtain the thioaldehydes (**6**) successfully, the above procedure, including the purification of crude thioaldehydes by column chromatography, had to be carried out continuously.

Use of the Vilsmeier reagent prepared from *N*-methylformanilide and $POCl_3$ (large excess; *ca.* 3 mol equiv.) followed by solvolysis of the resulting Vilsmeier salt with methanolic NaHS improved the yield of (**6d**). In no cases could 3-amino-, -alkyl-, or -dialkylaminothioacroleins be obtained by this method of thioformylation.

Only the indole derivative[9] and indolizine and pyrrolothiazole derivatives have been reported as stable selenaldehydes.[10] Attempts by Okazaki and co-workers to synthesize 2,4,6-tri(t-butyl)selenobenzaldehyde[11] were unsuccessful since the selenobenzaldehyde was too unstable to be isolated. The direct conversion of aldehydes into selenaldehydes[13] has been developed very recently as an efficient means for generating selenaldehydes. K. Okuma and co-workers[3m] synthesized a series of selenaldehydes by the reaction of phosphonium ylides and elemental selenium; these were obtained as gem-bis(dialkylamino) derivatives on treatment with *sec*-amines *in situ*.

In the present study, we also attempted the synthesis of enamino selenaldehydes using Vilsmeier salts and aqueous NaHSe. The selenaldehydes, however, were also highly unstable and very sensitive to light. None of them corresponded to thioaldehydes (**3**). The 2-alkoxycarbonyl enamino selenaldehydes (using Teflon flasks and separating funnels for the solvolysis with aqueous NaHSe) were found to be stable for a short time in benzene solution.

The selenaldehyde pentacarbonyltungsten(0) complexes (**7**) were sufficiently stable to permit their isolation and they had definite melting points. The complexes gradually decomposed on storage in light and did so much more rapidly in solvents such as CH_2Cl_2 and $CHCl_3$. In contrast, pentacarbonyl(selenobenzaldehyde)tungsten complex[12] is much less stable.

Two geometric isomers (**3A**) and (**3C**) and their respective rotamers (**3B**) and (**3D**) are possible for the thioaldehydes (**3**). All *N*-alkylamino thioaldehydes (**3**) were found to possess an imino hydrogen according to their i.r. and ^{1}H n.m.r. spectra. The i.r. (KBr) absorption band near 3 200 cm^{-1} is attributable to NH stretching. No definite absorption band corresponding to enethiolic SH stretching could be observed. This is consistent with the inability to obtain *S*-alkylated derivatives from the thioaldehydes. The signals of thioformyl protons in the ^{1}H n.m.r. spectra ($CDCl_3$) appeared at *ca.* δ 10—10.5. A weak signal upfield, always evident at *ca.* δ 10, <0.05 H, was ascribed to the thioformyl protons of the geometrical isomers or their rotamers with no intramolecular H-bonding in compounds (**3a**), (**3d**), (**3g**), (**3i**), or (**3k**—**l**).

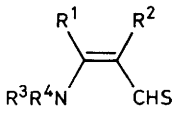
The n.m.r. spectra of the thioaldehydes (**3**) showed that the s-*trans* isomers (**3B**) and/or (**3C**) were present to a much lesser extent than the *cis*-s-*cis* isomer (**3A**), owing to hindered rotation around the C(1)–C(2) bond. No other weak peaks indicating the possible presence of *trans*-s-*cis* isomer (**3D**) could be observed in the ^{1}H n.m.r. spectra.

The ^{1}H n.m.r. spectra gave no indication of the presence of the iminoenethiol (**3E**) and imino thioformyl nitrile (**3F**) forms

Table 1. Preparation of simple enamino thioaldehydes (**6**)

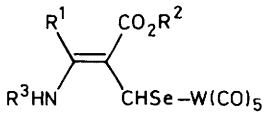
Enamino thioaldehyde	Enamine R¹	R²	R³	R⁴	Vilsmeier[a] reagent	Reaction conditions: Vilsmeier salt formation[b]	Reaction conditions: Solvolysis	Isolated yield (%) (eluant for c.c.)
(6a)	Ph	H	c-C_6H_{11}	H	$DMF–POCl_3$	i, 35 °C, 4 h; ii, r.t., 20 h (DMF)	NaHS–MeOH r.t., 1 h	38[c] (——)
(6b)	Ph	H	$(CH_2)_5$		$DMF–POCl_3$	i, 0 °C, 1 h; ii, 35 °C, 3 h; iii, r.t., 20 h (DMF)	NaHS–MeOH r.t., 1 h	37 (C_6H_6–MeCN, 8:1)
(6c)	Ph	H	$O(CH_2CH_2)_2$		$DMF–POCl_3$	i, 0 °C, 1 h; ii, 35° C, 3 h; iii, r.t., 20 h (DMF)	NaHS–MeOH r.t., 1 h	42 (C_6H_6–THF, 5:1)
(6d)	$(CH_2)_3$		$O(CH_2CH_2)_2$		$DMF–POCl_3$	i, −15 °C, 1 h; ii, r.t., 20 h (DMF)	aq. NaHS r.t., 15 min	49 (C_6H_6–MeCN–ether, 8:1:1)
(6e)	Ph	Ph	C_3H_7	H	$MFA–POCl_3$	i, 0 °C, 1 h; ii, r.t., 20 h (THF)	NaHS–MeOH 40 °C, 1 h	44 (C_6H_{14}–C_6H_6–THF, 16:3:1)
(6f)	Ph	Ph	C_6H_{13}	H	$MFA–POCl_3$	i, 0 °C, 1 h; ii, r.t., 20 h (THF)	NaHS–MeOH 40 °C, 1 h	51 (C_6H_{14}–C_6H_6–THF, 16:3:1)
(6g)	Ph	Ph	$(CH_2)_4$		$MFA–POCl_3$	i, 0 °C, 1 h; ii, 30 °C, 18 h (THF)	NaHS–MeOH 30 °C, 1 h	43 (C_6H_6–THF, 9:1)
(6h)	Ph	Ph	c-C_6H_{11}	H	$MFA–POCl_3$[d]	i, 0 °C, 1 h; ii, 30 °C, 18 h (THF)	NaHS–MeOH 40 °C, 1 h	87 (C_6H_6–THF, 19:1)
(6i)	Ph	Ph	$O(CH_2CH_2)_2$		$DMF–POCl_3$	i, 0 °C, 1 h; r.t., 20 h (DMF)	NaHS–MeOH r.t., 1 h	71 (C_6H_6–THF, 9:1)
(6j)	*o*-$C_6H_4CH_2$		$(CH_2)_5$		$DMF–POCl_3$	i, r.t., 20 h (DMF)	NaHS–MeOH r.t., 1 h	56 (C_6H_6–MeCN, 8:1)

[a] MFA = *N*-Methylformanilide. [b] Solvent in parentheses. [c] Yield by solvolysis of the isolated Vilsmeier salt (**1u**) was 41% (overall yield) (see Experimental section). [d] The enamine–MFA–$POCl_3$ = 1:1:3 mol equiv.



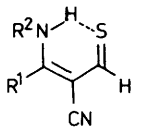
(**6**)

	R¹	R²	R³	R⁴
a;	Ph	H	*c*-C_6H_{11}	H
b;	Ph	H	$(CH_2)_5$	
c;	Ph	H	$(CH_2CH_2)_2O$	
d;	$(CH_2)_3$		$(CH_2CH_2)_2O$	
e;	Ph	Ph	C_3H_7	H
f;	Ph	Ph	C_6H_{13}	H
g;	Ph	Ph	$(CH_2)_4$	
h;	Ph	Ph	*c*-C_6H_{11}	H
i;	Ph	Ph	$(CH_2CH_2)_2O$	
j;	*o*-$C_6H_4CH_2$		$(CH_2)_5$	

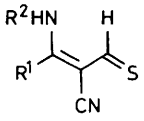


(**7**)

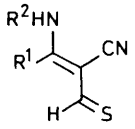
a; $R^1 = R^2 = Me$, $R^3 = H$
b; $R^1 = Ph$, $R^2 = Et$, $R^3 = H$
c; $R^1 = Ph$, $R^2 = Et$, $R^3 = Ph$



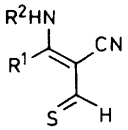
(**3A**)
cis–S–*cis*



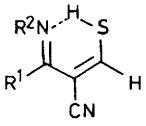
(**3B**)
cis–S–*trans*



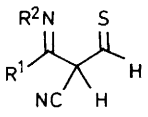
(**3C**)
trans–S–*trans*



(**3D**)
trans–S–*cis*



(**3E**)



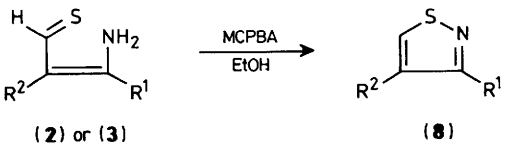
(**3F**)

of the thioaldehydes. From amino-unsubstituted enamino thioaldehydes (**2**) and (**3**), however, isothiazole derivatives were obtained in high yields by their oxidation with an organic peracid. Thus the imino enethiol form (**3E**) may possibly be present in a trace amount, at least temporarily. The thioaldehydes (**2**) showed an n.m.r. spectrum which was quite similar to those of compounds (**3**) (see Experimental section).

Enamino thioaldehydes are generally considered to be vinyl analogues of thioformamides. However, from their spectral data (particularly n.m.r. and electronic spectra) they resemble genuine thioaldehydes. This is supported by the results of the chemical reactions described below.

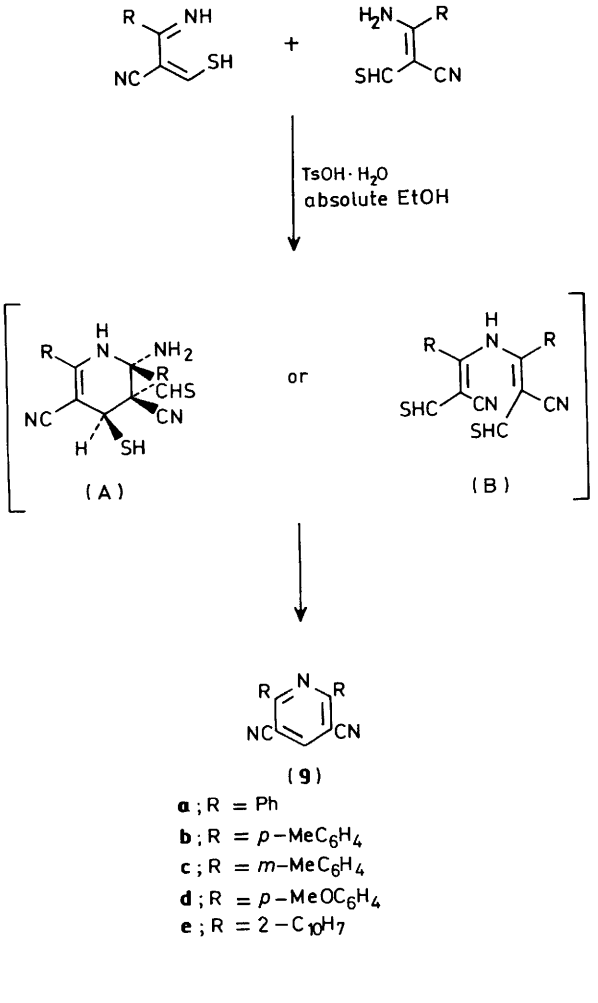
The chemical reactions of these enamino thioaldehydes, either with each other or with other reagents[7a,7c,11] (except for the trapping reactions[3] of unstable species) have been little studied owing to the scarcity of stable thioaldehydes. The following reactions of the 2-cyano enamino thioaldehydes (**3**) and 2-alkoxycarbonyl thioaldehydes (**2**) were examined: (1) oxidation with MCPBA, (2) bimolecular cyclisation reactions, (3) hydrolysis, and (4) reactions with primary amines.

