Polarized Ethylenes. IV [1]. Synthesis of Polarized Ethylenes Using Thioamides and Methyl Dithiocarboxylates and Their Application to Syntheses of Pyrazoles, Pyrimidines, Pyrazolo[3,4-*d*]pyrimidines, and 5-Aza[2.2.3]cyclazines

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Polarized ethylenes having both electron-donating (an amino or a methylthio group) and electron-accepting (cyano, carbamoyl, methyl ester) groups on the adjacent two olefinic carbon atoms were prepared by the condensation of *S*-alkylthioamidinium salts or methyl dithiocarboxylates with the corresponding active methylene compounds in good yields. These polarized ethylenes were alternatively synthesized by the reaction of thioamides or methyl dithiocarboxylates with tetracyanoethylene oxide in good yields. Reactions of these polarized ethylenes with hydrazine or guanidine derivatives occurred smoothly to give the corresponding pyrazole and pyrimidine derivatives in good yields. The synthesis of 5-aza[2.2.3]cyclazine derivatives using polarized ethylenes is also described.

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Dithiocarboxylic acids and thioamides are most useful and successful in various synthetic applications of the thiocarbonyl derivatives [2-14]. In this paper, useful and convenient synthetic method of polarized ethylenes, which are important starting compounds for the synthesis of heterocyclic compounds, from thioamides and dithiocarboxylates is described, and furthermore the studies on synthesis of 5-aza[2.2.3]cyclazines are reported along with their some new reactions. Thioamides and methyl dithiocarboxylates using in this paper are shown in Figure 1.

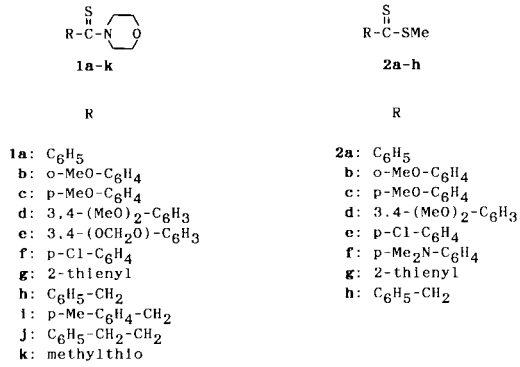


Fig. 1 Thioamides and dithiocarboxylates

Synthesis of Polarized Ethylenes.

Ethylenes having electron-donating groups on an olefinic carbon atom and electron-accepting groups on another carbon atom of the olefin are one of most important and interesting compounds from both synthetic and theoretical points of view [15] (Figure 2). Among these compounds, for example, ketene dithioacetals [16-20], ethoxymethylene compounds [21-23], and aminomethylene compounds [24-26] are widely used for the preparation of heterocyclic compounds.

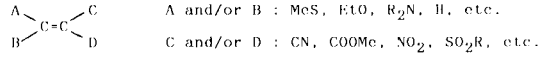
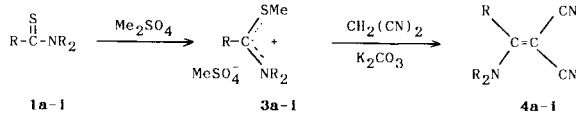


Fig. 2 Polarized ethylenes

Thioamides are easily activated with suitable aklylating reagents, giving the corresponding *S*-alkylthioamidium salts. They are allowed to react efficiently with nucleophilic reagents such as Grignard reagents and amino compounds to give the corresponding displacement products of the alkylthio group [27-31]. However reactions of these *S*-alkylthioamidium salts with active methylene compounds to give β-amino acrylonitrile derivatives are not almost known, and they are not sufficiently used in organic synthesis [27,28]. Therefore we attempted a synthesis of polarized ethylenes as electrophilic reagents.

Reactions of **3a-i**, readily prepared by treatment of thioamide derivatives **1a-i** with dimethyl sulfate without solvent, with active methylene compounds such as malononitrile in the presence of potassium carbonate in dimethyl sulfoxide gave the corresponding dicyanoethylene compounds **4a-i** in good yields (Scheme 1, Table 1).



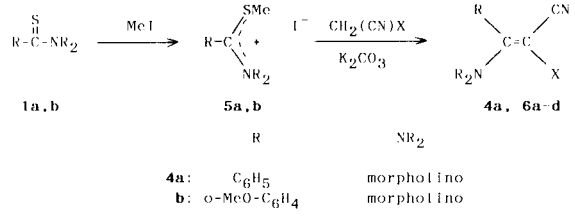
Scheme 1

The displacement reaction of methylthioamidium iodides **5a,b**, which were prepared by treatment of thio-

Table 1. 3-Amino-2-cyanoacrylonitriles

	R	mp(°C)	Yield(%)
4a	C_6H_5	178	79
b	o-MeO-C_6H_4	107	87
c	p-MeO-C_6H_4	114	60
d	3,4-$(MeO)_2$-C_6H_3	151	43
e	3,4-(OCH_2O)-C_6H_3	187	57
f	p-Cl-C_6H_4	153	88
g	thienyl	145	83
h	C_6H_5-CH_2	113	59
i	p-Me-C_6H_4-CH_2	120	58

amide derivatives **1a,b** with methyl iodide, with active methylene compounds (malononitrile, methyl cyanoacetate, cyanoacetamide) smoothly occurred in the presence of potassium carbonate in DMSO to give the corresponding polarized ethylenes **4a** and **6a-d**, though the yields were not so good (Scheme 2, Table 2).



Scheme 2

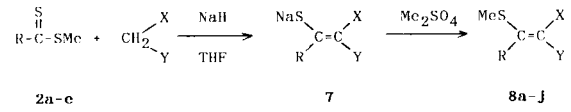
Table 2. Synthesis of Polarized Ethylenes

Entry	Product	R	X	Conditions[a] Time(hr), Solvent		mp(°C)	Yield(%)[b]
1	**4a**	Ph	CN	24	CH_2Cl_2	178	54
2	**4a**	Ph	CN	1	DMSO	178	46
3	**6a**	Ph	COOMe	24	CH_2Cl_2	116	43
4	**b**	Ph	$CONH_2$	24	CH_2Cl_2	182	16
5	**c**	o-MeO-C_6H_4	COOMe	24	CH_2Cl_2	117	35
6	**d**	o-MeO-C_6H_4	$CONH_2$	36	CH_2Cl_2	140	19

[a]All reactions were carried out at room temperature. [b]Yield after isolation by recrystallization.

Next, we explored a synthetic method of the new polarized ethylenes bearing methylthio groups as the electron-donating group. In general, this type of polarized ethylene derivatives are synthesized by the displacement reaction of suitable Grignard reagents with appropriately functionalized ketene dithioacetals, extensively used in the synthesis of heterocyclic compounds [16-20, 32-35].

Methyl dithiocarboxylates **2a-e**, which are readily prepared from the corresponding thioamides or Grignard reagents and carbon disulfide [36], are allowed to react with malononitrile in the presence of sodium hydride in tetrahydrofuran at reflux followed by the methylation with methyl iodide to give the corresponding 1-methylthio-2,2-dicyanoethylene derivatives **8a-e** in moderate yields (Scheme 3). Reactions of **2a-e** with other active methylene compounds (cyanoacetamide, methyl cyanoacetate, phenylacetonitrile) also afforded the corresponding polarized ethylene compounds **8f-j** in 13-86% yields.

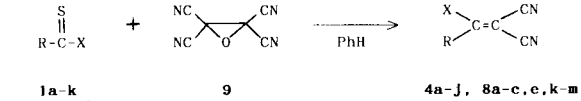


Scheme 3

Table 3. 2-Cyano-3-methylthioacrylonitriles

	R	X	Y	mp(°C)	Yield(%)
8a	C_6H_5	CN	CN	95	51
b	o-MeO-C_6H_4	CN	CN	75	87
c	p-MeO-C_6H_4	CN	CN	102	46
d	3,4-$(MeO)_2$-C_6H_3	CN	CN	90	30
e	p-Cl-C_6H_4	CN	CN	155	56
f	C_6H_5	CN	$CONH_2$	207	38
g	p-MeO-C_6H_4	CN	$CONH_2$	130	55
h	p-Cl-C_6H_4	CN	$CONH_2$	196	64
i	p-Me_2N-C_6H_4	CN	COOMe	120	13
j	p-Me_2N-C_6H_4	CN	C_6H_5	112	86

Moreover we found a novel and simple preparation of polarized ethylenes bearing push-pull substituents by the reaction of thioamides **1a-k** or methyl dithiocarboxylates **2a-c,e-h** with tetracyanoethylene oxide (**9**). Although it has been reported that the reaction of thiocarbonyl derivatives with tetracyanoethylene oxide give stable thiocarbonyl ylides, thiazoles, and dicyanomethylene compounds, the preparation of the polarized ethylenes using dicyanomethylenation with tetracyanoethylene oxide has been unknown hitherto [17-41]. Thioamides **1a-k** were allowed to react with tetracyanoethylene oxide at room temperature in benzene with stirring to give the corresponding dicyanoethylene compounds **4a-j** very smoothly. In addition, reactions of methyl dithiocarboxylates **2a-c,e-h** with tetracyanoethylene oxide also occurred under the similar condi-



Scheme 4

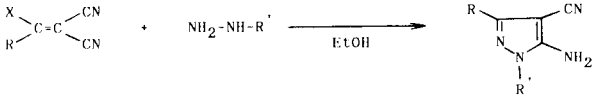
Table 4. Synthesis of 2-methylthio-1,1-dicyanoethylenes

Product	R	X	mp(°C)	% Yield
4a:	C_6H_5	morpholino	178	69
b:	o-MeO-C_6H_4	morpholino	95	91
c:	p-MeO-C_6H_4	morpholino	114	84
d:	3,4-$(MeO)_2$-C_6H_3	morpholino	151	90
e:	3,4-(OCH_2O)-C_6H_3	morpholino	187	82
f:	p-Cl-C_6H_4	morpholino	153	85
g:	2-thienyl	morpholino	145	88
h:	C_6H_5-CH_2	morpholino	113	77
i:	p-Me-C_6H_4-CH_2	morpholino	120	75
j:	C_6H_5-CH_2CH_2	morpholino	111	79
k:	methylthio	morpholino	121	62
8a:	C_6H_5	methylthio	95	78
b:	o-MeO-C_6H_4	methylthio	75	67
c:	p-MeO-C_6H_4	methylthio	95	72
e:	p-Cl-C_6H_4	methylthio	155	82
k:	p-Me_2N-C_6H_4	methylthio	116	91
l:	2-thienyl	methylthio	102	78
m:	C_6H_5-CH_2	methylthio	oil	68

tions to yield the corresponding 2-methylthio-1,1-dicyanoethylene derivatives **8a-c,e,k-m** in good yields (Scheme 4). The results are listed in Table 4.