(1) *Oxidation with* m-*Chloroperbenzoic Acid* (*MCPBA*).—The thioaldehydes (**2**) and (**3**), possessing no substituted amino nitrogen atoms, gave on oxidation with MCPBA in ethanolic solution at 65 °C the corresponding isothiazoles (**8**) in good



(2) or (3) (8)

a; R^1 = Me, R^2 = CO_2Me
b; R^1 = Et, R^2 = CO_2Me
c; R^1 = Ph, R^2 = CO_2Et
d; R^1 = *m*-MeC_6H_4, R^2 = CO_2Et
e; R^1 = Me, R^2 = CN
f; R^1 = Ph, R^2 = CN
g; R^1 = *p*-MeC_6H_4, R^2 = CN
h; R^1 = *m*-MeC_6H_4, R^2 = CN
i; R^1 = *p*-$MeOC_6H_4$, R^2 = CN
j; R^1 = 2-$C_{10}H_7$, R^2 = CN



(A) (B)

(9)

a ; R = Ph
b ; R = *p*-MeC_6H_4
c ; R = *m*-MeC_6H_4
d ; R = *p*-$MeOC_6H_4$
e ; R = 2-$C_{10}H_7$

(10)

Scheme 2.

yield. The reactions proceeded smoothly to completion under reflux using 1.5 mol equiv. of MCPBA.

Use of iodine instead of MCPBA gave only an intractable tarry material. Treatment with sulphur powder partially oxidised the thioaldehydes to isothiazoles with recovery possible in most cases. Alkylamino analogues also gave tarry material on oxidation.

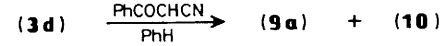
The formation of isothiazoles from the enamino thioaldehydes indicated the possibility of synthesizing enamino thioaldehydes from isothiazoles. Recently, Hassan and co-workers [13] reported that isothiazolium salts with substituents on the 3- or 5-position, or both, gave enamino thioaldehydes on treatment with benzylamine, but they neither isolated nor characterised the products.

I.r., ^{1}H n.m.r., and electronic spectra, together with elemental analyses of compounds (**8**), were in good agreement with their proposed structures.

(2) *Bimolecular Cyclisation Reactions.*—The amino-unsubstituted thioaldehydes (**3d**), (**3g**), and (**3i**), when refluxed in absolute ethanol at 80 °C in the presence of a strong acid, gave 3,5-dicyano-2,6-diarylpyridines (**9a**—**c**) (Scheme 2) in moderate yields. One possible pathway is that the tetrahydropyridine derivative (**A**) is first formed by a Diels–Alder type cycloaddition between tautomeric iminoenethiol and enamino thioaldehyde, followed by elimination of ammonia and dithioformic acid to give the pyridines.

Another possible mechanism could be the elimination of ammonia from two molecules of enamino thioaldehyde to form the intermediate (**B**) (Scheme 2). This would in turn produce the final product through several cyclisation steps. Strong acids such as sulphuric or *p*-toluenesulphonic acid may be necessary to promote elimination of the leaving molecules leading to the final product.

The ^{1}H n.m.r. spectra of these pyridines were fully consistent with the proposed symmetrical structures. The ^{13}C n.m.r. spectrum of (**9c**) was also in good agreement with the structure proposed. In the bimolecular cyclisation with 2-cyanothiocinnamaldehyde (**3d**) a by-product, 6-amino-5-benzoyl-3-cyano-2-phenylpyridine (**10**) was always obtained in low yield (best yield 22%). This compound may possibly be formed by reaction of the thioaldehyde (**3d**) and benzoylacetonitrile produced by decarbonylation of the 3-ketoaldehyde [2-cyanobenzoylacetaldehyde, formed by a two-step hydrolysis of (**3d**)]. The yield of compound (**10**) was reduced when the thioaldehyde (**3d**) was allowed to react with benzoylacetonitrile under the same reaction conditions. Compound (**10**) was separately



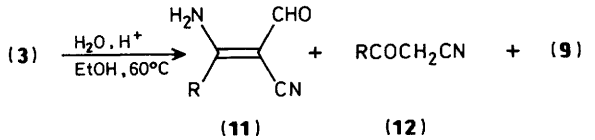
(**3d**) (**9a**) + (**10**)

synthesized (in 41% yield) by treatment of (**3d**) with benzoylacetonitrile anion together with pyridine derivative (**9a**) (yield 37.5%).

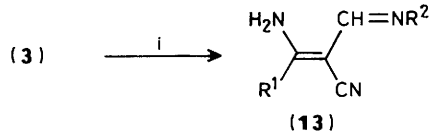
(3) *Hydrolysis.*—We decided to investigate which of the two functional groups, enamino or thioformyl, was more susceptible to hydrolysis. Thus, when each enamino thioaldehyde (**3**) in 95% ethanol was refluxed at 60 °C in the presence of sulphuric acid, the enamino aldehydes (**11**) were obtained as major products in moderate yields accompanied by aroylacetonitriles (**12**) produced by further hydrolysis of the enamino aldehydes (**11**) and decarbonylation of unstable 2-cyano 3-keto aldehydes. In addition to hydrolysis, bimolecular cyclisation also occurred to some extent to give the pyridine derivatives (**9a**—**b**) and (**9d**—**e**). The results are shown in Table 2. The direct synthesis of the 2-cyano enamino aldehydes (**11**) from the corresponding Vilsmeier salts (**1**) was also investigated. More vigorous hydrolysis was found necessary to convert the Vilsmeier salts into the enamino aldehydes (**11**) and this direct hydrolysis was noted to be effective for a limited number of cases (see Experimental section).

(4) *Reactions with Primary Amines.*—The thioaldehydes (**3g**), (**3i**), and (**3k**—**l**) were each mixed with 1 mol equiv. of a primary amine in ethanol and the resulting clear solution was allowed to stand overnight at room temperature. The corresponding imines (**13**) were formed in good yields (Scheme 3).

Table 2. Hydrolysis of Thioaldehydes (**3**)



	R	%(11)	%(12)	%(9)
a	Ph	57.5	14	28
b	*p*-MeC_6H_4	53	2	13
c	*p*-$MeOC_6H_4$	46	37	14
d	2-$C_{10}H_7$	58	0	7



a; R^1 = *p*-MeC_6H_4, R^2 = Ph
b; R^1 = *m*-MeC_6H_4, R^2 = Ph
c; R^1 = *m*-MeC_6H_4, R^2 = c-C_6H_{11}
d; R^1 = *p*-$MeOC_6H_4$, R^2 = Ph
e; R^1 = *p*-$MeOC_6H_4$, R^2 = c-C_6H_{11}
f; R^1 = 2-$C_{10}H_7$, R^2 = Ph
g; R^1 = 2-$C_{10}H_7$, R^2 = c-C_6H_{11}

Scheme 3. *Reagents and conditions:* i, R^2NH_2, room temp.

The reactions of some of these enamino thioaldehydes (**2**) and (**3**) with various carbanions are now being studied and the results will be reported elsewhere.

Experimental

M.p.s and b.p.s are uncorrected. ^1H N.m.r. spectra were determined with a JEOL JNM-GX270-FT spectrometer operating at 270 MHz with tetramethylsilane as internal standard. I.r. spectra were determined with a JASCO A-302 spectrophotometer. U.v. and visible spectra were obtained on a Hitachi 557 double-wavelength double-beam spectrophotometer. Molecular weights were determined with a Hitachi Perkin-Elmer 115 molecular weight apparatus. When the crude products to be chromatographed were sparingly soluble in the appropriate eluant they were pre-adsorbed on silica gel. All solvents used for reactions and column chromatography were dried and distilled before use. Ether refers to diethyl ether throughout.

Starting Materials.—3-Aminocinnamic acid esters were prepared by the usual method from arylmagnesium bromide and ethyl cyanoacetate.[14] Ethyl 3-amino-3′-methylcinnamate (56%), b.p. 110 °C/0.15 mmHg, $\nu_{max.}$(KBr) 3 430, 3 315, 2 965, 1 730, 1 656, 1 607, 1 550, 1 306, and 1 160 cm^{-1}; $\delta_H(CDCl_3)$ 7.6—7.0 (4 H, m, C_6H_4), 4.91 (1 H, s, vinylic H), 4.12 (2 H, q, CH_2CH_3), 2.33 (3 H, s, 3′-CH_3), and 1.24 (3 H, t, CH_2CH_3). Ethyl 3-amino-3-(1-naphthyl)acrylate (3%) [non-volatile residue was flash-chromatographed (×3) on silica gel using the following eluant systems: first, benzene–acetonitrile (18:1); second, benzene; and finally, ether–hexane (2:1)], b.p. 161 °C/0.1 mmHg, $\nu_{max.}$(KBr) 3 480, 3 440, 3 330, 3 045, 2 985, 1 740, 1 662, 1 609, 1 551, 1 399, 1 310, and 1 176 cm^{-1}; $\delta_H(CDCl_3)$ 8.22 and 4.90 (each 0.5 H, each br s, NH_2), 8.20—7.30 (8 H, m, $C_{10}H_7$ and vinylic H), 4.13 (2 H, q, CH_2), and 1.26 (3 H, t, CH_3); *m/z* 241 (M^+, 53%), 168 ($M^+ - CO_2C_2H_5$, 100%), and 155 ($M^+ - 86$, 33%).

The enamino nitriles were prepared by known preparative methods.[15] Simple enamines and imines were also prepared by the usual method using toluene-*p*-sulphonic acid monohydrate as catalyst[16] and purified by fractional distillation followed by repeated flash-chromatography on silica gel. An example of the preparation of new enamines is as follows. A mixture of deoxybenzoin (3.9 g, 20 mmol), cyclohexylamine (4.0 g, 40 mmol), toluene-*p*-sulphonic acid monohydrate (0.19 g, 1 mmol), and toluene (50 ml) was refluxed for 1 day in a flask (200 ml) fitted with a Dean–Stark trap fitted with NaOH. After volatile material had been removed from the reaction mixture, the residue was fractionally distilled to obtain a fraction (4.75 g, b.p. 154 °C/0.15 mmHg), which was flash-chromatographed on silica gel using hexane–ether (9:1) as eluant to give pure *α-cyclohexylaminostilbene* (isolated yield 81%), b.p. 147 °C/0.25 mmHg, $\nu_{max.}$(KBr) 3 070, 3 040, 2 940, 2 860, 1 630, 1 600, 1 500, and 1 449 cm^{-1}; $\delta_H(CDCl_3)$ 8.0—6.4 (*ca.* 10.5 H, m, Ph × 2 and vinylic H), 3.81 (0.6 H, s, N=CCH_2Ph), 3.57 [*ca.* 1 H, m, =NCH(CH_2)$_2$], 2.92 (*ca.* 0.4 H, br s, NH), and 1.9—1.05 [10 H, m, $(CH_2)_5$]; *m/z* 277 (M^+, 2%), 186 ($M^+ - 91$, 17%), 104 (100%). Other new enamines and imines were prepared in the same way: *α-propylaminostilbene* (21%), b.p. 124.5 °C/0.15 mmHg; $\nu_{max.}$(KBr) 3 335w, 3 070, 2 970, 2 940, 2 885, 1 672, 1 596, 1 580, 1 450, 1 220, and 1 180 cm^{-1}; $\delta_H(CDCl_3)$ 8.0—7.2 (*ca.* 11 H, m, Ph × 2 and vinylic H), 3.86 (*ca.* 0.2 H, br s, NH), 3.56—3.40 (2 H, 3 × t, NC$H_2$$CH_2$$CH_3$ in each tautomer), 1.82—1.55 (2 H, mixed sextuplets, $NCH_2CH_2CH_3$ in each tautomer), and 1.02—0.82 (3 H, mixed triplets, CH_3); *α-hexylaminostilbene* (53%) b.p. 152 °C/0.15 mmHg; $\nu_{max.}$(KBr) 3 330w, 3 065, 3 030, 2 940, 2 860, 1 674, 1 625, 1 598, 1 580, 1 450, and 1 222 cm^{-1}; $\delta_H(CDCl_3)$ 8.26—7.20 (*ca.* 10 H, Ph × 2 and vinylic H), 3.60 and 3.44 (0.15 H and 1.85 H, each t, NC$H_2$$C_5H_{11}$ in each tautomer), 2.03 (0.15 H, br s, NH), 1.70 (2 H, quintet, $NCH_2CH_2C_4H_9$), 1.34—1.10 (6 H, m, $NC_2H_4C_3H_6CH_3$), and 1.25 (3 H, t, $NC_5H_{11}CH_3$); *1-piperidinoindene* (16%), b.p. 87 °C/0.1 mmHg; $\nu_{max.}$(KBr) 3 070, 3 030, 2 945, 2 860, 2 800, 1 715, 1 597, 1 574, 1 467, 1 454, 1 443, 1 375, and 1 244 cm^{-1}; $\delta_H(CDCl_3)$ 7.73—7.11 (4 H, m, ArH), 5.46 (1 H, t, NC=CH), 3.24 (2 H, d, NC=CHCH_2), 3.00 [4 H, t, N(CH_2)$_2$], 1.72 (4 H, quintet, 3′-H_2 and 5′-H_2), and 1.56 (2 H, t, 4′-H_2); *m/z* 199 (M^+, 69%) and 115 ($M^+ - 84$, 100%).