Synthesis of Pyrazoles and Pyrimidines.

It is well known that the reaction of polarized ethylenes like ketene dithioacetals with bifunctionalized amines such as hydrazine or amidine derivatives gives the corresponding pyrazole or pyrimidine derivatives [42-47]. The heterocyclic compounds, thus obtained, are not only interesting from a viewpoint of biological activities but also important and useful as the starting materials for the synthesis to other heterocyclic compounds. Therefore, we attempted to prepare pyrazole and pyrimidine derivatives using **4** and **8**. Reactions of **4a-i** with hydrazine hydrate gave the corresponding 3-substituted 5-aminopyrazole-4-carbonitrile derivatives **10a-h** on heating at 100° for 5 hours in good yield. In contrast, reactions of morpholino compounds **4a-i** with phenylhydrazine did not occur under the similar conditions. However this problem can be readily solved by use of methylthioethylene compounds **8a,c,k** instead of **4a-i** since dicyanoethylenes bearing the methylthio group is generally more active towards nucleophiles than those of the morpholino group. Namely, reactions of **8a,c,k** with phenylhydrazine gave the corresponding 5-amino-1-arylpyrazoles-4-carbonitriles **10j-m** at reflux for 1 hour in ethanol, as illustrated in Table 5 (Scheme 5).



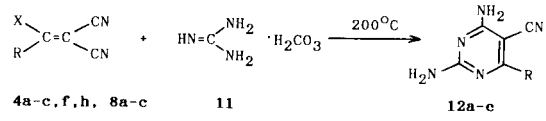
4a-l, 8a,c,k 10a-l

Scheme 5

Table 5. 5-Aminopyrazole-4-carbonitriles

Product	R	R'	mp(°C)	% Yield
10a:	C_6H_5	H	203	74
b:	o-MeO-C_6H_4	H	192	88
c:	p-MeO-C_6H_4	H	158	69
d:	3,4-$(MeO)_2$-C_6H_3	H	175	51
e:	3,4-(OCH_2O)-C_6H_3	H	215	65
f:	p-Cl-C_6H_4	H	221	82
g:	2-thienyl	H	255	91
h:	C_6H_5-CH_2	H	141	98
i:	p-Me-$C_6H_4CH_2$	H	162	98
j:	C_6H_5	C_6H_5	160	46
k:	p-MeO-C_6H_4	C_6H_5	190	43
l:	p-Cl-C_6H_4	C_6H_5	189	64

Reactions of **4a-c,f,h** with guanidine carbonate (**11**) on heating at 200° for 2 hours gave the corresponding 2,4-diaminopyrimidine-5-carbonitrile derivatives **12a-e** in 52-90% yield (Scheme 6). The results are summarized in Table 6.



4a-c,f,h, 8a-c 11 12a-c

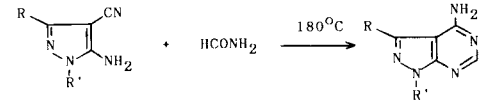
Scheme 6

Table 6. Synthesis of pyrazoles

Product	R	mp(°C)	% Yield
12a:	C_6H_5	300	85
b:	o-MeO-C_6H_4	218	70
c:	p-MeO-C_6H_4	245	83
d:	p-Cl-C_6H_4	281	90
e:	C_6H_5-CH_2	228	52

Synthesis of Pyrazolo[3,4-*d*]pyrimidines.

Pyrazolo[3,4-*d*]pyrimidines are of considerable chemical and pharmacological importance, because of purine analogs [48]. In particular, hypoxanthine analogue, allopurinol, is a known inhibitor of xanthine oxidase in vivo [44]. Other related pyrazolo[3,4-*d*]pyrimidine, including the xanthine analogue (oxyallopurinol) and the thiohypoxanthine analogue (thiopurinol), have similar inhibitory effect on xanthine oxidase. Many compounds of this type also reveal anti-tumor and anti-leukemic activity. Recently, several 3-substituted pyrazolo[3,4-*d*]pyrimidine derivatives have also shown pharmacological activity like allopurinol, which namely is the inhibor of xanthine oxidase. Compounds **10** are the key intermediates for the preparation of pyrazolo[3,4-*d*]pyrimidine derivatives. It has been known the synthesis of 4-aminopyrazolo[3,4-*d*]pyrimidine by the cyclization of 5-aminopyrazole-4-carbonitrile with formamide [49,50]. So we tried the application of the above reaction to synthesis 3-substituted pyrazolo[3,4-*d*]pyrimidine derivatives. The reaction of **10a** with formamide also smoothly occurred at 180° for 2 hours to give the desired



10a,c,d,f,h,j,k,l 13a-h

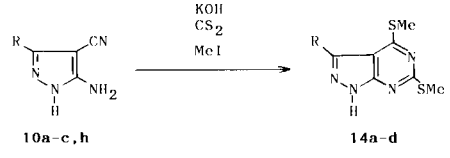
Scheme 7

Table 7. 4-Aminopyrazolo[3,4-d]pyrimidines

	R	R'	mp(°C)	Yield(%)
13a:	C_6H_5	H	276	53
b:	p-MeO-C_6H_4	H	298	60
c:	3,4-$(MeO)_2$-C_6H_3	H	290	42
d:	p-Cl-C_6H_4	H	357	50
e:	C_6H_5-CH_2	H	277	87
f:	C_6H_5	C_6H_5	242	42
g:	p-MeO-C_6H_4	C_6H_5	220	82
h:	p-Cl-C_6H_4	C_6H_5	278	83

corresponding 4-amino-3-phenylpyrazolo[3,4-*d*]pyrimidine (**13a**) in good yields (Scheme 7). Other 3-substituted 4-aminopyrazolo[3,4-*d*]pyrimidine derivatives **3b-h** were also prepared from **10b,c,d,f,j-l** in a manner similar to that of the preparation of **13a** (Table 7).

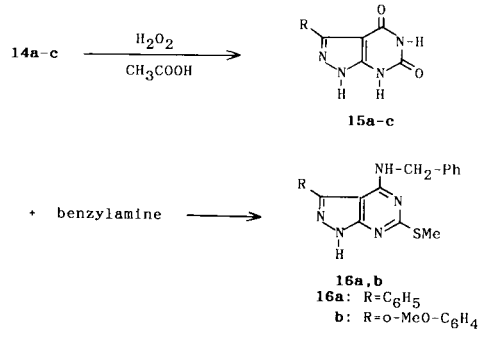
It is well known that the reaction of *o*-aminobenzonitrile with carbon disulfide in the presence of an appropriate base like sodium hydroxide gives cyclized products, quinazoline derivatives [57,64]. We tried the application of above reaction to synthesis of pyrazolo[3,4-*d*]pyrimidines. Compounds **10a-c,h** were allowed to react with carbon disulfide in the presence of potassium hydroxide as a base in dimethyl sulfoxide (DMSO), followed by treatment with methyl iodide to give the desired product, 4,6-bis(methylthio)pyrazolo[3,4-*d*]pyrimidines **14a-d** in good yields. Treatment of **14a-c** with 30% hydrogen peroxide in acetic acid afforded 4,6-hydroxy(or 4,6-dioxo)pyrazolo[3,4-*d*]pyrimidines **15a-c** in quantitative yields. The displacement of the methylthio group in **12a,b** with benzylamine smoothly occurs to yield the corresponding 4-benzylaminopyrazolo-[3,4-*d*]pyrimidine derivatives **16a,b** in good yields (Scheme 8). In general, the 4-chloro group on the pyrimidine ring is more reactive than that of the 2-chloro group in the 2,4-dichloropyrimidine derivatives [42,51,52]. So it is suggested that the methylthio group at the 4-position in the pyrimidine is more active than that at the 2-position towards nucleophiles like amines [53].



10a-c,h **14a-d**

Table 8. 4,6-Bis(methylthio)pyrazolo[3,4-d]pyrimidines

	R	mp(°C)	Yield(%)
14a	C_6H_5	218	77
b	*o*-MeO-C_6H_4	200	64
c	*p*-MeO-C_6H_4	248	81
d	C_6H_5-CH_2	176	60

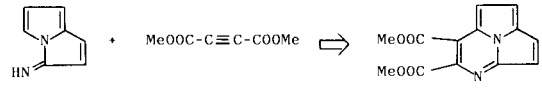


Scheme 8

Synthesis of 5-Aza[2.2.3]cyclazines.

5-Aza[2.2.3]cyclazine is an interesting aromatic compound involving delocalized 10π-electrons from the theoretical point of view, similarly to other 1-, 2-, or 6-aza-[2.2.3]cyclazines and [2.2.3]cyclazines [54-58]. Therefore synthesis of a variety of 5-azacyclazines by use of readily available starting materials is highly desirable for the investigation of aza[2.2.3]cyclazine chemistry. Boekelheide and Kertelj have first reported the synthesis of 5-aza[2.2.3]-cyclazine derivatives by the [8 + 2] cycloaddition reaction of 7-methyl-2-phenylpyrrolo[1,2-*c*]pyrimidine with dimethyl acetylenedicarboxylate (DMAD) in the presence of palladium on charcoal, which contains a phenyl and a methyl group in the 6- and 2-positions, respectively [59]. However, access to desired 5-aza[2.2.3]cyclazine derivatives from pyrrolo[1,2-*c*]pyrimidines is difficult at present, because the preparation of suitably designed pyrrolo[1,2-*c*]pyrimidine derivatives is still limited.

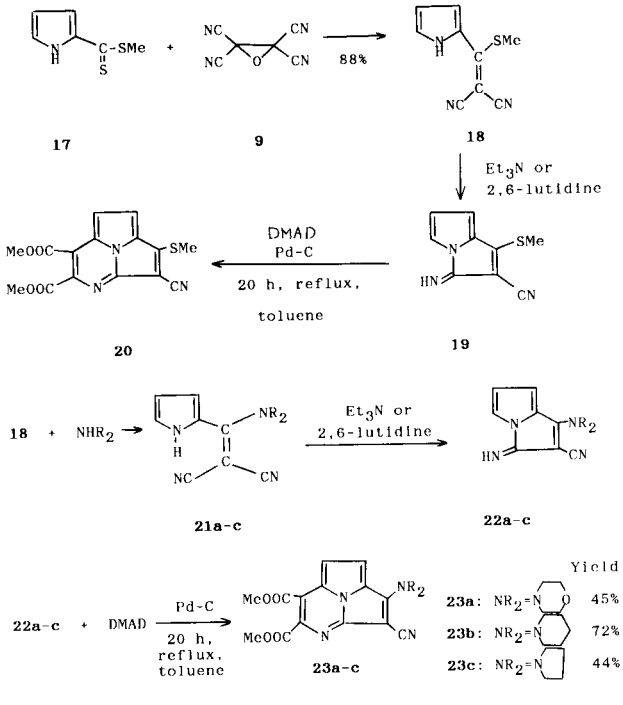
Jessep and Leaver reported a convenient and unique [8 + 2] cycloaddition reaction of 3-dimethylaminomethylene-3*H*-pyrrolizine bearing an exo-methylene group with DMAD to give dimethyl [2.2.3]cyclazine-5,6-dicarboxylate [60]. Therefore we attempted a novel synthesis of 5-aza-[2.2.3]cyclazines by the [8 + 2] cycloaddition reaction of in situ generated cyclic exo-imino tetraene compounds, 3-imino-3*H*-pyrrolizine derivatives, with DMAD (Scheme 9).



Scheme 9

In an extension of the studies on polarized ethylenes [61], we applied this reaction to the preparation of 2-cyano-3-pyrrol-2-yl)-3-methylthioacrylonitrile which is an important precursor for the synthesis of 5-aza[2.2.3]cyclazines. Methyl pyrrole-2-dithiocarboxylate (**17**), readily prepared from the Grignard reagent of pyrrole and carbon disulfide, is allowed to react with tetracyanoethylene oxide (**9**) in benzene with stirring at room temperature to give a desired dicyanomethylene derivative **18** in 88% yield. Cyclization of **18** to 2-cyano-3-imino-1-methylthio-3*H*-pyrrolizine (**19**) occurred smoothly, when the mixture of **18** and triethylamine or 2,6-lutidine was heated at reflux, and then the reaction temperature was elevated ultimately up to *ca.* 150° by removal of the base [62]. Without isolation of **19**, treatment of the reaction mixture with DMAD in the presence of 5% palladium on charcoal in toluene at reflux for 20 hours gave the [8 + 2] cycloaddition product, dimethyl 4-cyano-3-methylthio-5-aza[2.2.3]cyclazine-6,7-dicarboxylate (**20**), in 23% yield. 3-Amino-5-aza[2.2.3]cyclazine derivatives **23a-c** were also obtained from the corre-

sponding 1-amino-3-imino-3*H*-pyrrolizine derivatives **22a-c** and DMAD. Compounds **21a-c** were readily prepared by the displacement of the methylthio group of **18** with the corresponding amines such as morpholine, piperidine, and pyrrolidine, respectively, followed by cyclization at heating in the presence of triethylamine or 2,6-lutidine in a manner similar to the preparation of **19** (Scheme 10). The vicinal coupling constant between C_1-H and C_2-H (7.62 and 7.86 pm, $J_{1,2}$ = 4.5 Hz) of **20** in the ^{1}H nmr spectrum is similar to the corresponding value of 2-methylthio-1-aza[2.2.3]cyclazine (7.21 and 7.53 ppm, $J_{3,4}$ = 4.4 Hz). The chemical shift of the methyl protons of the methylthio group of **20** is also shown in low field region similar to that of the corresponding methylthio group in 2-methylthio-1-aza[2.2.3]cyclazine [63]. The nmr data apparently indicate that 5-aza[2.2.3]cyclazine derivatives **20** and **23a-c** are typical aromatic compounds.



Scheme 10

In conclusion, the utility of the present method for preparing polarized ethylenes **4,6,8,18** which were otherwise inaccessible was mostly displaced by the ready availability of starting materials and simple manipulation of the conversion. The activated ethylenes **4,6,8** are also very useful reagents for the preparation of a variety of heterocyclic compounds such as pyrazoles and pyrimidines. The present synthetic method of 5-aza[2.2.3]cyclazine by the [8 + 2] cycloaddition of heterocycles bearing exo-imino group with DMAD will provide a convenient and useful method for the synthesis of various other aza[2.2.3]cyclazine derivatives.

EXPERIMENTAL

All melting points were determined in a capillary tube and are uncorrected. Infrared (ir) spectra were recorded in potassium bromide pellets on JASCO IRA-2 spectrometer and SHIMADZU IR-460 and ultraviolet (uv) absorption spectra were determined in 95% ethanol on a Hitachi EP-S2 spectrometer. Nuclear magnetic resonance (nmr) spectra were obtained on JNM-PS-100(100 MHz), JNM-FX-90Q(90 MHz), and JNM-PMX-60SI(60 MHz) spectrometers with tetramethylsilane as an internal standard. Mass (ms) spectra were recorded on a JMS-01SG and JMS-303D mass spectrometers.

2-Cyano-3-morpholino-3-phenylacrylonitrile (**4a**).

A mixture of 1.04 g (5 mmoles) of phenylthiomorpholide (**1a**) and 1.26 g (10 mmoles) of dimethyl sulfate was heated at 100° for 30 minutes. This imidium salts **3a** was used in the next step without purification. This crude product **3a** was mixed with 0.66 g (10 mmoles) of malononitrile, 20 ml of dimethyl sulfoxide, and 1.38 g (10 mmoles) of potassium carbonate. This mixture was stirred at room temperature for 2 hours and stirring was continued at 70° for 20 minutes. After cooling to room temperature, the reaction mixture was poured into 200 ml of water. The resulting precipitate was collected by filtration and recrystallized from methanol to give 0.95 g (4.0 mmoles) of **4a** as colorless needles, mp 178°, in 79% yield. Compound **4a** was also prepared from **5a** in manner similar to that described for the synthesis of **6a** (See Table 2); ir (potassium bromide): ν max cm^{-1} 2190 (CN), 1595 (C = C); uv (ethanol): λ max nm (log ϵ) 236 (4.01), 314 (4.16); ^{1}H nmr (deuteriochloroform): δ 3.70 (8H, bs, N-(CH_2-CH_2)$_2$O), 7.59 (5H, s, phenyl-H).

Anal. Calcd. for $C_{14}H_{13}N_3O$: C, 70.27; H, 5.48; N, 17.56. Found: C, 70.49; H, 5.52; N, 17.50.

2-Cyano-3-(2-methoxyphenyl)-3-morpholinoacrylonitrile (**4b**).

This compound (1.17 g, 4.4 mmoles) was synthesized in 87% yield from *o*-methoxyphenylthiomorpholide (**1b**) (1.19 g, 5 mmoles) and malononitrile (0.66 g, 10 mmoles) in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 107°; ir (potasssium bromide): ν max cm^{-1} 2170 (CN), 1595 (C = C); uv (ethanol): λ max nm (log ϵ) 217 (4.17), 311 (4.28); ^{1}H nmr (deuteriochloroform): δ 3.71 (8H, bs, N-(CH_2-CH_2)$_2$-O), 3.89 (3H, s, OMe), 6.95-7.66 (4H, m, phenyl-H).

Anal. Calcd. for $C_{15}H_{17}N_3O_2$: C, 66.90; H, 5.61; N, 15.61. Found: C, 66.88; H, 5.52; N, 15.66.

2-Cyano-3-(4-methoxyphenyl)-3-morpholinoacrylonitrile (**4c**).

This compound (0.81 g, 3 mmoles) was synthesized in 60% yield from *o*-methoxyphenylthiomorpholide (**1c**) (1.19 g, 5 mmoles) and malononitrile (0.66 g, 10 mmoles) in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 114°; ir (potassium bromide): ν max cm^{-1} 2190 (CN), 1600 (C = C); uv (ethanol): λ max nm (log **e**) 223 (4.13), 298 (4.28); ^{1}H nmr (deuteriochloroform): δ 3.75 (8H, bs, N-(CH_2-CH_2)$_2$-O), 3.87 (3H, s, OMe), 7.01 (2H, d, J = 8.4 Hz, 2,6-H or 3,5-H), 7.39 (2H, d, J = 8.4 Hz, 2,6-H or 3,5-H).

Anal. Calcd. for $C_{15}H_{17}N_3O_2$: C, 66.90; H, 5.61; N, 15.61. Found: C, 66.78; H, 5.61; N, 15.55.

2-Cyano-3-(3,4-dimethoxyphenyl)-3-morpholinoacrylonitrile (**4d**).

This compound (0.64 g, 2.2 mmoles) was synthesized in 43% yield from 3,4-dimethoxyphenylthiomorpholide (**1d**) (1.34 g, 5 mmoles) and malononitrile (0.66 g, 10 mmoles) in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 151°; ir (potassium bromide): ν max cm^{-1} 2180 (CN), 1595 (C=C); uv (ethanol): λ max nm (log ϵ) 230 (4.16), 311 (4.29); ^{1}H nmr (deuteriochloroform): δ 3.74 (8H, bs, N-(CH_2-CH_2)$_2$-O), 3.91 (6H, s, OMe), 6.88 (1H, s, 2-H), 7.00 (2H, s, 5,6-H).

Anal. Calcd. for $C_{16}H_{17}N_3O_3$: C, 64.20; H, 5.72; N, 14.04. Found: C, 64.25; H, 5.78; N, 13.97.

2-Cyano-3-(3,4-methylenedioxyphenyl)-3-morpholinoacrylonitrile (**4e**).

This compound (0.81 g, 2.9 mmoles) was synthesized in 57% yield from 3,4-methylenedioxyphenylthiomorpholide (**1e**) (1.26 g, 5 mmoles) and malononitrile (0.66 g, 10 mmoles) in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 187°; ir (potassium bromide): ν max cm^{-1} 2180 (CN), 1600 (C=C); uv (ethanol): λ max nm (log ϵ) 233 (4.12), 311 (4.32); ^{1}H nmr (deuteriochloroform): δ 3.73 (8H, bs, N-(CH_2-CH_2)$_2$O), 6.08 (2H, s, O-CH_2-O), 6.84 (1H, s, 2-H), 6.94 (2H, s, 5,6-H).

Anal. Calcd. for $C_{15}H_{13}N_3O_3$: C, 63.60; H, 4.63; N, 14.83. Found: C, 62.81; H, 4.38; N, 14.64.

3-(4-Chlorophenyl)-2-cyano-3-morpholinoacrylonitrile (**4f**).