The enamines and imines used here contained a small quantity of starting ketone, even after repeated chromatography.

Preparation of the 2-Alkoxycarbonyl Enamino Thioaldehydes (**2a—g**)*: Solvolysis of the Vilsmeier Salts* (**1**) *with Sodium Hydrogen Sulphide.—General procedure.* A solution of phosphoryl chloride (0.5 ml, 5.5 mmol) in dimethylformamide (DMF) (1.5 ml) was added dropwise during 10 min to a stirred solution of an enamino ester (5 mmol) in tetrahydrofuran (THF) (10 ml) with the temperature maintained at 0 °C. The resulting mixture was stirred at this temperature for a further 1 h at room temperature and then for 4 h at 30 °C; it was then allowed to stand overnight in a refrigerator. Addition of ether in portions at 0 °C precipitated a highly hygroscopic yellowish white to yellow solid from which ether was removed by decantation. The solid remaining was washed several times with ether until the ether layer became clear. The solid was then dissolved in dichloromethane (250 ml) in a separating funnel (1 l) and to this was added aqueous sodium hydrogen sulphide (2M; 25 ml). The mixture was shaken vigorously and the water layer was extracted with dichloromethane (30 ml). The combined organic extracts were washed with water (×6), dried ($MgSO_4$) and evaporated to give orange crystals (or an oil when R^1 = Pr). Compound (**2a**) was obtained pure [t.l.c. comparison with a thick solution of crude (**2a**)], which was purified only by recrystallisation. Column chromatography of the orange residue (**2b—g**) on silica gel [Merck, 60 (70—230 mesh)] using

benzene–ether (8:1) or benzene–acetonitrile (8:1) as eluant gave the pure thioaldehydes (**2**). The work-up procedure from the solvolysis of the Vilsmeier salts with sodium hydrogen sulphide to purification of each crude thioaldehyde by column chromatography was finished without interval. Compound (**2c**) has a low melting point and was purified by chromatography followed by distillation under reduced pressure using a heating block.

Methyl 3-*amino*-2-*thioformylcrotonate* (**2a**). Yield 83%, m.p. 110.5—111 °C (from benzene–hexane); $\nu_{max.}$(KBr) 3 300, 1 643, 1 442, 1 361, 1 279, 1 248, and 1 030 cm^{-1}; $\lambda_{max.}$(EtOH) 216 (log ε 4.17), 256 (4.09), and 354.5 nm (4.32); $\delta_H(CDCl_3)$ 13.94 and 6.83 (1 H, each br s, NH_2), 10.97 (1 H, s, CHS), 3.79 (3 H, s, OCH_3), and 2.58 (3 H, s, CH_3) (Found: C, 45.5; H, 5.9; N, 8.9; S, 20.05. $C_6H_9NO_2S$ requires C, 45.3; H, 5.7; N, 8.8; S, 20.1%).

Methyl 3-*amino*-2-*thioformylpent*-2-*enoate* (**2b**). Yield 48%, m.p. 52.5—53 °C (from hot benzene–hexane); $\nu_{max.}$(KBr) 3 355, 1 679, 1 635, 1 427, 1 392, 1 308, 1 252, 1 228, 1 025, and 994 cm^{-1}; $\lambda_{max.}$(EtOH) 216 (log ε 4.16), 257 (4.07), and 355 nm (4.32); $\delta_H(CDCl_3)$ 14.20 and 6.70 (1 H, each br s, NH_2), 10.97 (1 H, s, CHS), 3.79 (3 H, s, OCH_3), 3.00 (2 H, q, CH_2), and 1.30 (3 H, t, CH_3) (Found: C, 48.4; H, 6.5; N, 7.6; S, 18.5. $C_7H_{11}NO_2S$ requires C, 48.5; H, 6.4; N, 8.4; S, 18.5%).

Ethyl 3-*amino*-2-*thioformylhex*-2-*enoate* (**2c**). Yield 71%, m.p. 25—26 °C, b.p. 144 °C/0.23 mmHg; $\nu_{max.}$(KBr) 3 315br, 1 695, 1 671, 1 630, 1 459, 1 440, 1 363, 1 260, 1 240, 1 117, and 1 030 cm^{-1}; $\lambda_{max.}$(EtOH) 217 (log ε 4.13), 259 (4.09), and 357 (4.25); $\delta_H(CDCl_3)$ 14.00 and 6.97 (1 H, each br s, NH_2), 10.94 (1 H, s, CHS), 4.25 (2 H, q, OCH_2), 2.88 (2 H, t, $CH_2CH_2CH_3$), 1.71 (2 H, sext, $CH_2CH_2CH_3$), 1.33 (3 H, t, OCH_2CH_3), and 1.05 (3 H, t, $CH_2CH_2CH_3$) (Found: C, 53.9; H, 7.8; N, 6.7; S, 15.75. $C_9H_{15}NO_2S$ requires C, 53.7; H, 7.5; N, 7.0; S, 15.9%).

Ethyl 3-*amino*-3-*phenyl*-2-*thioformylacrylate* (**2d**). Yield 69%, m.p. 135.5—137 °C (from hot benzene–hexane); $\nu_{max.}$(KBr) 3 275, 1 656, 1 629, 1 460, 1 440, 1 364, 1 344, 1 280, and 1 028 cm^{-1}; $\lambda_{max.}$(EtOH) 215 (log ε 4.20), 2.63 (4.03), 369 (4.32), and 458 nm (3.43); $\delta_H(CDCl_3)$ 13.67 and 6.65 (1 H, each br s, NH_2), 10.87 (1 H, s, CHS), 7.5—7.2 (5 H, m, Ph), 3.90 (2 H, q, OCH_2), and 0.93 (3 H, t, CH_3) (Found: C, 61.3; H, 5.7; N, 6.1; S, 13.4. $C_{12}H_{13}NO_2S$ requires C, 61.25; H, 5.6; N, 5.95; S, 13.6%).

Ethyl 3-*amino*-2-*thioformyl*-3-(p-*tolyl*)*acrylate* (**2e**). Yield 83%, m.p. 90.5—92 °C (from hot benzene–hexane); $\nu_{max.}$(KBr) 3 260sh, 3 225, 1 670, 1 632, 1 444, 1 360, 1 278, 1 239, 1 161, 1 120, 1 110, 1 024, and 981 cm^{-1}; $\lambda_{max.}$(EtOH) 215 (log ε 4.25), 267 (4.10), and 371 nm (4.35); $\delta_H(CDCl_3)$ 13.45 and 6.98 (each 1 H, each br s, NH_2), 10.81 (1 H, s, CHS), 7.23 (4 H, s, C_6H_4), 3.88 (2 H, q, CH_2), 2.40 (3 H, s, 4′-CH_3), and 0.93 (3 H, t, CH_2CH_3) (Found: C, 62.6; H, 6.1; N, 5.9; S, 12.8. $C_{13}H_{15}NO_2S$ requires C, 62.6; H, 6.1; N, 5.6; S, 12.8%).

Ethyl 3-*amino*-2-*thioformyl*-3-(m-*tolyl*)*acrylate* (**2f**). Yield 80%, m.p. 142—143 °C (from hot benzene–hexane); $\nu_{max.}$(KBr) 3 290, 1 655, 1 624, 1 469, 1 440, 1 396, 1 366, 1 350, 1 283, 1 220, and 1 035 cm^{-1}; $\lambda_{max.}$(EtOH) 236 (log ε 4.04), 369 (4.33), and 459 nm (2.43); $\delta_H[(CD_3)_2SO]$ 13.14 and 10.11 (1 H, each br s, NH_2), 10.55 (1 H, s, CHS), 7.40—7.20 (4 H, m, C_6H_4), 3.82 (2 H, q, CH_2), 2.37 (3 H, s, 3′-CH_3), and 0.79 (3 H, t, CH_2CH_3) (Found: C, 62.7; H, 6.2; N, 5.5; S, 12.6. $C_{13}H_{15}NO_2S$ requires C, 62.6; H, 6.1; N, 5.6; S, 12.8%).

Ethyl 3-*amino*-3-(1-*naphthyl*)-2-*thioformylacrylate* (**2g**). Yield 35%, m.p. 145.5—146.5 °C (from benzene–hexane); $\nu_{max.}$(KBr) 3 285, 1 658, 1 623, 1 467, 1 442, 1 382, 1 364, 1 348, 1 273, 1 040, and 1 023 cm^{-1}; $\lambda_{max.}$(EtOH) 219 (log ε 4.87), 262 (4.10), and 368 nm (4.38); $\delta_H(CDCl_3)$ 13.83 and 7.07 (each 1 H, each br s, NH_2), 10.93 (1 H, s, CHS), 7.90—7.22 (7 H, m, $C_{10}H_7$), 3.34 (2 H, q, CH_2), and 0.40 (3 H, t, CH_3) (Found: C, 67.3; H, 5.3; N, 5.1; S, 11.2. $C_{16}H_{15}NO_2S$ requires C, 67.3; H, 5.3; N, 4.9; S, 11.2%).

Preparation of the 2-*Cyano Enamino Thioaldehydes* (**3a**—**m**)

Method A: Solvolysis of the Vilsmeier Salts (**1**) *with Sodium Hydrogen Sulphide.—General procedure.* The thioaldehydes (**3**) were prepared by a similar procedure to that used in the preparation of compounds (**2**). The resulting mixture was stirred for an additional 2 h at −15 °C and kept overnight in a refrigerator (< −15 °C). The work-up procedure was the same as that for compounds (**2**); purification by column chromatography was performed within half a day. Newly synthesized thioaldehydes prepared were (**3b**—**f**) and (**3m**). Spectral data of known compounds (**3**)[5] was recorded again using high performance instruments.

For the preparation of thioaldehyde (**3d**), it was necessary to complete the procedure, including formation of the corresponding Vilsmeier salt, within 24 h because the crude thioaldehyde when set aside overnight at this stage gave only an orange oil that failed to solidify even after purification by chromatography. The yield of thioaldehyde (**3i**) was greatly reduced unless the quantity of solvent used in the preparation of the Vilsmeier salt was half that used in the other reactions. Acetone was used for the molecular weight measurements.

3-*Amino*-2-*cyanothiocrotonaldehyde* (**3a**) Yield 60%, m.p. 137—138 °C (from dichloromethane–hexane); $\nu_{max.}$(KBr) 3 220, 2 220, 1 648, 1 448, 1 372, 1 242, 1 005, 935, 907, and 756 cm^{-1}; $\lambda_{max.}$(EtOH) 247 (log ε 3.91) and 364.5 nm (4.18); $\delta_H(CDCl_3)$ 13.17 and 6.88 (1 H, each br s, NH_2), 10.48 (1 H, s, CHS), and 2.43 (3 H, s, CH_3); *M* (VPO; vapour phase osmometry), 125.6 (theory, 126.19) (Found: C, 47.8; H, 4.9; N, 22.0; S, 25.1. Calc. for $C_5H_6N_2S$: C, 47.6; H, 4.8; N, 22.2; S, 25.4%).

2-*Cyano*-3-*methylaminothiocrotonaldehyde* (**3b**). Yield 61%, m.p. 79.5—80.5 °C (decomp.) (from THF–hexane); $\nu_{max.}$(KBr) 2 800, 2 220, 1 606, 1 496, 1 318, 1 230, 967, 920, and 830 cm^{-1}; $\lambda_{max.}$(EtOH) 247 (log ε 3.91) and 371 nm (4.32); $\delta_H(CDCl_3)$ 14.12 (1 H, br s, NH), 10.20 (1 H, s, CHS), 3.18 (3 H, d, NCH_3), and 2.41 (3 H, s, CH_3); *M* (VPO), 140.5 (140.22) (Found: C, 51.6; H, 5.8; N, 20.1; S, 22.9. $C_6H_8N_2S$ requires C, 51.4; H, 5.75; N, 20.0; S, 22.9%).

2-*Cyano*-3-*ethylaminothiocrotonaldehyde* (**3c**). Yield 73%, m.p. 124.5—125 °C (from THF–hexane); $\nu_{max.}$(KBr) 2 960, 2 920, 2 760, 2 220, 1 620, 1 511, 1 463, 1 365, 1 312, 1 235, 1 059, 939, and 798 cm^{-1}; $\lambda_{max.}$(EtOH) 247 (log ε 3.92) and 372 nm (4.32); $\delta_H(CDCl_3)$ 14.17 (1 H, br s, NH), 10.19 (1 H, s, CHS), 3.56 (2 H, dq, NCH_2), 2.40 (3 H, s, CH_3), and 1.41 (3 H, t, NCH_2CH_3); *M* (VPO), 153.9 (154.25) (Found: C, 54.4; H, 6.65; N, 17.9; S, 20.9. $C_7H_{10}N_2S$ requires C, 54.5; H, 6.5; N, 18.2; S, 20.8%).

3-*Amino*-2-*cyanothiocinnamaldehyde* (**3d**). Yield 53%, m.p. 120—121 °C (from benzene–hexane); $\nu_{max.}$(KBr) 3 230, 2 925, 2 220, 1 634, 1 490, 1 446, 1 428, 1 360, 1 258, 1 175, 1 145, 995, 874, 778, 744, and 698 cm^{-1}; $\lambda_{max.}$(EtOH) 257 (log ε 3.93) and 374 nm (4.35); $\delta_H(CDCl_3)$ 13.35 and 6.63 (*ca.* 1 H, each br s, NH_2), 10.68 (1 H, s, CHS), 10.40 (0.04 H, s, isomer CHS), 7.5—7.6 (5 H, m, Ph), and 5.9 (0.08 H, br s, isomer NH_2); *M* (VPO), 189.6 (188.24) (Found: C, 64.0; H, 4.3; N, 14.7; S, 17.1. $C_{10}H_8N_2S$ requires C, 63.8; H, 4.3; N, 14.9; S, 17.0%).

2-*Cyano*-3-*methylaminothiocinnamaldehyde* (**3e**). Yield 81%, m.p. 131—132 °C (from dichloromethane–hexane); $\nu_{max.}$(KBr) 3 200, 3 095, 3 020, 2 930, 2 200, 1 590, 1 458, 1 420, 1 394, 1 352, 1 300, 1 149, 1 048, 976, 763, and 700 cm^{-1}; $\lambda_{max.}$(EtOH) 218 (log ε 4.19), 255 (3.88), and 374 nm (4.36); $\delta_H(CDCl_3)$ 14.30 (*ca.* 1 H, br s, NH), 10.38 (*ca.* 1 H, s, CHS), 9.89 (0.01 H, s, isomer CHS), 7.3—7.6 (5 H, m, Ph), 5.9 (0.01 H, br s, isomer NH), and 2.98 (3 H, d, NCH_3); *M* (VPO), 201.2 (202.27) (Found: C, 65.5; H, 5.2; N, 13.6; S, 15.6. $C_{11}H_{10}N_2S$ requires C, 65.3; H, 5.0; N, 13.9; S, 15.85%).

2-*Cyano*-3-*ethylaminothiocinnamaldehyde* (**3f**). Yield 70%, m.p. 90—91.5 °C (from benzene–hexane); $\nu_{max.}$(KBr) 2 980, 2 930, 2 750, 2 200, 1 590, 1 570, 1 470, 1 352, 1 300, 1 172, 1 036,

996, 936, 898, 851, 769, and 708 cm^{-1}; $\lambda_{max.}$(EtOH) 219 (log ε 4.03), 254 (3.89), and 377 nm (4.36); $\delta_H(CDCl_3)$ 14.37 (*ca.* 1 H, br s, NH), 10.37 (*ca.* 1 H, s, CHS), 9.88 (0.01 H, s, isomer CHS), 7.3—7.6 (5 H, m, Ph), 6.73 (0.01 H, br s, isomer NH), 3.33 (2 H, q, NCH_2), and 2.28 (3 H, t, NCH_2CH_3); *M* (VPO), 220.8 (216.32) (Found: C, 66.6; H, 5.7; N, 12.7; S, 15.0. $C_{12}H_{12}N_2S$ requires C, 66.6; H, 5.6; N, 13.0; S, 14.9%).

3-*Amino*-2-*cyano*-4′-*methylthiocinnamaldehyde* (**3g**). Yield 83%, m.p. 155—156 °C (from dichloromethane–hexane); $\nu_{max.}$(KBr) 3 270, 2 200, 1 630, 1 448, 1 344, 1 249, 1 192, 1 168, 1 141, 999, 882, 824, and 700 cm^{-1}; $\lambda_{max.}$(EtOH) 265 (log ε 3.90) and 378 nm (4.36); $\delta_H(CDCl_3)$ 13.28 and 6.82 (0.95 H, each br s, NH_2), 10.59 (0.95 H, s, CHS), 9.91 (0.05 H, s, isomer CHS), 7.37 and 7.29 (2 H, each *ca.* d, C_6H_4), 6.18 (0.1 H, br s, isomer NH_2), and 2.44 (3 H, s, CH_3); *M* (VPO), 202.5 (202.27) (Found: C, 65.4; H, 4.95; N, 14.05; S, 16.0. Calc. for $C_{11}H_{10}N_2S$: C, 65.3; H, 5.0; N, 13.9; S, 15.85%).

2-*Cyano*-3-*methylamino*-4′-*methylthiocinnamaldehyde* (**3h**). Yield 62%, m.p. 127—128 °C (from THF–hexane); $\nu_{max.}$(KBr) 3 200, 3 100, 3 030, 2 200, 1 597, 1 440, 1 422, 1 398, 1 377, 1 300, 1 146, 1 044, 978, 820, 778, and 717 cm^{-1}; $\lambda_{max.}$(EtOH) 261 (log ε 3.86) and 379 nm (4.38); $\delta_H(CDCl_3)$ 14.26 (1 H, br s, NH), 10.35 (1 H, s, CHS), 7.37 and 7.29 (2 H, each *ca.* d, C_6H_4), 2.99 (3 H, d, NCH_3), and 2.93 (3 H, d, CH_3); *M* (VPO), 216.0 (216.32) (Found: C, 66.7; H, 5.6; N, 12.7; S, 14.7. Calc. for $C_{12}H_{12}N_2S$: C, 66.6; H, 5.6; N, 12.95; S, 14.8%).

3-*Amino*-2-*cyano*-3′-*methylthiocinnamaldehyde* (**3i**). Yield 69%, m.p. 125.5—126.5 °C (from dichloromethane–hexane); $\nu_{max.}$(KBr) 3 250, 2 940, 2 200, 1 632, 1 460, 1 400, 1 354, 1 260, 1 209, 1 178, 1 138, 1 010, 996, 794, 720, 706, 688, and 675 cm^{-1}; $\lambda_{max.}$(EtOH) 261 (log ε 3.88) and 376 nm (4.35); $\delta_H(CDCl_3)$ 13.36 and 6.63 (*ca.* 1 H, each br s, NH_2), 10.66 (*ca.* 1 H, s, CHS), 10.34 (0.03 H, s, isomer CHS), 7.44 (4 H, s, C_6H_4), 5.9 (0.06 H, br s, isomer NH_2), and 2.45 (3 H, s, CH_3); *M* (VPO), 203.3 (202.27) (Found: C, 65.5; H, 5.1; N, 14.3; S, 16.0. Calc. for $C_{11}H_{10}N_2S$: C, 65.3; H, 5.0; N, 13.9; S, 15.85%).

2-*Cyano*-3-*methylamino*-3′-*methylthiocinnamaldehyde* (**3j**). Yield 75%, m.p. 123—124 °C (from benzene–hexane); $\nu_{max.}$(KBr) 3 230, 2 210, 1 564vs, 1 436, 1 418, 1 375vs, 1 292, 1 136, 1 140, 980, 896, 784, and 714 cm^{-1}; $\lambda_{max.}$(EtOH) 258 (log ε 3.79) and 378 nm (4.36); $\delta_H(CDCl_3)$ 14.27 (*ca.* 1 H, br s, NH), 10.36 (*ca.* 1 H, s, CHS), 9.90 (0.04 H, s, isomer CHS), 7.0—7.5 (4 H, m, C_6H_4), 5.9 (0.04 H, br s, isomer NH), 2.97 (3 H, d, NCH_3), and 2.45 (3 H, s, CH_3); *M* (VPO), 221.8 (216.32) (Found: C, 66.3; H, 5.6; N, 12.7; S, 14.55. Calc. for $C_{12}H_{12}N_2S$: C, 66.6; H, 5.6; N, 13.0; S, 14.8%).

3-*Amino*-2-*cyano*-4′-*methoxythiocinnamaldehyde* (**3k**). Yield 88%, m.p. 184—185 °C (from dichloromethane–hexane); $\nu_{max.}$(KBr) 3 390, 2 900, 2 210, 1 632, 1 608, 1 452, 1 353, 1 308, 1 272, 1 188, 1 150, 1 027, 996, 890, 848, and 708 cm^{-1}; $\lambda_{max.}$(EtOH) 222 (log ε 4.20), 266 (3.74), 297 (3.74), and 381 nm (4.43); $\delta_H(CDCl_3)$ 13.30 and 6.56 (*ca.* 1 H, each br s, NH_2), 10.63 (*ca.* 1 H, s, CHS), 10.39 (*ca.* 0.01 H, s, isomer CHS), 7.65 and 7.05 (2 H, each *ca.* d, C_6H_4), 5.85 (0.01 H, br s, isomer NH_2), and 3.89 (3 H, s, CH_3); *M* (VPO), 216.8 (218.27) (Found: C, 60.7; H, 4.75; N, 12.7; S, 15.1. Calc. for $C_{11}H_{10}N_2OS$: C, 60.5; H, 4.6; N, 12.8; S, 14.7%).

2-(1-*Amino*-2-*cyano*-2-*thioformylvinyl*)*naphthalene* (**31**). Yield 70%, m.p. 168.5—169.5 °C (from chloroform–hexane); $\nu_{max.}$(KBr) 3 250, 2 210, 1 630, 1 479, 1 445, 1 422, 1 358, 1 342, 1 256, 1 230, 1 142, 1 116, 1 004, 912, 860, 812, 748, and 700 cm^{-1}; $\lambda_{max.}$(EtOH) 250 (log ε 4.09), 255 (4.09), 265 (4.11), and 381 nm (4.41); $\delta_H(CDCl_3)$ 13.44 and 6.74 (*ca.* 1 H, each br s, NH_2), 10.71 (*ca.* 1 H, s, CHS), 10.47 (0.03 H, s, isomer CHS), 7.6—8.2 (7 H, m, $C_{10}H_7$), and 6.0 (0.06 H, br s, isomer NH_2); *M* (VPO) 233.6 (238.32) (Found: C, 70.3; H, 4.4; N, 11.7; S, 13.3. Calc. for $C_{14}H_{10}N_2S$: C, 70.6; H, 4.2; N, 11.8; S, 13.45%).

2-(2-*Cyano*-1-*methylamino*-2-*thioformylvinyl*)*naphthalene* (**3m**). Yield 52%, m.p. 145—146 °C (from dichloromethane–hexane); $\nu_{max.}$(KBr) 3 230, 2 200, 1 575, 1 565, 1 416, 1 372, 1 298, 1 142, 1 120, 1 040, 984, 813, 752, and 712 cm^{-1}; $\lambda_{max.}$(EtOH) 221 (log ε 4.87), 250 (4.09), and 378 nm (4.36); $\delta_H(CDCl_3)$ 14.36 (*ca.* 1 H, br s, NH), 10.41 (*ca.* 1 H, s, CHS), 9.93 (0.02 H, s, isomer CHS), 7.3—8.1 (7 H, m, $C_{10}H_7$), 5.5 (0.02 H, br s, isomer NH), and 2.99 (3 H, d, NCH_3); *M* (VPO), 252.8 (252.35) (Found: C, 71.7; H, 4.75; N, 11.4; S, 13.0. $C_{15}H_{12}N_2S$ requires C, 71.4; H, 4.8; N, 11.1; S, 12.7%).