This compound (1.20 g, 4.4 mmoles) was synthesized in 88% yield from 4-chlorophenylthiomorpholide (**1f**) (1.21 g, 5 mmoles) and malononitrile (0.66 g, 10 mmoles) in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 153°; ir (potassium bromide): ν max cm^{-1}; 2190 (CN), 1588 (C=C); uv (ethanol): λ max nm (log ϵ) 250 (4.12), 311 (4.14); ^{1}H nmr (deuteriochloroform): δ 3.74 (8H, bs, N-(CH_2-CH_2)$_2$-O), 7.34 (2H, d, J = 8.4 Hz, 2,6-H or 3,5-H), 7.47 (2H, d, J = 8.4 Hz, 2,6-H or 3,5-H).

Anal. Calcd. for $C_{14}H_{12}ClN_3O$: C, 61.43; H, 4.42; Cl, 12.95, N, 15.35. Found: C, 61.27; H, 4.32; Cl, 13.07; N, 15.35.

2-Cyano-3-morpholino-3-(2-thienyl)acrylonitrile (**4g**).

This compound (1.02 g, 4.2 mmoles) was synthesized in 83% yield from 2-thienylthiomorpholide (**1g**) (1.07 g, 5 mmoles) and malononitrile (0.66 g, 10 mmoles) in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give yellow needles, mp 145°; ir (potassium bromide): ν max cm^{-1} 2180 (CN), 1525 (C=C); uv (ethanol: λ max nm (log ϵ) 244 (3.82), 312 (4.14); ^{1}H nmr (deuteriochloroform): δ 3.75 (8H, bs, N-(CH_2-CH_2)$_2$-O), 7.10-7.35 (1H, m, 4-H), 7.58-7.78 (2H, m, 3,5-H).

Anal. Calcd. for $C_{12}H_{11}N_3OS$: C, 58.76; H, 4.52; N, 17.13; S, 13.07. Found: C, 58.52; H, 4.44; N, 16.94; S, 12.96.

3-Benzyl-2-cyano-3-morpholinoacrylonitrile (**4h**).

This compound (0.75 g, 3.0 mmoles) was synthesized in 59% yield from benzylthiomorpholide (**1h**) (1.11 g, 5 mmoles) and malononitrile (0.66 g, 10 mmoles) in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 113°; ir (potassium bromide): ν max cm^{-1} 2180 (CN), 1555 (C=C); uv (ethanol): λ max nm (log ϵ) 297 (4.31); ^{1}H nmr (deuteriochloroform): δ 3.58-3.61 (8H, m, N-(CH_2-CH_2)$_2$-O), 4.00 (2H, s, CH_2), 7.40 (5H, s, phenyl-H).

Anal. Calcd. for $C_{15}H_{15}N_3O$: C, 71.13; H, 5.97; N, 16.59. Found: C, 71.02; H, 5.91; N, 16.61.

2-Cyano-3-(4-methylbenzyl)-3-morpholinoacrylonitrile (**4i**).

This compound (0.78 g, 2.9 mmoles) was synthesized in 58% yield from 4-methylbenzylthiomorpholide (**1i**) (1.18 g, 5 mmoles) and malononitrile (0.66 g, 10 mmoles) in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 120°; ir (potassium bromide): ν max cm^{-1} 2180 (CN), 1545 (C=C); uv (ethanol): λ max nm (log ϵ) 297 (4.01); ^{1}H nmr (deuteriochloroform): δ 2.32 (3H, s, Me), 3.56-3.61 (8H, m, N-(CH_2-CH_2)$_2$-O), 3.94 (2H, s, CH_2), 6.96-7.35 (4H, m, 2,3,5,6-H).

Anal. Calcd. for $C_{16}H_{17}N_3O$: C, 71.89; H, 6.41; N, 15.72. Found: C, 71.96; H, 6.36; N, 15.66.

Methyl 2-Cyano-3-morpholino-3-phenylacrylate (**6a**).

A mixture of 2.07 g (10 mmoles) of phenylthiomorpholide (**1a**) and 2.84 g (20 mmoles) of methyl iodide was refluxed in methanol for 1 hour. This imidium salts **5a** was used in the next step without purification because of sufficient pure. The imidium salt (1.1 g, 5 mmoles) was mixed with 0.5 g (5 mmoles) of methyl cyanoacetate, 20 ml of dichloromethane, and 2.8 g (20 mmoles) of potassium carbonate. After stirring at room temperature for 24 hours, the mixture was poured into 50 ml of water, the organic layer was extracted by 30 ml of dichloromethane. After removal of solvent, this product was recrystallized from methanol to give 0.585 g (2.2 mmoles) of **5a** as colorless needles, mp 116°, in 43% yield; ir (potassium bromide): ν max cm^{-1} 2190 (CN), 1690 (CO); uv (ethanol): λ max nm (log ϵ) 242 (3.96), 329 (4.09); ^{1}H nmr (deuteriochloroform): δ 3.28-3.96 (8H, m, N-(CH_2-CH_2)-O), 3.78 (3H, s, OMe), 7.18-7.61 (5H, m, phenyl-H).

Anal. Calcd. for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92; N, 10.29. Found: C, 65.94; H, 5.95; N, 10.27.

2-Cyano-3-morpholino-3-phenylacrylamide (**6b**).

This compound (0.205 g, 0.8 mmole) was synthesized in 16% yield from phenylthiomorpholide (**1a**) (1.04 g, 5 mmoles) and 2-cyanoacetamide (0.42 g, 5 mmoles) in a manner similar to that described for the preparation of **6a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 182°; ir (potassium bromide): ν max cm^{-1} 3360, 3185 (NH_2), 2190 (CN); uv (ethanol): λ max nm (log ϵ) 242 (4.03), 339 (4.05); ^{1}H nmr (deuteriochloroform): δ 3.26-3.88 (8H, m, N-(CH_2-CH_2)$_2$-O), 5.61 (2H, bs, NH_2), 7.26-7.65 (5H, m, phenyl-H).

Anal. Calcd. for $C_{14}H_{15}N_3O_2$: C, 65.35; H, 5.88; N, 16.33. Found: C, 65.33; H, 5.86; N, 16.36.

Methyl 2-Cyano-3-morpholino-3-(2-methoxyphenyl)acrylate (**6c**).

This compound (0.531 g, 1.75 mmoles) was synthesized in 35% yield from 2-methoxyphenylthiomorpholide (**1d**) (1.19 g, 5 mmoles) and methyl cyanoacetate (0.5 g, 5 mmoles) in a manner similar to that described for the preparation of **6a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 117°; ir (potassium bromide): ν max cm^{-1} 2200 (CN), 1705 (CO); uv (ethanol): λ max nm (log ϵ) 232 (4.01, shoulder), 260 (3.55, shoulder), 323 (4.16); ^{1}H nmr (deuteriochloroform): δ 3.20-3.98 (8H, m, N-(CH_2-CH_2)$_2$-O), 3.76 (3H, s, COOMe), 3.87 (3H, s, 2-OMe), 6.92-7.59 (4H, m, phenyl-H).

Anal. Calcd. for $C_{16}H_{18}N_2O_4$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.78; H, 5.93; N, 9.12.

2-Cyano-3-(2-methoxyphenyl)-3-morpholinoacrylamide (**6d**).

This compound (0.272 g, 0.95 mmole) was synthesized in 19% yield from 2-methoxyphenylthiomorpholide (**1b**) (1.19 g, 5 mmoles) and 2-cyanoacetamide (0.42 g, 5 mmoles) in a manner similar to that described for the preparation of **6a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 140°; ir (potassium bromide): ν max cm^{-1} 3395, 3180 (NH_2), 2190 (CN); uv (ethanol): λ max nm (log ϵ) 232 (4.05, shoulder), 255 (3.72, shoulder), 324 (4.12); ^1H nmr (deuteriochloroform): δ 3.12-3.98 (8H, m, N-(CH_2-CH_2)$_2$-O), 3.88 (3H, s, OMe), 5.64 (2H, bs, NH_2), 6.84-7.58 (4H, m, phenyl-H).

Anal. Calcd. for $C_{15}H_{17}N_3O_3$: C, 62.71; H, 5.96; N, 14.62. Found: C, 62.72; H, 5.94; N, 14.72.

2-Cyano-3-methylthio-3-phenylacrylonitrile (**8a**).

Malononitrile (0.99 g, 15 mmoles) was added to a suspension of sodium hydride (50%, 0.72 g, 15 mmoles) in 50 ml of absolute tetrahydrofuran (THF) and the mixture was stirred for 30 minutes at room temperature. Methyl phenyldithiocarboxylate (**2a**) (1.68 g, 10 mmoles) was added to the above mixture. The whole was stirred for 1 hour and then refluxed for 2 hours. After evaporation of the THF, the residue was dissolved in 100 ml of water. Dimethyl sulfate (1.89 g, 15 mmoles) was added dropwise to the solution and the mixture was stirred for 2 hours at room temperature. The precipitate was collected by filtration and recrystallized from methanol to give 1.02 g (51%) of colorless needles, mp 95°; ir (potassium bromide): ν max cm^{-1} 2220 (CN), 1597 (C=C); uv (ethanol): λ max nm (log ϵ) 278 (3.86, shoulder), 322 (4.14); ^1H nmr (deuteriochloroform): δ 2.22 (3H, s, SMe), 7.47 (5H, s, phenyl-H).

Anal. Calcd. for $C_{11}H_8N_2S$: C, 65.97; H, 4.03; N, 13.99; S, 16.01. Found: C, 65.94; H, 3.99; N, 14.00; S, 16.19.

2-Cyano-3-(2-methoxyphenyl)-3-methylthioacrylonitrile (**8b**).

This compound (1.97 g, 8.7 mmoles) was synthesized in 87% yield from methyl 2-methoxyphenyldithiocarboxylate (**2b**) (1.98 g, 10 mmoles), malononitrile (0.99 g, 15 mmoles) and dimethyl sulfate (1.89 g, 15 mmoles) in a manner similar to that described for the preparation of **8a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 75°; ir (potassium bromide): ν max cm^{-1} 2200 (CN), 1594 (C=C); uv (ethanol): λ max nm (insufficient solubility) 253, 318: λ min nm 237, 266; ^1H nmr (deuteriochloroform): δ 2.15 (3H, s, SMe), 3.89 (3H, s, OMe), 6.98-7.16 (3H, m, 3,5,6-H), 7.40-7.60 (1H, m, 4-H).