Method B: Thioformylation of Enamino Nitriles with Potassium Dithioformate.—(a) *Improved preparation of potassium dithioformate.* Potassium dithioformate was prepared conveniently in high yield by an improvement in Engler's method.[17] To dried methanol (400 ml), potassium (40 g, 1.03 mol) was added with cooling. Dry hydrogen sulphide was passed through the solution for 2 h, the colour of the solution turning to yellow-green. Excess of hydrogen sulphide was removed under reduced pressure in N_2 at 40 °C from the solution and then methanol (400 ml) was added to the latter followed by more potassium (40 g, 1.03 mol). The resulting mixture was warmed to 70 °C in a water-bath and to this chloroform (125 g, 1.06 mol) was added at a rate such that the mixture continued to reflux gently. The solution turned from yellow to orange and was, after being refluxed for an additional 10 min, kept overnight at room temperature. The insoluble matter which separated was filtered off and the resulting solution was concentrated under reduced pressure (< 40 °C). Acetone (400 ml) was then added to precipitate insoluble matter. The acetone solution was then concentrated to dryness to give brown material (44 g, 74%), which was dissolved in ethanol (500 ml) and then diluted gradually with hexane (1.5 l) to give pure non-hygroscopic potassium dithioformate as golden-yellow long-needles, m.p. 197—198 °C (lit.,[17] 196 °C).

(b) *Preparation of 2-cyano enamino thioaldehydes by the reaction of enamino nitriles with potassium dithioformate: General procedure.* A mixture of enamino nitrile (3 mmol), potassium dithioformate (3 mmol), sodium 1,1-dimethylpropoxide (6 mmol), and dried THF (25 ml) was stirred at room temperature for 24 h. Water (25 ml) was added to the reaction mixture which was then washed several times with ether. Any ether remaining was removed under reduced pressure and the solution was acidified with 2M hydrochloric acid with cooling to 0 °C. The resulting orange-red crystals which separated were dissolved in ether. The ether layer was dried ($MgSO_4$) magnesium sulphate and evaporated to give a red oil, which was washed with benzene–hexane to give orange-red crystals. Recrystallisation from hot benzene or ethanol–water gave orange-yellow crystals of pure 2-cyano enamino thioaldehydes. Yields: (**3a**), 23%; (**3g**), 76%; (**3h**), 45%; (**3i**), 64%; (**3j**), 37%; and (**3l**), 64% respectively. The thioaldehyde (**3d**) could not be prepared by this method and (**3a**) was obtained only occasionally in low yield when a mixed solvent, THF–MeOH (10:1, v/v), was used.

Isolation of 2,2-Disubstituted 6-Amino-3-cyanopyridines (**4**).—The ether washings from the above experiment were combined and washed with water, dried ($MgSO_4$) and evaporated to give pale yellow crystals. The following were recrystallised from hot ethanol:

3-*Acetimidoyl*-2-*amino*-5-*cyano*-6-*methylpyridine* (**4a**). Yield 27%, m.p. 226—227 °C; $\nu_{max.}$(KBr) 3 260, 3 080, 2 210, 1 622, 1 440, 1 125, 932, and 770 cm^{-1}; $\lambda_{max.}$(EtOH) 218 (log ε 4.46), 279 (4.23), and 336 nm (3.91) (Found: C, 61.8; H, 5.7; N, 32.45. $C_9H_{10}N_4$ requires C, 62.1; H, 5.8; N, 32.2%).

2-*Amino*-3-*benzimidoyl*-5-*cyano*-6-*phenylpyridine* (**4b**). Yield 17%, m.p. 211—212 °C; $\nu_{max.}$(KBr) 3 280, 3 255, 3 120, 2 215, 1 630, 1 600, 1 518, 1 440, 1 422, 1 370, 1 331, 1 183, 853, and 755 cm^{-1}; $\lambda_{max.}$(EtOH) 218sh (log ε 4.37), 252.5 (4.35), 282 (4.16), and 352 nm (4.02) (Found: C, 76.2; H, 4.8; N, 18.9. $C_{19}H_{14}N_4$ requires C, 76.5; H, 4.7; N, 18.8%).

2-*Amino*-3-*anisimidoyl*-5-*cyano*-6-(4-*methoxyphenyl*)*pyridine* (**4c**). Yield 15%, m.p. 150—151 °C; $\nu_{max.}$(KBr) 3 420, 3 270, 2 219, 1 602, 1 510, 1 435, 1 300, 1 253, 1 174, 1 025, and 830 cm^{-1}; $\lambda_{max.}$(EtOH) 224.5 (log ε 4.47), 281 (4.43), and 356 nm (4.20) (Found: C, 70.1; H, 5.2; N, 15.5. $C_{21}H_{18}N_4O_2$ requires C, 70.4; H, 5.1; N, 15.6%).

2-*Amino*-5-*cyano*-3-*naphthimidoyl*-6-(2-*naphthyl*)*pyridine* (**4d**). Yield 31%, m.p. 213—214 °C; $\nu_{max.}$(KBr) 3 360, 3 280, 3 170, 2 219, 1 640, 1 635, 1 600, 1 514, 1 293, 1 223, 1 177, 1 125, and 789 cm^{-1}; $\lambda_{max.}$(EtOH) 218 (log ε 4.87), 248 (4.65), and 281 (4.46), 360 nm (4.25) (Found: C, 81.3; H, 4.7; N, 14.3. $C_{27}H_{18}N_4$ requires C, 81.4; H, 4.55; N, 14.1%).

Isolation of 3-*acetyl*-2-*amino*-5-*cyano*-6-*methylpyridine* (**5a**). The aqueous solution from the preparation of the 2-cyano enamino thioaldehydes was acidified and extracted with ether. The combined ether extracts were dried and evaporated to give an oil which solidified on addition of water–ethanol (15%). Recrystallisation from hot benzene gave pale yellow crystals, m.p. 221—222 °C; $\nu_{max.}$(KBr) 3 365, 3 255, 3 120, 2 225, 1 660, 1 630, 1 538, 1 440, 1 371, 1 240, 942, and 780 cm^{-1}; $\lambda_{max.}$(EtOH) 218 (log ε 4.42), 220 (4.41), 267 (4.30), and 348 nm (3.87) (Found: C, 61.5; H, 5.2; N, 24.2. $C_9H_9N_3O$ requires C, 61.7; H, 5.2; N, 24.0%).

2-*Amino*-3-*benzoyl*-5-*cyano*-6-*phenylpyridine* (**5b**). Crude (**5b**) was obtained as an oil from the above aqueous solution in a similar procedure to that used for (**5a**). To this oil was added ethanol–hexane to precipitate starting material: this was filtered off and the mother liquor was concentrated and extracted with hot hexane. Removal of hexane left (**5b**) (4%), which was recrystallised from hot ethanol to give pale yellow crystals, m.p. 227 °C; $\nu_{max.}$(KBr) 3 360, 3 280, 3 180, 2 235, 1 640, 1 580, 1 519, 1 443, 1 320, 1 310, 1 235, 997, and 780 cm^{-1}; $\lambda_{max.}$(EtOH) 222 (log ε 4.28), 266 (4.44), 282sh (4.32), and 370 nm (4.12) (Found: C, 76.3; H, 4.4; N, 13.9. $C_{19}H_{13}N_3O$ requires C, 76.2; H, 4.4; N, 14.0%).

2-*Amino*-5-*cyano*-3-(m-*toluoyl*)-6-(m-*tolyl*)*pyridine* (**5c**). Compound (**5c**) was obtained, similarly to compound (**5a**), as a residue which was sparingly soluble in water–ethanol (15%). Recrystallisation from hot ethanol gave pale yellow crystals of (**5c**), m.p. 181—181.5 °C; $\nu_{max.}$(KBr) 3 360, 3 290, 3 180, 2 230, 1 638, 1 584, 1 517, 1 428, 1 318, 1 284, 1 247, 1 201, 1 172, and 780 cm^{-1}; $\lambda_{max.}$(EtOH) 226sh (log ε 4.30), 270 (4.42), 286sh (4.30), and 365 nm (4.14) (Found: C, 76.8; H, 5.5; N, 13.1. $C_{21}H_{17}N_3O$ requires C, 77.0; H, 5.2; N, 12.8%).

Preparation of Simple Enamino Thioaldehydes (**6a**—**j**) *from Imines and Enamines*.—Enamino thioaldehydes (**6a**—**j**) were also synthesized by a similar method to that used in the preparation of the thioaldehydes (**2**) and (**3**). To attain the best yield for these enamino thioaldehydes, the imines and enamines employed were re-distilled just before use. The Vilsmeier salts were prepared at a higher temperature (see Table 1) and freshly prepared methanolic NaHS solution was used for the solvolysis of the salts [with the exception of (**6a**) and (**6d**), which were obtained by the same procedure used for compounds (**2**) and (**3**)]. Best results were obtained when the preparative procedure was completed in < 12 h.

3-(*Cyclohexylamino*)*thiocinnamaldehyde* (**6a**). *Isolation of* 3-*Cyclohexylamino*-3-*phenylallylidene*-(N,N-*dimethyl*)-*ammonium Phosphorodichloridate* (**1u**).—To a solution of 1-phenylvinylcyclohexylamine (1.005 g, 5 mmol) dissolved in DMF (5 ml) was added a mixture of phosphoryl chloride (0.5 ml, 5.5 mmol) and DMF (2.5 ml) dropwise over 10 min at −10 °C; the resulting mixture was then set aside for 4 h at 35 °C, and then overnight at room temperature. The Vilsmeier salt was precipitated by addition of ether (150 ml) in portions; the ether layer was decanted off and saturated brine (10 ml) was added. The solid was collected, washed with ether, dried, and recrystallised from ethanol–hexane to give the Vilsmeier salt (**1u**), (0.99 g, 51%), m.p. 153—157 °C (Found: C, 52.2; H, 6.6; N, 7.4. $C_{17}H_{25}Cl_2N_2PO_2$ requires C, 52.2; H, 6.4; N, 7.4%).

The enamino thioaldehyde (**6a**) was obtained in the following manner. Compound (**1u**) was dissolved in methanolic 2M NaHS and the solution was stirred for 15 min at room temperature. Ether (20 ml × 3) was added and the mixture was dried ($MgSO_4$), and evaporated to dryness under reduced pressure to give light orange crystals (0.502 g, 41% overall yield). Crude thioaldehyde (**6a**) was chromatographically pure (t.l.c.) and purified by recrystallisation from hot hexane, m.p. 100—101 °C (rapid heating), 108—109 °C (slow heating); $\nu_{max.}$(KBr) 2 940, 2 850, 2 685br, 1 605, 1 590, 1 566, 1 530, 1 486, 1 353, 1 343, 1 248, 1 215, and 1 105 cm^{-1}; $\lambda_{max.}$(EtOH) 254 (log ε 3.70), and 381 nm (4.51); $\delta_H(CDCl_3)$ 15.25 and 5.74 (*ca.* 0.95 H and 0.05 H, each br s, NH), 9.95 (*ca.* 0.05 H, d, *J* 12 Hz, *cis*-s- or *trans*-s-*trans* isomer CHS), 9.70 (*ca.* 0.95 H, d, *J* 9 Hz, *cis*-s-*cis* isomer CHS), 7.5—7.3 (5 H, m, Ph), 6.66 (*ca.* 0.05 H, d, *J* 12 H, *cis*-s- or *trans*-s-*trans* isomer vinylic H), 6.14 (*ca.* 0.95 H, d, *J* 9 Hz, *cis*-s-*cis* isomer vinylic H), 3.54 (1 H, m, N-CH), and 2.15—1.2 [10 H, m, $(CH_2)_5$]; $\delta_C(CDCl_3)$ 210.5 p.p.m. (CHS) (Found: C, 73.2; H, 8.1; N, 5.9; S, 13.4. $C_{15}H_{19}NS$ requires C, 73.4; H, 7.8; N, 5.7; S, 13.1%).

It was not usually possible to isolate the Vilsmeier salt (**1u**) and in such cases the yield of (**6a**) from solvolysis was reduced (35—38%).

Reaction conditions and procedures for the preparation of the enamino thioaldehydes (**6a**—**j**) are given in Table 1.

3-*Piperidinothiocinnamaldehyde* (**6b**). M.p. 136—137 °C (from benzene–hexane); $\nu_{max.}$(KBr) 2 960, 2 850, 1 520vs, 1 469, 1 283, 1 256, 1 235, and 950vs cm^{-1}; $\lambda_{max.}$(EtOH) 247 (log ε 3.80) and 385 nm (4.70); $\delta_H(CDCl_3)$ 9.47 (1 H, d, *J* 12 Hz, CHS), 7.5—7.2 (5 H, m, Ph), 6.80 (1 H, d, *J* 12 Hz, vinylic H), 3.68 and 3.15 [each 2 H, each br s, $N(CH_2)_2$], 1.76 [4 H, br s, $N(CH_2CH_2)_2$], and 1.52 [2 H, br s, $N(CH_2CH_2)_2CH_2$]; $\delta_C(CDCl_3)$ 209.17 p.p.m. (CHS) (Found: C, 72.7; H, 7.6; N, 6.3; S, 13.9. $C_{14}H_{17}NS$ requires C, 72.7; H, 7.4; N, 6.05; S, 13.9%).