Anal. Calcd. for $C_{12}H_8N_2OS$: C, 62.60; H, 4.38; N, 12.17; S, 13.90. Found: C, 62.15; H, 4.34; N, 12.23; S, 13.77.

2-Cyano-3-(4-methoxyphenyl)-3-methylthioacrylonitrile (**8c**).

This compound (1.04 g, 4.6 mmoles) was synthesized in 46% yield from methyl 4-methoxyphenyldithiocarboxylate (**2c**) (1.98 g, 10 mmoles), malononitrile (0.99 g, 15 mmoles) and dimethyl sulfate (1.89 g, 15 mmoles) in a manner similar to that described for the preparation of **8a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 95°; ir (potasssium bromide): ν max cm^{-1} 2220 (CN), 1600 (C=C); uv (ethanol): λ max nm (log ϵ) 254 (3.76), 280 (3.78, shoulder), 318 (4.16); ^1H nmr (deuteriochloroform): δ 2.14 (3H, s, SMe), 3.87 (3H, s, OMe), 6.94-7.41 (4H, m, 2,3,5,6-H).

Anal. Calcd. for $C_{12}H_7N_2OS$: C, 62.59; H, 4.38; N, 12.16; S, 13.92. Found: C, 62.49; H, 4.44; N, 12.38; S, 13.57.

2-Cyano-3-(3,4-dimethoxyphenyl)-3-methylthioacrylonitrile (**8d**).

This compound (0.78 g, 3 mmoles) was synthesized in 30% yield from methyl 3,4-dimethoxyphenyldithiocarboxylate (**2d**) (2.28 g, 10 mmoles), malononitrile (0.99 g, 15 mmoles) and dimethyl sulfate (1.89 g, 15 mmoles) in a manner similar to that described for the preparation of **8a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 90°; ir (potassium bromide): ν max cm^{-1} 2210 (CN); uv (ethanol): λ max nm (log ϵ) 260 (3.89), 315 (4.16); ^1H nmr (deuteriochloroform): 2.34 (3H, s, SMe), 3.93 (3H, s, OMe), 3.95 (3H, s, OMe), 6.90-7.15 (3H, m, 2,5,6-H).

Anal. Calcd. for $C_{13}H_{12}N_2O_2S$: C, 59.99; H, 4.65; N, 10.77; S, 12.30. Found: C, 59.81; H, 4.66; N, 10.95; S, 12.35.

3-(4-Chlorophenyl)-2-cyano-3-methylthioacrylonitrile (**8e**).

This compound (1.32 g, 5.6 mmoles) was synthesized in 56% yield from methyl 4-chlorophenyldithiocarboxylate (**2e**) (2.03 g, 10 mmoles), malononitrile (0.99 g, 15 mmoles) and dimethyl sulfate (1.89 g, 15 mmoles) in a manner similar to that described for the preparation of **8a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 155°; ir (potassium bromide): ν max cm^{-1} 2210 (CN), 1582 (C=C); uv (ethanol): λ max nm (log ϵ) 294 (4.04, shoulder), 324 (4.14); ^1H nmr (deuteriochloroform): δ 2.28 (3H, s, SMe), 7.32 (2H, d, J = 8.79 Hz, 2,6-H or 3,5-H), 7.54 (2H, d, J = 8.79 Hz, 2,6-H or 3,5-H).

Anal. Calcd. for $C_{11}H_7ClN_2S$: C, 56.29; H, 3.01; N, 11.94; S, 13.66. Found: C, 55.99; H, 3.00; N, 11.75; S, 13.69.

2-Cyano-3-methylthio-3-phenylacrylamide (**8f**).

This compound (0.73 g, 3.76 mmoles) was synthesized in 38% yield from methyl phenyldithiocarboxylate (**2a**) and cyanoacetamide (1.26 g, 15 mmoles) in a manner similar to that described for the preparation of **8a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 209°; ir (potassium bromide): ν max cm^{-1} 3360, 3160 (NH), 2200 (CN), 1620 (CO); uv (ethanol): λ max nm (log ϵ) 238 (4.25), 314 (3.69); ^1H nmr (deuteriochloroform): δ 1.88 (3H, s, SMe), 5.81 (2H, bs, NH_2), 7.15-7.27 (2H, m, phenyl-), 7.46-7.54 (3H, m, phenyl-H).

Anal. Calcd. for $C_{11}H_{10}N_2OS$: C, 60.53; H, 4.62; N, 12.84; S, 14.81. Found: C, 60.30; H, 4.63; N, 12.78; S, 14.81.

2-Cyano-2-(4-methoxyphenyl)-3-methylthioacrylamide (**8g**).

This compound (1.36 g, 5.5 mmoles) was synthesized in 55% yield from methyl *p*-methoxyphenyldithiocarboxylate (**2c**) (1.99 g, 10 mmoles) and cyanoacetamide (1.26 g, 15 mmoles) in a manner similar to that described for the preparation of **8a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 130°; ir (potassium bromide): ν max cm^{-1} 3402, 3280, 3210 (NH), 2200 (CN), 1665 (CO); uv (ethanol): λ max nm (log ϵ) 243 (3.64), 313 (4.23); ^1H nmr (deuteriochloroform): δ 1.88 (3H, s, SMe), 3.87 (3H, s, OMe), 5.77 (2H, bs, NH_2), 6.96-7.54 (4H, m, phenyl-H).

Anal. Calcd. for $C_{12}H_{12}O_2N_2S$: C, 58.05; H, 4.87; N, 11.28; S, 12.91. Found: C, 58.01; H, 4.86; N, 11.29; S, 12.71.

3-(4-Chlorophenyl)-2-cyano-3-methylthioacrylamide (**8h**).

This compound (2.25 g, 6.4 mmoles) was synthesized in 64% yield from methyl 4-chlorophenyldithiocarboxylate (**2e**) (2.02 g, 10 mmoles) and cyanoacetate (1.26 g, 15 mmoles) in a manner similar to that described for the preparation of **8a**. An analytical sample was recrystallized from methanol to give colorless

needles, mp 196°; ir (potassium bromide): ν max cm^{-1} 3380, 3200 (NH_2), 2205 (CN), 1680 (CO); uv (ethanol): λ max nm (log ϵ) 245 (4.06), 313 (4.23); ^1H nmr (deuteriochloroform): δ 1.91 (2H, s, SMe 2/3), 2.06 (1H, s, SMe 1/3), 7.09-7.55 (4H, m, phenyl-H).

Anal. Calcd. for $C_{11}H_9ClON_2S$: C, 52.28; H, 3.59; Cl, 14.03; N, 11.08; S, 12.69. Found: C, 52.12; H, 3.60; Cl, 13.86; N, 11.00; S, 12.51.

Methyl 2-Cyano-3-(4-*N,N*-dimethylaminophenyl)-3-methylthioacrylate (**8i**).

This compound (0.36 g, 1.3 mmoles) was synthesized in 13% yield from methyl 4-*N,N*-dimethylaminophenyldithiocarboxylate (**2f**) (2.11 g, 10 mmoles), methyl cyanoacetate (1.49 g, 15 mmoles) and dimethyl sulfate (1.89 g, 15 mmoles) in a manner similar to that described for the preparation of **8a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 120°; ir (potassium bromide): ν max cm^{-1} 2250 (CN), 1680 (CO); uv (ethanol): λ max nm (log ϵ) 264 (4.25), 318 (4.20), 390 (4.01); ^1H nmr (deuteriochloroform): δ 2.02 (3H, s, SMe), 3.01 (6H, s, NMe_2), 3.84 (3H, s, OMe), 6.71 (2H, d, J = 8.8 Hz, 2,6-H), 7.15 (2H, d, J = 8.8 Hz, 3,5-H).

Anal. Calcd. for $C_{14}H_{16}N_2O_2S$: C, 60.85; H, 5.84; N, 10.14; S, 11.60. Found: C, 60.50; H, 5.89; N, 9.84; S, 11.40.

3-(4-*N,N*-Dimethylphenyl)-3-methylthio-2-phenylacrylonitrile (**8j**).

This compound (2.53 g, 8.6 mmoles) was synthesized in 86% yield from methyl 4-*N,N*-dimethylaminophenyldithiocarboxylate (**2f**) (2.11 g, 10 mmoles), phenylacetonitrile (1.76 g, 15 mmoles) and dimethyl sulfate (1.89 g, 15 mmoles) in a similar manner to that described for the preparation of **8a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 112°; ir (potassium bromide): ν max cm^{-1} 2180 (CN); uv (ethanol): λ max nm (log ϵ) 263 (4.21), 317 (4.11), 380 (4.21); ^1H nmr (deuteriochloroform): 2.18 (3H, s, SMe), 3.03 (6H, s, NMe_2), 6.53 (2H, d, J = 9.0 Hz, 2,6-H), 7.01 (2H, d, J = 9.0 Hz, 3,5-H), 7.18 (5H, s, phenyl-H).

Anal. Calcd. for $C_{18}H_{18}N_2S$: C, 73.43; H, 6.16; N, 9.52; S, 10.89. Found: C, 73.50; H, 6.23; N, 9.35; S, 10.83.

General Procedure for the Reaction of Thiocarbonyl Compounds with Tetracyanoethylene Oxide.

A freshly prepared tetracyanoethylene oxide [64] (0.346 g, 2.4 mmoles) was added dropwise during 10 minutes to a solution of (2 mmoles) of the thiocarbonyl compounds while the mixture was stirred at 0°. After stirring for 3-5 hours at room temperature, the precipitate that appeared was collected by filtration and was recrystallized from the appropriate solvent such as methanol or benzene to give the corresponding acrylonitrile compounds. The filtrate (benzene solution) was chromatographed on a column of aluminium oxide using benzene as an eluent to give the corresponding acrylonitrile compounds. If the desired compounds did not appear in the reaction mixture, the product was obtained by chromatography on an aluminium oxide column followed by the crystallization from an appropriate solvent such as methanol. The results are listed in Table 4.

2-Cyano-3-morpholino-5-phenylbut-2-enylacrylonitrile (**4j**).

This compound was synthesized in 79% from **1j** and **9** in a manner similar to the above described method. An analytical sample was recrystallized from methanol to give colorless needles, mp 111°; ir (potassium bromide): ν max cm^{-1} 2190 (CN), 1560 (C=C); uv (ethanol): λ max nm (log ϵ) 300 (4.28); ^1H nmr (deuteriochloroform): δ 2.86-2.95 (4H, m, CH_2-CH_2), 3.61 (8H, s, N-(CH_2-CH_2)$_2$-O), 7.20-7.37 (5H, s, phenyl-H).