3-*Morpholinothiocinnamaldehyde* (**6c**). M.p. 138.5—139.5 °C (from benzene–hexane); $\nu_{max.}$(KBr) 2 960, 2 890, 2 840, 1 520vs, 1 230vs, 1 112vs, and 960vs cm^{-1}; $\lambda_{max.}$(EtOH) 254 (log ε 3.75) and 385 nm (4.69); $\delta_H(CDCl_3)$ 9.73 (1 H, d, *J* 12 Hz, CHS), 7.5—7.3 (5 H, m, Ph), 6.72 (1 H, d, *J* 12 Hz, vinylic H), and 3.7—3.2 [8 H, br, $N(CH_2CH_2)_2O$]; $\delta_C(CDCl_3)$ 212.28 p.p.m. (CHS) (Found: C, 66.9; H, 6.5; N, 6.3; S, 13.5. Calc. for $C_{13}H_{15}NOS$: C, 66.9; H, 6.5; N, 6.0; S, 13.7%).

2-*Morpholinocyclopent*-1-*ene*-1-*thiocarbaldehyde* (**6d**). M.p. 116—117 °C (from benzene–hexane); $\nu_{max.}$(KBr) 1 546vs, 1 463, 1 440, 1 362, 1 240, 1 120, and 931 cm^{-1}; $\lambda_{max.}$(EtOH) 249sh (log ε 3.34) and 405 nm (4.61); $\delta_H(CDCl_3)$ 10.41 (s, 1 H, CHS), 3.9—3.75 [8 H, m, $N(CH_2CH_2)_2O$], 2.85 (2 H, t, 3-H_2), 2.71 (2 H, t, 5-H_2), and 1.89 (2 H, t, 4-H_2); $\delta_C(CDCl_3)$ 197.37 p.p.m. (CHS) (Found: C, 60.9; H, 7.9; N, 7.1; S, 16.5. Calc. for $C_{10}H_{15}NOS$: C, 60.9; H, 7.7; N, 7.1; S, 16.25%).

β-*Propylamino*-cis-*stilbene*-α-*thiocarbaldehyde* (**6e**). M.p. 107.5—108.5 °C (from benzene–hexane); $\nu_{max.}$(KBr) 2 700br, 1 584, 1 564vs, 1 515, 1 491, 1 477, 1 291, and 1 100 cm^{-1}; $\lambda_{max.}$(EtOH) 242 (log ε 4.10), 268sh (3.85), and 402 nm (4.31); $\delta_H(CDCl_3)$ 15.14 and 5.56 (*ca.* 0.93 H and 0.07 H, each br s, NH), 9.98 (0.07 H, s, isomer CHS), 9.86 (*ca.* 0.97 H, s, CHS), 7.5—6.8 (10 H, m, Ph × 2), 3.21 (2 H, q, $NHCH_2$), 1.68 (2 H, q, $NHCH_2CH_2$), and 1.00 (3 H, t, CH_3); $\delta_C(CDCl_3)$ 192.93 p.p.m. (CHS) (Found: C, 76.55; H, 6.9; N, 4.7; S, 11.4. $C_{18}H_{19}NS$ requires C, 76.8; H, 6.8; N, 5.0; S, 11.4%).

β-*Hexylamino*-cis-*stilbene*-α-*thiocarbaldehyde* (**6f**). M.p. 70 °C (from hot hexane); $\nu_{max.}$(KBr) 2 650br, 1 582, 1 571, 1 472, 1 465, 1 295, 1 280, 1 258, and 1 099 cm^{-1}; $\lambda_{max.}$(EtOH) 242 (log ε 4.10), 268 (3.85), and 402 nm (4.29); $\delta_H(CDCl_3)$ 15.15 and 5.52 (*ca.* 0.95

H and 0.05 H, each br s, NH), 9.99 (0.05 H, s, isomer CHS), 9.85 (*ca.* 0.95 H, s, CHS), 7.5—7.0 (10 H, m, Ph × 2), 3.24 (2 H, q, $NHCH_2$), 1.7—1.2 [8 H, m, $NHCH_2(CH_2)_4$], and 0.87 (3 H, t, CH_3); $\delta_C(CDCl_3)$ 192.85 p.p.m. (CHS) (Found: C, 77.75; H, 8.0; N, 4.2; S, 10.0. $C_{21}H_{25}NS$ requires C, 78.0; H, 7.8; N, 4.3; S, 9.9%).

β-*Pyrrolidin*-1-*ylstilbene*-α-*thiocarbaldehyde* (**6g**). M.p. 163.5—164 °C (from dichloromethane–hexane); $\nu_{max.}$(KBr) 1 503vs, 1 492, 1 444, 1 383vs, 1 336, 1 307, 1 105, and 989 cm^{-1}; $\lambda_{max.}$(EtOH) 263 (log ε 3.91), 394 nm (4.59); $\delta_H(CDCl_3)$ 9.86 (1 H, s, CHS), 7.5—7.2 (10 H, m, Ph × 2), 3.06 and 2.79 [each 2 H, each br s, $N(CH_2)_2$], and 1.70 [4 H, br s, $N(CH_2CH_2)_2$]; $\delta_C(CDCl_3)$ 209.03 p.p.m. (CHS) (Found: C, 77.5; H, 6.4; N, 4.8; S, 11.1. Calc. for $C_{19}H_{19}NS$: C, 77.8; H, 6.5; N, 4.8; S, 10.9%).

β-*Cyclohexylamino*-cis-*stilbene*-α-*thiocarbaldehyde* (**6h**). M.p. 136.5 °C (from hot EtOH); $\nu_{max.}$(KBr) 2 930, 2 850, 2 565br, 1 588vs, 1 568, 1 504, 1 491, 1 474, 1 322, 1 296vs, 1 262, 1 095, 880, 759, and 702 cm^{-1}; $\lambda_{max.}$(EtOH) 242 (log ε 4.11), 268sh (3.86), and 404 nm (4.34); $\delta_H(CDCl_3)$ 15.25 and 5.40 (*ca.* 0.97 H and 0.03 H, each br s, NH), 9.96 (*ca.* 0.03 H, s, *cis*-s- or *trans*-s-*trans* isomer CHS), 9.82 (*ca.* 0.97 H, s, *cis*-s-*cis* isomer CHS), 7.5—6.8 (10 H, s, Ph × 2), 3.40 (1 H, m, NHC*H*), and 1.8—0.9 [10 H, m, $(CH_2)_5$]; $\delta_C(CDCl_3)$ 192.22 p.p.m. (CHS) (Found: C, 78.2; H, 7.3; N, 4.1. Calc. for $C_{21}H_{23}NS$: C, 78.5; H, 7.2; N, 4.4%).

The best yield was obtained when 3 mol equiv. of phosphoryl chloride was used for each equimolar amount of *N*-methylformanilide and the enamine. The thioaldehyde (**6h**) was not obtained, even in trace amounts, when *N*,*N*-dimethylthioformamide was employed instead of *N*,*N*-dimethylformamide in the preparation of the Vilsmeier reagent.

β-*Morpholinostilbene*-α-*thiocarbaldehyde* (**6i**). M.p. 170—171 °C (from dichloromethane–hexane); $\nu_{max.}$(KBr) 1 507, 1 480vs, 1 437, 1 378, 1 352, 1 302vs, 1 260, 1 119, 1 102, and 980vs cm^{-1}; $\lambda_{max.}$(EtOH) 244 (log ε 3.87), 278 (3.99), and 409 nm (4.44); $\delta_H(CDCl_3)$ 10.14 (*ca.* 0.9 H, s, *cis*-s-*cis* isomer CHS), 8.91 (*ca.* 0.1 H, s, *cis*-s- or *trans*-s-*trans* isomer CHS), 7.55—7.2 (10 H, m, Ph × 2), and 3.9—2.8 [8 H, m, 2 × t, q, $N(CH_2CH_2)_2O$]; $\delta_C(CDCl_3)$ 213.59 and 190.62 p.p.m. (each isomer CHS) (Found: C, 73.4; H, 6.5; N, 4.2; S, 10.4. Calc. for $C_{19}N_{19}NOS$: C, 73.8; H, 6.2; N, 4.5; S, 10.4%).

3-*Piperidinoindene*-2-*thiocarbaldehyde* (**6j**). M.p. 159—159.5 °C (from hot benzene–hexane); $\nu_{max.}$(KBr) 1 604vs, 1 597vs, 1 441, 1 329, 1 318vs, 1 263, 1 249, 1 197, 1 098, and 1 018 cm^{-1}; $\lambda_{max.}$(EtOH) 225 (log ε 4.08), 275 (3.69), 306sh (4.08), 319 (4.25), 331 (4.31), and 444 nm (4.29); $\delta_H(CDCl_3)$ 8.33 (1 H, s, CHS), 7.5—7.3 (4 H, m, ArH), 3.73 (2 H, s, 1-H_2), 3.60 [4 H, br s, $N(CH_2)_2$], and 1.71 [6 H, s, $NCH_2(CH_2)_3CH_2$]; $\delta_C(CDCl_3)$ 210.34 p.p.m. (CHS) (Found: C, 73.15; H, 7.2; N, 5.6; S, 13.0. $C_{15}H_{17}NS$ requires C, 74.0; H, 7.0; N, 5.8; S, 13.2%).

Enamino Selenaldehyde Pentacarbonyltungsten(0) *Complexes* (**7a—c**).—*General procedure*. To a solution of an enamino ester (5 mmol) in THF (5 ml), was added dropwise a mixture of DMF (2 ml) and phosphoryl chloride (0.5 ml, 5 mmol) over 20 min at 0 °C. The resulting mixture was set aside for an additional 1 h at 0 °C before being stirred for 1 h at room temperature. The following day, ether (300 ml) was added in portions at 0 °C to the reaction mixture and the ether was removed by decantation to leave a viscous oil which was dissolved in dichloromethane (200 ml). Freshly prepared aqueous NaHSe (1M; 50 ml) was added to the solution and the mixture was shaken vigorously for 5 min. Tetraethylammonium pentacarbonyliodotungstate(0) (3.195 g, 5.5 mmol) was added to the organic layer and the mixture shaken to give a clear solution to which aqueous $AgNO_3$ (0.1M; 60 ml) was added; the mixture was shaken immediately and vigorously for 5 min. The organic layer, after removal of AgI by suction, was washed with water (× 6), quickly dried ($MgSO_4$) with vigorous shaking for 1 min, and evaporated under reduced pressure to give dark purple crystals of the enamino selenaldehyde complex. The complexes were purified by column chromatography on silica gel [Merck 60 (70—230 mesh)] with benzene–acetonitrile (8:1) as eluant. Dark purple eluate was evaporated under reduced pressure in the dark to give dark purple crystals which were recrystallised from dichloromethane–hexane.

Flasks, separating funnels, columns, and all other vessels were made of polypropylene or Teflon because glassware accelerated the decomposition of both the selenaldehydes and the complexes.

Pentacarbonyl(*methyl* 3-*amino*-2-*selenoformylcrotonate*)-*tungsten* (**7a**). Yield 8%, m.p. 112—113.5 °C; $\nu_{max.}$(KBr) 3 400, 3 190, 2 070, 1 920vs, 1 845, 1 670, 1 611, 1 410, 1 306, 1 242, 1 100, 1 039, 982, 861, 811, 591, and 578 cm^{-1}; $\lambda_{max.}$(cyclohexane) 228 (log ε 4.74), 243 (4.67), 330 (4.20), and 487 nm (4.19); $\delta_H(CDCl_3)$ 12.47 (1 H, s, CHSe), 11.10 and 7.26 (1 H, each br s, NH_2), 3.87 (3 H, s, OCH_3), and 2.63 (3 H, s, CH_3) (Found: C, 24.9; H, 1.55; N, 2.4. $C_{11}H_9NO_7SeW$ requires C, 24.9; H, 1.7; N, 2.6%).

Pentacarbonyl(*ethyl* 3-*amino*-2-*selenoformylcinnamate*)-*tungsten* (**7b**). Yield 13%, m.p. 119.5—120.5 °C; $\nu_{max.}$(KBr) 3 400, 3 285, 3 215, 2 060, 1 920vs, 1 880, 1 680, 1 627, 1 484, 1 470, 1 450, 1 382, 1 303, 1 198, 1 109, 1 016, 702, 632, 596, and 575 cm^{-1}; $\lambda_{max.}$(cyclohexane) 230 (log ε 4.72), 243sh (4.69), 334 (4.23), and 502 nm (4.12); $\delta_H(CDCl_3)$ 12.04 (1 H, s, CHSe), 10.84 and 6.66 (1 H, each br s, NH_2), 7.67—7.44 (5 H, m, Ph), 4.45 (2 H, q, CH_2), and 1.45 (3 H, t, CH_3) (Found: C, 33.8; H, 2.2; N, 2.0. $C_{17}H_{13}NO_7SeW$ requires C, 33.7; H, 2.2; N, 2.3%).

Pentacarbonyl(*ethyl* 3-*anilino*-2-*selenoformylcinnamate*)-*tungsten* (**7c**). Yield 22.5%, m.p. 112 °C (rapid heating), 117—119 °C (slow heating); $\nu_{max.}$(KBr) 3 420br, 2 055, 1 910vs, 1 855, 1 662, 1 551, 1 393, 1 260, 1 212, 1 135, 1 018, 823, 592, and 578 cm^{-1}; $\lambda_{max.}$(cyclohexane) 232 (log ε 4.68), 248 (4.64), 363 (4.39), and 582 nm (4.24); $\delta_H(CDCl_3)$ 13.18 (1 H, s, CHSe), 11.85 (1 H, s, NH), 7.53—6.83 (10 H, m, Ph × 2), 4.47 (2 H, q, CH_2), and 1.48 (3 H, t, CH_3) (Found: C, 40.6; H, 2.5; N, 1.9. $C_{23}H_{17}NO_7SeW$ requires C, 40.5; H, 2.5; N, 2.1%).

Oxidation of 2-*Alkoxycarbonyl- and* -*Cyano Enamino Thioaldehydes with MCPBA: Formation of Isothiazoles* (**8a—j**).—4-*Methoxycarbonyl*-3-*methylisothiazole* (**8a**). To a solution of methyl 3-amino-2-thioformylcrotonate (**2a**) (318 mg, 2 mmol) in ethanol (30 ml), was added *m*-chloroperbenzoic acid (518 mg, 3 mmol) in ethanol (10 ml) dropwise with stirring at room temperature. The solution was warmed for 3 h at 70 °C and, after being cooled, was diluted with ether (200 ml). The ethereal solution was washed with 0.1M sodium hydroxide (× 3) and once with water, dried ($MgSO_4$), and evaporated to dryness in the dark to give colourless material. This material contained no impurities (t.l.c. analysis), yield 259 mg (82.5%). Recrystallisation from hot hexane in the dark gave pure isothiazole (**8a**) as white crystals, m.p. 50.5—51 °C; $\nu_{max.}$(KBr) 3 140, 2 930, 2 860, 1 710vs, 1 514, 1 443, 1 415, 1 368, 1 352, 1 263, and 1 252 cm^{-1}; $\lambda_{max.}$(EtOH) 255 nm (log ε 3.95); $\delta_H(CDCl_3)$ 9.25 (1 H, s, 5-H), 3.91 (3 H, s, OCH_3), and 2.74 (3 H, s, 3-CH_3) (Found: C, 46.0; H, 4.6; N, 8.6; S, 20.5. $C_6H_7NO_2S$ requires C, 45.85; H, 4.5; N, 8.9; S, 20.4%).

For the oxidation of compound (**2d**), the reaction mixture was warmed at 75 °C and for the formation of compounds (**8e—i**), the mixtures were warmed for 2 h at 65 °C.

3-*Ethyl*-4-*methoxycarbonylisothiazole* (**8b**). Yield 84%, m.p. 54.5—55 °C (from benzene–hexane); $\nu_{max.}$(KBr) 3 120, 2 965, 2 930, 1 708vs, 1 509, 1 440, 1 410, and 1 318 cm^{-1}; $\lambda_{max.}$(EtOH) 255 nm (log ε 3.93); $\delta_H(CDCl_3)$ 9.26 (1 H, s, 5-H), 3.89 (3 H, s, OCH_3), 3.16 (2 H, q, CH_2), and 1.34 (3 H, t, CH_2CH_3) (Found: C, 48.9; H, 5.3; N, 7.9; S, 18.8. $C_7H_9NO_2S$ requires C, 49.1; H, 5.3; N, 8.2; S, 18.7%).

4-*Ethoxycarbonyl*-3-*phenylisothiazole* (**8c**). Yield 97%, b.p. 80 °C/0.09 mmHg; $\nu_{max.}$(neat) 3 075, 2 975, 1 718vs, 1 494, 1 412, and 1 260vs cm^{-1}; $\lambda_{max.}$(EtOH) 254 nm (log ε 4.01); $\delta_H(CDCl_3)$ 9.32 (1 H, s, 5-H), 7.65—7.24 (5 H, m, Ph), 4.25 (2 H, q, CH_2), and 1.23 (3 H, t, CH_3) (Found: C, 61.9; H, 4.7; N, 5.8; S, 13.5. $C_{12}H_{11}NO_2S$ requires C, 61.8; H, 4.75; N, 6.0; S, 13.7%).

4-*Ethoxycarbonyl*-3-(m-*tolyl*)*isothiazole* (**8d**). Yield 94%, b.p. 128 °C/0.2 mmHg; $\nu_{max.}$(neat) 3 100, 2 970, 2 915, 1 718vs, 1 500, 1 488, 1 430, 1 400, 1 329, and 1 264 cm^{-1}; $\lambda_{max.}$(EtOH) 254 nm (log ε 4.00); $\delta_H(CDCl_3)$ 9.03 (1 H, s, 5-H), 7.12—6.91 (4 H, m, C_6H_4), 3.94 (2 H, q, CH_2), 2.09 (3 H, s, 3′-CH_3), and 0.93 (3 H, t, CH_2CH_3) (Found: C, 63.3; H, 5.4; N, 5.7. $C_{13}H_{13}NO_2S$ requires C, 63.1; H, 5.3; N, 5.7%).

4-*Cyano*-3-*methylisothiazole* (**8e**). Slightly viscous colourless oil (78%), b.p. 105 °C/20 mmHg; $\nu_{max.}$(KBr) 3 090, 2 915, 1 515, 1 416, and 1 338 cm^{-1}; $\lambda_{max.}$(EtOH) 257 nm (log ε 3.93); $\delta_H(CDCl_3)$ 9.12 (1 H, s, 5-H) and 2.67 (3 H, s, CH_3) (Found: C, 48.3; H, 3.3; N, 22.3. $C_5H_4N_2S$ requires C, 48.4; H, 3.3; N, 22.6%).

4-*Cyano*-3-*phenylisothiazole* (**8f**). Yield 95%, m.p. 54.5—55 °C (from hot EtOH–hexane); $\nu_{max.}$(KBr) 3 110, 3 100, 2 240, 1 487, 1 443, 1 405, and 1 330 cm^{-1}; $\lambda_{max.}$(EtOH) 252 nm (log ε 4.09); $\delta_H(CDCl_3)$ 9.30 (1 H, s, 5-H) and 8.07—7.51 (5 H, m, Ph) (Found: C, 64.3; H, 3.2; N, 14.75. $C_{10}H_6N_2S$ requires C, 64.5; H, 3.25; N, 15.0%).

4-*Cyano*-3-(p-*tolyl*)*isothiazole* (**8g**). Yield 80%, m.p. 104.5—105 °C (from hot EtOH); $\nu_{max.}$(KBr) 3 070, 2 905, 2 220, 1 613, 1 484, 1 406, and 1 330 cm^{-1}; $\lambda_{max.}$(EtOH) 237 (log ε 4.07), 258 nm (4.20); $\delta_H(CDCl_3)$ 9.26 (1 H, s, 5-H), 7.95 and 7.31 (each 2 H, each *ca.* d, C_6H_4), and 2.42 (3 H, s, CH_3); *m/z* 200 (M^+, 35%) (Found: C, 65.9; H, 4.3; N, 13.9; S, 15.8. $C_{11}H_8N_2S$ requires C, 66.0; H, 4.0; N, 14.0; S, 16.0%).

4-*Cyano*-3-(m-*tolyl*)*isothiazole* (**8h**). Yield 84%, m.p. 87.5—88 °C (from hot EtOH); $\nu_{max.}$(KBr) 3 095, 2 225, 1 581, 1 492, 1 404, and 1 330 cm^{-1}; $\lambda_{max.}$(EtOH) 236 (log ε 4.05), 255 nm (4.10); $\delta_H(CDCl_3)$ 9.27 (1 H, s, 5-H), 7.85—7.45 (4 H, m, C_6H_4), and 2.45 (3 H, s, CH_3); *m/z* 200 (M^+, 100%) (Found: C, 65.9; H, 4.1; N, 13.95; S, 15.95. $C_{11}H_8N_2S$ requires C, 66.0; H, 4.0; N, 14.0; S, 16.0%).

4-*Cyano*-3-(p-*methoxyphenyl*)*isothiazole* (**8i**). Yield 92%, m.p. 120.5—121 °C (from hot EtOH); $\nu_{max.}$(KBr) 3 100, 2 930, 2 230, 1 611, 1 524, 1 490, 1 400, 1 260, and 1 183 cm^{-1}; $\lambda_{max.}$(EtOH) 238 (log ε 4.03), 272 nm (4.25); $\delta_H(CDCl_3)$ 9.26 (1 H, s, 5-H), 8.05 and 7.01 (2 H, each *ca.* d, C_6H_4), and 3.88 (3 H, s, CH_3); *m/z* 216 (M^+, 100%) (Found: C, 61.1; H, 3.6; N, 12.9; S, 14.7. $C_{11}H_8N_2OS$ requires C, 61.1; H, 3.7; N, 12.95; S, 14.8%).

4-*Cyano*-3-(2-*naphthyl*)*isothiazole* (**8j**). Yield 88%, m.p. 119.5—120 °C (from hot EtOH); $\nu_{max.}$(KBr) 3 100, 2 240, 1 602, 1 496, 1 405, 1 360, and 1 351 cm^{-1}; $\lambda_{max.}$(EtOH) 213 (log ε 4.50), 248 (4.57), 278sh (4.12), 286 (4.18), 294 nm (4.12); *m/z* 236 (M^+, 100%) (Found: C, 71.4; H, 3.6; N, 11.7; S, 13.3. $C_{14}H_8N_2OS$ requires C, 71.2; H, 3.4; N, 11.9; S, 13.6%).

Bimolecular Cyclizations of 3-*Amino*-2-*cyanothiocinnamaldehydes: Formation of Symmetrically Substituted Pyridines* (**9**).—3,5-*Dicyano*-2,6-*diphenylpyridine* (**9a**). A mixture of 3-amino-2-cyanothiocinnamaldehyde (**3d**) (376.5 mg, 2 mmol), 99% toluene-*p*-sulphonic acid monohydrate (384 mg, 2 mmol), and anhydrous ethanol (10 ml) was refluxed for 24 h at 80 °C and then cooled. Hexane (200 ml) was added to the cooled reaction mixture to precipitate white crystals which were collected, washed with hexane, dried, and subjected to column chromatography on silica gel with acetonitrile–benzene (1:25, v/v) as eluant to give (**9a**) (115 mg, 43%) from the first eluate; m.p. 238—239.5 °C (from hot ethyl acetate–hexane); $\nu_{max.}$(KBr) 3 060, 2 220, 1 584, 1 570, 1 516, and 1 421 cm^{-1}; $\lambda_{max.}$(EtOH) 221 (log ε 4.22), 278 nm (4.49); $\delta_H(CDCl_3)$ 8.39 (1 H, s, 4-H) and 8.12—7.53 (10 H, m, Ph × 2) (Found: C, 80.9; H, 4.1; N, 14.7. $C_{19}H_{11}N_3$ requires C, 81.1; H, 3.9; N, 14.9%).

6-*Amino*-5-*benzoyl*-3-*cyano*-2-*phenylpyridine* (**10**) was also obtained from the second eluate (65 mg, 22%); m.p. 233—233.5 °C (from hot ethyl acetate–hexane); $\nu_{max.}$(KBr) 3 340, 3 260, 3 165, 2 215, 1 636, 1 572, 1 518, and 1 442 cm^{-1}; $\lambda_{max.}$(EtOH) 221 (log ε 4.29), 264 (4.43), 282sh (4.31), and 367 nm (4.08); $\delta_H([^2H_6]DMSO)$ 8.19 (2 H, s, NH_2), 8.04 (1 H, s, 4-H), and 7.92—7.56 (10 H, s, Ph × 2) (Found: C, 76.25; H, 4.25; N, 14.0. $C_{19}H_{13}N_3O$ requires C, 76.2; H, 4.4; N, 14.0%).