Anal. Calcd. for $C_{16}H_{17}N_3O$: C, 71.88; H, 6.41; N, 15.72. Found: C, 72.00; H, 6.42; N, 15.61.

2-Cyano-3-methylthio-3-morpholinoacrylonitrile (**4l**).

This compound was synthesized in 62% yield from **1k** and **9**. An analytical sample was recrystallized from methanol to give colorless needles, mp 121°; ir (potassium bromide): ν max cm^{-1} 2200 (CN), 1520 (C=C); uv (ethanol): λ max nm (log ϵ) 277 (3.85), 316 (4.22); ^1H nmr (deuteriochloroform): δ 2.63 (3H, s, SMe), 3.85 (8H, s, N-(CH_2-CH_2)$_2$-O).

Anal. Calcd. for $C_9H_{11}N_3OS$: C, 51.65; H, 5.30; N, 20.08; S, 15.32. Found: C, 51.67; H, 5.25; N, 20.04; S, 15.57.

2-Cyano-3-(4-*N,N*-dimethylaminophenyl)-3-methylthioacrylonitrile (**8k**).

This compound was synthesized in 91% from **2f** and **9**. An analytical sample was recrystallized from methanol to give colorless needles, mp 116°; ir (potassium bromide): ν max cm^{-1} 2225 (CN), 1606 (C=C); uv (ethanol): λ max nm (log ϵ) 258 (4.09), 323 (4.05), 430 (4.43); ^1H nmr (deuteriochloroform): δ 2.38 (3H, s, SMe), 3.09 (6H, s, NMe_2), 6.73 (2H, d, J = 8.79 Hz, 2,6-H, or 3,5-H), 7.45 (2H, d, J = 8.79 Hz, 2,6-H or 3,5-H).

Anal. Calcd. for $C_{13}H_{13}N_3S$: C, 64.17; H, 5.39; N, 17.27; S, 13.18. Found: C, 64.07; H, 5.40; N, 17.18; S, 13.01.

2-Cyano-3-methylthio-3-(2-thienyl)acrylonitrile (**8l**).

This compound was synthesized in 78% from **2g** and **9**. An analytical sample was recrystallized from methanol to give colorless needles, mp 102°; ir (potassium bromide): ν max cm^{-1} 2200 (CN), 1520 (C=C); uv (ethanol): λ max nm (log ϵ) 222 (3.95), 348 (4.18); ^1H nmr (deuteriochloroform): δ 2.60 (3H, s, SMe), 7.25 (1H, m, 4H), 7.68-7.83 (2H, m, 3,5-H).

Anal. Calcd. for $C_9H_7N_2S_2$: C, 52.17; H, 2.90; N, 13.52; S, 31.04. Found: C, 52.40; H, 2.93; N, 13.58; S, 31.09.

3-Benzyl-2-cyano-3-methylthioacrylonitrile (**8m**).

This compound was synthesized in 68% yield from **2h** and **9**. An analytical sample was recrystallized from methanol to give colorless oil; ir (potassium bromide): ν max cm^{-1} 2200 (CN), 1508 (C=C); uv (ethanol): λ max nm (log ϵ) 313 (4.22); ^1H nmr (deuteriochloroform): δ 2.50 (3H, s, SMe), 4.13 (2H, s, CH_2), 7.10-7.50 (5H, m, phenyl-H).

Anal. Calcd. for $C_{12}H_{10}N_2S$: C, 67.26; H, 4.70; N, 13.27; S, 14.96. Found: C, 67.08; H, 4.64; N, 13.10; S, 14.97.

5-Amino-3-phenyl-1*H*-pyrazole-4-carbonitrile (**10a**).

A mixture of 2.39 g (10 mmoles) of **4a** and 0.75 g (15 mmoles) of hydrazine hydrate was heated at 100° for 1 hour. This reaction product was recrystallized from methanol to give 1.36 g (7.4 mmoles) of **10a** as colorless needles, mp 203°, in 74% yield; ir (potassium bromide): ν max cm^{-1} 3170 (NH_2, w), 2210 (CN); uv (ethanol): λ max nm (log ϵ) 232 (4.25), 252 (4.14, shoulder); ^1H nmr (deuteriochloroform): δ 6.17 (2H, bs, NH_2), 7.33-7.53 (3H, m, 3,4,5-H), 7.70-7.90 (2H, m, 2,6-H).

Anal. Calcd. for $C_{10}H_8N_4$: C, 65.21; H, 4.38; N, 30.42. Found: C, 65.49; H, 4.38; N, 30.47.

5-Amino-3-(2-methoxyphenyl)-1*H*-pyrazole-4-carbonitrile (**10b**).

This compound (1.89 g, 8.8 mmoles) was synthesized in 88% yield from **4b** (2.69 g, 10 mmoles) and hydrazine hydrate (0.75 g, 15 mmoles) in a manner similar to that described for the preparation of **10a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 192°; ir (potassium bromide): λ max cm^{-1} 3200 (NH_2), 2200 (CN); uv (ethanol): 253 (3.99), 293 (3.85); ^1H nmr (deuteriochloroform): δ 3.81 (3H, s, OMe), 5.84 (2H, bs, NH_2), 6.91-7.55 (4H, m, 3,4,5,6-H).

Anal. Calcd. for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.71; N, 26.16. Found: C, 61.79; H, 4.63; N, 26.05.

5-Amino-3-(4-methoxyphenyl)-1*H*-pyrazole-4-carbonitrile (**10c**).

This compound (1.48 g, 6.9 mmoles) was synthesized in 69% yield from **3c** (2.69 g, 10 mmoles) and hydrazine hydrate (0.75 g, 15 mmoles) in a manner similar to that described for the preparation of **10a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 158°; ir (potassium bromide): ν max cm^{-1} 3180 (NH_2, w), 2210 (CN); uv (ethanol): λ max nm (log ε) 237 (4.01, shoulder), 264 (4.20); ^1H nmr (deuteriochloroform): δ 3.65 (3H, s, OMe), 6.12 (2H, s, NH_2), 7.24 (2H, d, J = 9.6 Hz, 2,6-H or 3,5-H), 7.38 (2H, d, J = 9.6 Hz, 2,6-H or 3,5-H), 8.05 (1H, s, NH).

Anal. Calcd. for $C_{11}H_{10}N_4O$: C, 63.15; H, 5.30; N, 24.55. Found: C, 63.09; H, 5.26; N, 24.54.

5-Amino-3-(3,4-dimethoxyphenyl)-1*H*-pyrazole-4-carbonitrile (**10d**).

This compound (1.25 g, 5.1 mmoles) was synthesized in 51% yield from **4d** (2.99 g, 10 mmoles) and hydrazine hydrate (0.75 g, 15 mmoles) in a manner similar to that described for the preparation of **10a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 175°; ir (potassium bromide): ν max cm^{-1} 3230 (NH_2, w), 2200 (CN); uv (ethanol): λ max nm (log ε) 268 (4.17), 292 (4.07, shoulder); ^1H nmr (deuteriochloroform): δ 3.83 (6H, s, OMe), 6.20 (2H, bs, NH_2), 7.18 (1H, d, J = 7.8 Hz, 5-H or 6-H), 7.40 (1H, s, 2-H), 7.46 (1H, d, J = 7.8 Hz, 5-H or 6-H), 8.00 (1H, bs, NH).

Anal. Calcd. for $C_{12}H_{12}N_4O_2$: C, 59.01; H, 4.95; N, 22.94. Found: C, 59.01; H, 4.89; N, 22.84.

5-Amino-3-(3,4-methylenedioxyphenyl)-1*H*-pyrazole-4-carbonitrile (**10e**).

This compound (1.48 g, 6.5 mmoles) was synthesized in 65% yield from **4e** (2.83 g, 10 mmoles) and hydrazine hydrate (0.75 g, 15 mmoles) in a manner similar to that described for the preparation of **10a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 215°; ir (potassium bromide): ν max cm^{-1} 3200 (NH_2), 2200 (CN); uv (ethanol): λ max nm (log ε) 269 (4.00), 301 (3.95); ^1H nmr (deuteriodimethyl sulfoxide): δ 6.07 (2H, s, O-CH_2-O), 6.28 (2H, bs, NH_2), 7.00 (1H, d, J = 9.0 Hz, 5-H or 6-H), 7.34 (1H, d, J = 9.0 Hz, 5-H or 6-H), 8.10 (1H, bs, NH).

Anal. Calcd. for $C_{11}H_8N_4O_2$: C, 57.89; H, 3.53; N, 24.55. Found: C, 57.70; H, 3.62; N, 24.17.

5-Amino-3-(4-chlorophenyl)-1*H*-pyrazole-4-carbonitrile (**10f**).

This compound (1.79 g, 8.2 mmoles) was synthesized in 82% yield from **4f** (2.74 g, 10 mmoles) and hydrazine hydrate (0.75 g, 15 mmoles) in a similar manner to that described for the preparation of **10a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 221°; ir (potassium bromide): ν max cm^{-1} 3180 (NH_2), 2210 (CN); uv (ethanol): λ max nm (log ε) 239 (4.26), 256 (4.23); ^1H nmr (deuteriochloroform): δ 6.54 (2H, bs, NH_2), 7.56 (2H, d, J = 9.0 Hz, 2,6-H or 3,5-H), 7.86 (2H, d, J = 9.0 Hz, 2,6-H or 3,5-H).

Anal. Calcd. for $C_{10}H_7ClN_4$: C, 54.93; H, 3.23; N, 25.62; Cl, 16.21. Found: C, 54.94; H, 3.25; N, 25.35; Cl, 16.31.

5-Amino-3-thien-2-yl-1*H*-pyrazole-4-carbonitrile (**10g**).

This compound (1.73 g, 9.1 mmoles) was synthesized in 91% yield from **4g** (2.45 g, 10 mmoles) and hydrazine hydrate (0.75 g, 15 mmoles) in a manner similar to that described for the preparation of **10a**. An analytical sample was recrystallized from methanol to give yellow needles, mp 255°; ir (potassium bromide): ν max cm^{-1} 3400, 3320 (NH); uv (ethanol): λ max nm (log ε) 225 (4.11), 262 (4.02), 278 (4.09); ^1H nmr (deuteriodimethyl sulfoxide): 7.00-7.80 (5H, m, 3,4,5-H and NH).

Anal. Calcd. for $C_6H_4N_4S$: C, 50.51; H, 3.18; N, 29.45; S, 16.86. Found: C, 50.43; H, 3.18; N, 29.28; S, 16.89.

5-Amino-3-benzyl-1*H*-pyrazole-4-carbonitrile (**10h**).

This compound (1.94 g, 9.8 mmoles) was synthesized in 98% yield from **4h** (2.53 g, 10 mmoles) and hydrazine hydrate (0.75 g, 10 mmoles) in a similar manner to that described for the preparation of **10a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 141°; ir (potassium bromide): δ max cm^{-1} 3200 (NH_2), 2200 (CN); uv (ethanol): λ max nm (log ε) 248 (3.73); ^1H nmr (deuteriodimethyl sulfoxide): δ 6.40 (2H, bs, NH_2), 7.15 (2H, s, CH_2), 7.30 (5H, s, phenyl-H), 8.50 (1H, bs, NH).

Anal. Calcd. for $C_{11}H_{10}N_4$: C, 66.66; H, 5.09; N, 28.27. Found: C, 66.72; H, 5.17; N, 28.06.

5-Amino-3-(4-methylbenzyl)-1*H*-pyrazole-4-carbonitrile (**10i**).

This compound (2.08 g, 9.8 mmoles) was synthesized in 98% yield from **4i** (2.67 g, 10 mmoles) and hydrazine hydrate (0.75 g, 15 mmoles) in a manner similar to that described for the preparation of **10a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 162°; ir (potassium bromide): ν max cm^{-1} 3200 (NH_2), 2200 (CN); uv (ethanol): λ max nm (log ε) 218 (4.24), 274 (2.77); ^1H nmr (deuteriodimethyl sulfoxide): δ 2.22 (3H, s, Me), 3.74 (2H, s, CH_2), 6.10 (2H, bs, NH_2), 7.07 (4H, s, Phenyl-H), 8.45 (1H, bs, NH).

Anal. Calcd. for $C_{12}H_{12}N_4$: C, 67.91; H, 5.70; N, 26.40. Found: C, 67.79; H, 5.63; N, 26.00.

5-Amino-1,3-diphenyl-1*H*-pyrazole-4-carbonitrile (**10j**).

A solution of 2.00 g (10 mmoles) of **8a** and 1.08 g (10 mmoles) of phenyl hydrazine in 20 ml of ethanol was refluxed for 1 hour. After evaporation of the solvent, the residue was recrystallized from methanol to give 1.20 g (4.6 mmoles) of **10j** as colorless needles, mp 160°, in 46% yield; ir (potassium bromide): ν max cm^{-1} 3440, 3340 (NH_2), 2190 (CN); uv (ethanol): λ max nm (log ε) 239 (4.44), 390 (2.85); ^1H nmr (deuteriochloroform): δ 6.80 (1H, bs, NH_2), 7.55 (10H, s, phenyl-H), 7.80 (1H, bs, NH_2).

Anal. Calcd. for $C_{16}H_{12}N_4$: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.73; H, 4.59; N, 21.34.

5-Amino-3-(4-methoxyphenyl)-1-phenylpyrazole-4-carbonitrile (**10k**).

This compound (1.25 g, 4.3 mmoles) was synthesized in 43% yield from **8c** (2.27 g, 10 mmoles) and phenylhydrazine (1.08 g, 10 mmoles) in a manner similar to that described for the preparation of **10i**. An analytical sample was recrystallized from methanol to give colorless needles, mp 190°; ir (potassium bromide): ν max cm^{-1} 3430, 3325 (NH_2), 2220 (CN); uv (ethanol): λ max nm (log ε)

242 (4.43), 259 (4.40), 284 (4.22, shoulder); ^{1}H nmr (deuteriochloroform): δ 3.86 (3H, s, OMe), 4.57 (4H, bs, NH_2), 6.96 (2H, d, J = 9.0 Hz, 2,6-H), 7.54 (5H, m, phenyl-H), 7.93 (2H, d, J = 9.0 Hz, 3,5-H).

Anal. Calcd. for $C_{17}H_{14}N_4O$: C, 70.33; H, 4.86; N, 19.30. Found: C, 70.32; H, 4.91; N, 19.27.

5-Amino-3-(4-chlorophenyl)-1-phenylpyrazole-4-carbonitrile (**10ℓ**).

This compound (1.89 g, 6.4 mmoles) was synthesized in 64% yield from **8e** (2.35 g, 10 mmoles) and phenylhydrazine (1.08 g, 10 mmoles) in a manner similar to that described for the preparation of **10j**. An analytical sample was recrystallized from methanol to give colorless needles, mp 189°; ir (potassium bromide): ν max cm^{-1} 3420, 3290 (NH_2), 2200 (CN); uv (ethanol): λ max nm (log ε) 241 (4.44), 420 (2.75); ^{1}H nmr (deuteriochloroform): δ 6.95 (1H, bs, NH_2), 7.35-7.80 (9H, m, phenyl-H), 8.18 (1H, bs, NH_2).

Anal. Calcd. for $C_{16}H_{11}ClN_4$: C, 65.20; H, 3.76; N, 19.01. Found: C, 64.90; H, 3.72; N, 19.16.

2,4-Diamino-6-phenylpyrimidine-4-carbonitrile (**12a**).

A mixture of 0.718 g (3 mmoles) of **4a** and 0.541 g (3 mmoles) of guanidine carbonate (**11**) was heated at 200° for 3 hours. After cooling, this product was washed two times with 10 ml of hot water, dried in air, and recrystallized from a mixture of methanol and benzene to give 0.539 g (2.6 mmoles) of **12a** as colorless needles, mp 300°, in 85% yield; ir (potassium bromide): ν max cm^{-1} 3450, 3380 (NH_2), 2200 (CN); uv (ethanol): λ max nm (log ε) 249 (4.47), 311 (3.85); ^{1}H nmr (deuteriodimethyl sulfoxide): δ 6.28 (2H, bs, NH_2), 6.50 (2H, bs, NH_2), 7.22-7.33 (5H, m, phenyl-H).

Anal. Calcd. for $C_{11}H_9N_5$: C, 62.55; H, 4.29; N, 33.16. Found: C, 62.00; H, 4.20; N, 33.29.

2,4-Diamino-6-(2-methoxyphenyl)pyrimidine-5-carbonitrile (**12b**).

This compound (0.507 g, 2.1 mmoles) was synthesized in 70% yield from **4b** (0.808 g, 3 mmoles) and guanidine carbonate (**11**) (0.541 g, 3 mmoles) in a manner similar to that described for the preparation of **12a**. An analytical sample was recrystallized from a mixture of methanol and benzene to give colorless needles, mp 218°; ir (potassium bromide): ν max cm^{-1} 3500, 3350 (NH_2), 2210 (CN); uv (ethanol): λ max nm (log ε) 251 (4.32), 300 (4.00).

Anal. Calcd. for $C_{12}H_{11}N_5O$: C, 55.59; H, 5.05; N, 27.02. Found: C, 55.28; H, 4.75; N, 26.86.

2,4-Diamino-6-(4-methoxyphenyl)pyrimidine-5-carbonitrile (**12c**).

This compound (0.601 g, 2.5 mmoles) was synthesized in 83% yield from **4c** (0.808 g, 3 mmoles) and guanidine carbonate (**11**) (0.541 g, 3 mmoles) in a manner similar to that described for the preparation of **12a**. An analytical sample was recrystallized from a mixture of methanol and benzene to give colorless needles, mp 245°; ir (potassium bromide): ν max cm^{-1} 3420, 3380 (NH_2), 2200 (CN); uv (ethanol): λ max nm (log ε) 259 (4.43), 286 (4.22), 320 (3.89, shoulder); ^{1}H nmr (deuteriochloroform): δ 3.85 (3H, s, OMe), 6.98 (4H, s, NH_2), 7.04 (2H, d, J = 9.0 Hz, 3,5-H or 2,6-H), 7.82 (2H, d, J = 9.0 Hz, 3,5-H or 2,6-H).

Anal. Calcd. for $C_{12}H_{11}N_5O$: C, 59.74; H, 4.60; N, 29.03. Found: C, 59.34; H, 4.58; N, 28.68.

2,4-Diamino-6-(4-chlorophenyl)pyrimidine-5-carbonitrile (**12d**).

This compound (0.666 g, 2.7 mmoles) was synthesized in 90% yield from **4f** (0.821 g, 3 mmoles) and guanidine carbonate (0.541 g, 3 mmoles) in a similar manner to that described for the preparation of **12a**. An analytical sample was recrystallized from a mixture of methanol and benzene to give colorless needles, mp 281°; ir (potassium bromide): ν max cm^{-1} 3430, 3375 (NH_2), 2200 (CN); uv (ethanol): λ max nm (log ε) 253 (4.54), 314 (3.86); ^{1}H nmr (deuteriochloroform): δ 3.55 (4H, bs, NH_2), 6.88-7.27 (4H, m, phenyl-H).

Anal. Calcd. for $C_{11}H_8ClN_5$: C, 53.80; H, 3.28; N, 28.52. Found: C, 53.56; H, 3.18; N, 28.55.

2,4-Diamino-6-benzylpyrimidine-5-carbonitrile (**12e**).

This compound (0.428 g, 1.6 mmoles) was synthesized in 52% yield from **4h** (0.760 g, 3 mmoles) and guanidine carbonate (0.541 g, 3 mmoles) in a manner similar to that described for the preparation of **12a**. An analytical sample was recrystallized from a mixture of methanol and benzene to give colorless needles, mp 228°; ir (potassium bromide): ν max cm^{-1} 3365, 3325 (NH_2), 2205 (CN); uv (ethanol): λ max nm (log ε) 242 (4.23), 250 (4.23, shoulder), 296 (3.88), 320 (3.37, shoulder); ^{1}H nmr (deuteriochloroform): δ 3.95 (2H, s, CH_2), 5.25 (4H, bs, NH_2), 7.13-7.31 (5H, m, phenyl-H).

Anal. Calcd. for $C_{12}H_{11}N_5$: C, 63.99; H, 4.92; N, 31.09. Found: C, 63.77; H, 4.88; N, 31.07.

4-Amino-3-phenylpyrazolo[3,4-*d*]pyrimidine (**13a**).