Compounds (**9b**) and (**9c**) were obtained in a similar manner to compound (**9a**); no 6-amino-5-benzoylpyridine (**10**) was formed (t.l.c. analysis). Compounds (**9d**) and (**9e**) were obtained as by-products on hydrolysis at 65 °C (see Hydrolysis).

3,5-*Dicyano*-2,6-*di*-p-*tolylpyridine* (**9b**). Yield 61%, m.p. 219—219.5 °C; $\nu_{max.}$(KBr) 3 050, 2 220, 1 610, 1 583, 1 564, 1 497, and 1 420 cm^{-1}; $\delta_H(CDCl_3)$ 8.37 (1 H, s, 4-H), 8.01 and 7.37 (4 H, each *ca.* d, C_6H_4 × 2), and 2.47 (6 H, s, CH_3 × 2) (Found: C, 81.5; H, 4.65; N, 13.65. $C_{21}H_{15}N_3$ requires C, 81.5; H, 4.9; N, 13.6%).

3,5-*Dicyano*-2,6-*di*-m-*tolylpyridine* (**9c**). Yield 52%, m.p. 165.5—166 °C; $\nu_{max.}$(KBr) 3 050, 2 220, 1 580, 1 518, and 1 424 cm^{-1}; $\lambda_{max.}$(EtOH) 229 (log ε 4.23) and 284 nm (4.48); $\delta_H(CDCl_3)$ 8.36 (1 H, s, 4-H), 7.88—7.37 (8 H, m, C_6H_4 × 2), and 2.47 (6 H, s, CH_3 × 2); $\delta_C(CDCl_3)$ 162.68, 147.53, 138.85, 135.93, 132.39, 129.82, 128.81, 126.44, 116.24, 105.19, and 12.50 p.p.m. (Found: C, 81.7; H, 4.9; N, 13.6. $C_{21}H_{15}N_3$ requires C, 81.5; H, 4.9; N, 13.6%).

Reaction of 2-*cyanothiocinnamaldehyde* (**3d**) *with benzoylacetonitrile.* To a mixture of sodium 1,1-dimethylpropoxide (264 mg, 2.4 mmol) was added freshly recrystallised benzoylacetonitrile (348 mg, 2.4 mmol), 3-amino-2-cyanothiocinnamaldehyde (**3d**) (366 mg, 2.0 mmol), and benzene (30 ml). The mixture was warmed at 60 °C for 16 h after which benzene was removed under reduced pressure to give a residue which was washed with water, dried, and chromatographed on silica gel using 11% acetonitrile–89% benzene as eluant to give compound (**9a**) (211 mg, 37.5%) and compound (**10**) (248 mg, 41%). Both compounds were purified by recrystallisation from hot ethyl acetate–hexane; i.r. spectra were completely identical with those of (**9a**) and (**10**) above.

Hydrolysis of 2-*Cyano Enamino Thioaldehyde.—General procedure.* A solution of 3-amino-2-cyanothiocinnamaldehyde (**3d**) (2 mmol) in ethanol (10 ml) containing sulphuric acid (1 mmol) was refluxed at 60 °C for 24 h. Triethylamine (404 mg, 4 mmol) was added to the cooled reaction mixture after which the solution was extracted with dichloromethane. The combined extracts were washed once with water, dried ($MgSO_4$), and evaporated under reduced pressure. The solid residue was adsorbed on silica gel (acetone) and chromatographed with benzene–acetonitrile (8:1) to give 3-amino-2-cyanocinnamaldehyde (**11a**) (99 mg, 57.5%), benzoylacetonitrile (**12a**) (20.5 mg, 14%), and compound (**9a**) (79 mg, 28%). The enamino thioaldehydes (**3g**) and (**3l**) were hydrolysed for 3 h at the same temperature and the mixed products were also column-chromatographed. The results of the 2-cyano enamino thioaldehydes (**3d**), (**3g**), (**3k**), and (**3l**), are given in Table 2. Other spectral data and elemental analyses for compounds (**11**) are as follows.

3-*Amino*-2-*cyanocinnamaldehyde* (**11a**). M.p. 167—168.5 °C (from hot ethyl acetate–hexane); $\nu_{max.}$(KBr) 3 320, 3 120, 2 200, 1 642, and 1 624 cm^{-1}; $\delta_H([^2H_6]acetone)$ 10.68 and 8.66 (1 H, each br s, NH_2), 9.41 (1 H, s, CHO), and 7.7—7.5 (5 H, m, Ph) (Found: C, 69.7; H, 4.8; N, 16.0. $C_{10}H_8N_2O$ requires C, 69.8; H, 4.7; N, 16.3%).

3-*Amino*-2-*cyano*-4′-*methylcinnamaldehyde* (**11b**). This was separated by flash column chromatography to prevent decomposition on the column, m.p. 203—203.5 °C (from hot ethyl acetate); $\nu_{max.}$(KBr) 3 300, 3 140, 2 200, 1 642, and 1 614

cm^{-1}; $\delta_H([^2H_6]acetone)$ 10.62 and 8.50 (1 H, each br s, NH_2), 9.39 (*ca.* 1 H, s, CHO), 7.62 and 7.41 (*ca.* 2 H, each *ca.* d, C_6H_4) and 2.42 (3 H, s, CH_3) (Found: C, 71.25; H, 5.4; N, 15.05. $C_{11}H_{10}N_2O$ requires C, 71.0; H, 5.4; N, 15.1%).

3-*Amino*-2-*cyano*-4′-*methoxycinnamaldehyde* (**11c**). M.p. 228—229 °C (from hot ethyl acetate–hexane); $\nu_{max.}$(KBr) 3 295, 3 125, 2 200, and 1 620 cm^{-1}; $\delta_H([^2H_6]acetone)$ 10.33 and 7.50 (*ca.* 1 H, each br s, NH_2), 9.35 (1 H, s, CHO), 7.62 and 7.21 (*ca.* 2 H, each *ca.* d, C_6H_4) and 3.84 (3 H, s, CH_3) (Found: C, 65.2; H, 5.0; N, 13.6. $C_{11}H_{10}N_2O_2$ requires C, 65.3; H, 5.0; N, 13.9%).

2-(1-*Amino*-2-*cyano*-2-*formylvinyl*)*naphthalene* (**11d**). M.p. 197.5—198 °C (from hot ethyl acetate); $\nu_{max.}$(KBr) 3 345, 3 195, 2 200, 1 638, and 1 618 cm^{-1}; $\delta_H(CDCl_3)$ 10.80 and 6.31 (1 H, each br s, NH_2), 9.50 (1 H, s, CHO), and 8.17—7.57 (7 H, m, $C_{10}H_7$) (Found: C, 75.8; H, 4.5; N, 12.6. $C_{14}H_{10}N_2O$: C, 75.7; H, 4.5; N, 12.6%).

Synthesis of Compounds (**11**) *by Hydrolysis of Vilsmeier Salts.*—Vilsmeier salts (**1d**) and (**1g**) were hydrolysed in aqueous 0.2M NaOH. The appropriate Vilsmeier salt from the corresponding enamino nitrile (10 mmol) was added gradually to aqueous 0.2M NaOH (37 ml). Additional aqueous NaOH (13 ml) was added to the above solution and the resulting aqueous solution was boiled for 10 min and then cooled to 0 °C. The crystalline solid which separated out was collected, washed with water, and dried *in vacuo*. Recrystallisation from hot ethyl acetate–hexane gave pure enamino aldehydes, yields: (**11a**), 58% and (**11b**), 65%. I.r. spectra (KBr) of these aldehydes (**11a**) and (**11b**) were fully consistent with those of the aldehydes obtained from thioaldehydes (**3d**) and (**3g**). Vilsmeier salts (**1a**) and (**1i**) gave no hydrolysed product. The i.r. spectra of compounds (**12**) were identical with those of authentic specimens. The i.r. spectra and m.p.s of compounds (**9a**) and (**9b**) isolated here were fully consistent with those of the corresponding compound (**9**) prepared by the bimolecular cyclisation reaction mentioned above.

3,5-*Dicyano*-2,6-*di*-p-*methoxyphenylpyridine* (**9d**). M.p. 220.5—221.5 °C (from hot ethyl acetate–hexane); $\nu_{max.}$(KBr) 3 050, 2 235, 1 604, 1 564, 1 500, and 1 432 cm^{-1}; $\delta_H(CDCl_3)$ 8.33 (1 H, s, 4-H), 8.15 and 7.17 (4 H, each *ca.* d, C_6H_4 × 2), and 3.91 (6 H, s, CH_3 × 2) (Found: C, 74.0; H, 4.4; N, 12.3. $C_{21}H_{15}N_3O_2$ requires C, 73.9; H, 4.4; N, 12.3%).

3,5-*Dicyano*-2,6-*di*-2-*naphthylpyridine* (**9e**). M.p. 195.5 °C (from hot ethyl acetate–hexane); $\nu_{max.}$(KBr) 3 050, 2 240, 1 580, 1 520, 1 449, and 1 422 cm^{-1} (Found: C, 84.8; H, 3.8; N, 10.7 $C_{27}H_{15}N_3$ requires C, 85.0; H, 4.0; N, 11.0%).

Reaction with Primary Amines: Formation of Imines (**13**).—A mixture of each 2-cyano enamino thioaldehyde (2 mmol) and the appropriate primary amine (2 mmol) in ethanol (10 ml) was kept overnight at room temperature until the thioaldehyde had disappeared (t.l.c.). Some white to pale yellow crystals separated out from the mixture. A small quantity of water was added to the reaction mixture. The resulting crystals were collected, washed with 75% ethanol, dried, and recrystallised.

3-*Amino*-2-(N-*phenylformimidoyl*)-4′-*methylcinnamonitrile* (**13a**). Yield 81%, m.p. 148—150.5 °C (from hot EtOH) (Found: C, 78.2; H, 6.1; N, 16.0. $C_{17}H_{15}N_3$ requires C, 78.1; H, 5.8; N, 16.1%).

3-*Amino*-2-(N-*phenylformimidoyl*)-3′-*methylcinnamonitrile* (**13b**). Yield 71%, m.p. 132—133.5 °C (from hot benzene) (Found: C, 78.2; H, 6.0; N, 15.9. $C_{17}H_{15}N_3$ requires C, 78.1; H, 5.8; N, 16.1%).

3-*Amino*-2-(N-*cyclohexylformimidoyl*)-3′-*methylcinnamonitrile* (**13c**). Yield 76%, m.p. 158—159 °C (from hot benzene) (Found: C, 76.3; H, 7.8; N, 15.7. $C_{17}H_{21}N_3$ requires C, 76.4; H, 7.9; N, 15.7%).

3-*Amino*-2-(N-*phenylformimidoyl*)-4′-*methoxycinnamonitrile* (**13d**). Yield 84%, m.p. 201—202 °C (from hot EtOH) (Found: C, 73.8; H, 5.2; N, 15.3. $C_{17}H_{15}N_3O$ requires C, 73.6; H, 5.45; N, 15.15%).

3-*Amino*-2-(N-*cyclohexylformimidoyl*)-4′-*methoxycinnamonitrile* (**13e**). Yield 85%, m.p. 122—123 °C (from hot EtOH) (Found: C, 72.2; H, 7.4; N, 14.9. $C_{17}H_{21}N_3O$ requires C, 72.05; H, 7.5; N, 14.8%).

2-[1-*Amino*-2-*cyano*-2-(N-*phenylformimidoyl*)*vinyl*]*naphthalene* (**13f**). Yield 89%, m.p. 188—189 °C (from hot benzene) (Found: C, 80.6; H, 5.1; N, 14.0. $C_{20}H_{15}N_3$ requires C, 80.8; H, 5.1; N, 14.1%).

2-[1-*Amino*-2-*cyano*-2-(N-*cyclohexylformimidoyl*)*vinyl*]-*naphthalene* (**13g**). Yield 84%, m.p. 129—130 °C (from benzene–hexane) (Found: C, 79.0; H, 7.0; N, 13.7. $C_{20}H_{21}N_3$ requires C, 79.2; H, 7.0; N, 13.85%).

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