A mixture of 2.0 g (10.9 mmoles) of **10a** and 2 ml of formamide was heated at 200° for 2 hours. After cooling, the solid was washed with 20 ml of water and recrystallized from a mixture of methanol and benzene to give 1.21 g (5.8 mmoles) of **13a**, colorless needles, mp 276°, in 53% yield; ir (potassium bromide): ν max cm^{-1} 3160 (NH_2); uv (ethanol): λ max nm (log ε) 254 (4.18), 276 (4.12, shoulder); ^{1}H nmr (deuteriodimethyl sulfoxide): δ 6.68 (2H, bs, NH_2), 7.60 (5H, s, phenyl-H), 8.27 (1H, s, NH).

Anal. Calcd. for $C_{11}H_9N_5$: C, 62.55; H, 4.30; N, 33.16. Found: C, 62.22; H, 4.23; N, 32.83.

4-Amino-3-(4-methoxyphenyl)pyrazolo[3,4-*d*]pyrimidine (**13b**).

This compound (1.35 g, 5.6 mmoles) was synthesized in 60% yield from **10c** (2.0 g, 9.3 mmoles) and formamide (2 ml) in a manner similar to that described for the preparation of **13a**. An analytical sample was recrystallized from a mixture of methanol and benzene to give colorless needles, mp 298°; ir (potassium bromide): ν max cm^{-1} 3420 (NH_2); uv (ethanol): λ max nm (log ε) 262 (4.20), 280 (4.11, shoulder); ^{1}H nmr (deuteriodimethyl sulfoxide): δ 3.88 (3H, s, OMe), 6.70 (2H, bs, NH_2), 7.16 (2H, d, J = 7.2 Hz, 2,6-H), 7.55 (2H, d, J = 7.2 Hz, 3,5-H), 8.26 (1H, s, NH).

Anal. Calcd. for $C_{12}H_{11}N_5O$: C, 59.74; H, 4.60; N, 29.03. Found: C, 59.66; H, 4.62; N, 28.93.

4-Amino-3-(3,4-dimethoxyphenyl)pyrazolo[3,4-*d*]pyrimidine (**13c**).

This compound (0.93 g, 3.4 mmoles) was synthesized in 42% yield from **10d** (2.0 g, 8.2 mmoles) and formamide (2 ml) in a manner similar to that described for the preparation of **13a**. An analytical sample was recrystallized from a mixture of methanol and benzene to give colorless needles, mp 290°; ir (potassium bromide): ν max cm^{-1} 3400 (NH_2); uv (ethanol): λ max nm (insufficient solubility) 266, 285; λ min nm 250.

Anal. Calcd. for $C_{13}H_{13}N_5O_2$: C, 57.56; H, 4.83; N, 25.82. Found: C, 57.56; H, 4.86; N, 25.79.

4-Amino-3-(4-chlorophenyl)pyrazolo[3,4-*d*]pyrimidine (**13d**).

This compound (1.11 g, 4.5 mmoles) was synthesized in 50%

yield from **10f** (2.0 g, 9.1 mmoles) and formamide (2 ml) in a manner similar to that described for the preparation of **13a**. An analytical sample was recrystallized from a mixture of methanol and benzene to give colorless needles, mp 357°; ir (potassium bromide): ν max cm^{-1} 3060 (NH_2); uv (ethanol): λ max nm (log ϵ) 257 (4.29), 280 (4.21, shoulder).

Anal. Calcd. for $C_{11}H_8ClN_5$: C, 53.78; H, 3.28; Cl, 14.43; N, 28.51. Found: C, 54.01; H, 3.33; Cl, 14.31; N, 28.32.

4-Amino-3-benzylpyrazolo[3,4-*d*]pyrimidine (**13e**).

This compound (1.04 g, 4.6 mmoles) was synthesized in 87% yield from **10h** (1.0 g, 5.3 mmoles) and formamide (1 ml) in a manner similar to that described for the preparation of **13a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 277°; ir (potassium carbonate): ν max cm^{-1} 3455, 3305, 3080, 3005 (NH); uv (ethanol): λ max nm (log ϵ) 260 (3.95), 277 (3.93); ^1H nmr (deuteriochloroform + trifluoroacetic acid 5:1): δ 4.47 (2H, s, CH_2-Ph), 7.22-7.48 (5H, m, phenyl-H), 8.58 (1H, s, 6-H).

Anal. Calcd. for $C_{12}H_{11}N_5$: C, 63.99; H, 4.92; N, 31.09. Found: C, 63.91; H, 5.02; N, 30.91.

4-Amino-1,3-diphenylpyrazolo[3,4-*d*]pyrimidine (**13f**).

This compound (0.46 g, 1.60 mmoles) was synthesized in 42% yield from **10j** (1.0 g, 3.85 mmoles) and formamide (1 ml) in a manner similar to that described for the preparation of **13a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 242°; ir (potassium bromide): ν max cm^{-1} 3230 (NH); uv (ethanol): λ max nm (log ϵ) 258 (4.81); ^1H nmr (deuteriodimethyl sulfoxide): δ 6.89-7.57 (10H, m, phenyl-H), 8.63 (1H, s, 6-H).

Anal. Calcd. for $C_{17}H_{13}N_5$: C, 71.07; H, 4.56; N, 24.37. Found: C, 69.98; H, 4.41; N, 24.67.

4-Amino-1-phenyl-3-(4-methoxyphenyl)pyrazolo[3,4-*d*]pyrimidine (**13g**).

This compound (0.89 g, 2.82 mmoles) was synthesized in 82% yield from **10k** (1.0 g, 3.45 mmoles) and formamide (1 ml) in a manner similar to that described for the preparation of **13a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 220°; ir (potassium bromide): λ max cm^{-1} 3450, 3060 (NH); uv (ethanol): ν max nm (log ϵ) 242 (4.51), 299 (4.18); ^1H nmr (deuteriochloroform): δ 3.88 (3H, s, OMe), 5.52 (2H, bs, NH_2), 7.18 (2H, d, J = 8.0 Hz, phenyl-H), 7.26-7.65 (5H, m, phenyl-H), 8.21 (2H, d, J = 8.0 Hz), 8.45 (1H, s, 6-H).

Anal. Calcd. for $C_{18}H_{15}ON_5$: C, 68.13; H, 4.76; N, 22.07. Found: C, 68.13; H, 4.78; N, 22.23.

4-Amino-3-(4-chlorophenyl)-1-phenylpyrazolo[3,4-*d*]pyrimidine (**13h**).

This compound (0.90 g, 2.96 mmoles) was synthesized in 83% yield from **10l** (1.0 g, 3.45 mmoles) and formamide (1 ml) in a manner similar to that described for the preparation of **13a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 278°; ir (potassium bromide): λ max cm^{-1} 3480, 3060 (NH); uv (ethanol): ν max nm (log ϵ) 242 (4.40), 302 (4.18); ^1H nmr (deuteriochloroform): δ 5.50 (2H, bs, NH), 7.26-7.79 (7H, m, phenyl-H), 8.19 (2H, d, J = 8.0 Hz, phenyl-H), 8.49 (1H, s, 6-H).

Anal. Calcd. for $C_{17}H_{12}ClN_5$: C, 63.46; H, 3.76; N, 21.77. Found: C, 63.24; H, 3.73; N, 22.02.

4,6-Bis(methylthio)-3-phenylpyrazolo[3,4-*d*]pyrimidine (**14a**).

To a solution of 0.92 g (5 mmoles) of **10a** and 20% solution of potassium hydroxide (KOH: 1.12 g, H_2O: 4.5 ml) in 10 ml of dimethyl sulfoxide, stirred at 0°, 0.76 g (10 mmoles) of carbon disulfide was added in several portions during 30 minutes. After another 1 hour at room temperature, 2.13 g (15 mmoles) of methyl iodide was slowly added to the stirring solution over a period of 30 minutes and stirring was continued for 1 hour at room temperature. The reaction mixture was poured into 10 ml of ice-water. The precipitate that appeared was collected by filtration and washed several times with water. This crude product was recrystallized from methanol to give 1.11 g (3.9 mmoles) of colorless needles, mp 218°, in 77% yield; ir (potassium bromide): ν max cm^{-1} 3185 (NH), 1580, 1531, 1229; uv (ethanol): λ max nm (log ϵ) 257 (4.20), 300 (3.78, shoulder); ^1H nmr (deuteriochloroform): δ 2.60 (3H, s, SMe), 2.66 (3H, s, SMe), 7.45-7.54 (3H, m, 3,4,5-H), 7.69-7.80 (2H, m, 2,6-H).

Anal. Calcd. for $C_{13}H_{12}N_4S_2$: C, 54.14; H, 4.19; N, 19.43; S, 22.24. Found: C, 54.05; H, 4.23; N, 19.56; S, 22.35.

3-(2-Methoxyphenyl)-4,6-bis(methylthio)pyrazolo[3,4-*d*]pyrimidine (**14b**).

This compound (1.02 g, 3.2 mmoles) was synthesized in 64% yield from **10b** (1.07 g, 5 mmoles), carbon disulfide (0.76 g, 10 mmoles) and methyl iodide (2.13 g, 15 mmoles) in a manner similar to that described for the preparation of **14a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 200°; ir (potassium bromide); ν max cm^{-1} 3155, 3000 (NH), 1585, 1538, 1259; uv (ethanol): λ max nm (log ϵ) 220 (4.30, shoulder), 254 (4.43), 300 (4.18); ^1H nmr (deuteriochloroform): δ 2.54 (3H, s, SMe), 2.70 (3H, s, SMe), 3.79 (3H, s, OMe), 6.96-7.57 (4H, m, phenyl-H).

Anal. Calcd. for $C_{14}H_{13}N_4OS_2$: C, 52.98; H, 4.13; N, 17.65; S, 20.20. Found: C, 52.63; N, 4.39; N, 17.61; S, 20.08.

3-(4-Methoxyphenyl)-4,6-bis(methylthio)pyrazolo[3,4-*d*]pyrimidine (**14c**).

This compound (1.29 g, 4.1 mmoles) was synthesized in 81% yield from **10c** (1.07 g, 5 mmoles), carbon disulfide (0.76 g, 10 mmoles) and methyl iodide (2.13 g, 15 mmoles) in a manner similar to that described for the preparation of **14a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 248°; ir (potassium bromide): ν max cm^{-1} 3190, 3035 (NH), 1590, 1538, 1244; uv (ethanol): λ max nm (log ϵ) 236 (4.33), 260 (4.56), 305 (4.20); ^1H nmr (deuteriochloroform): δ 2.60 (3H, s, SMe), 2.66 (3H, s, SMe), 3.88 (3H, s, OMe), 7.01 (2H, d, J = 8.79 Hz, 2,6-H or 3,5-H), 7.69 (2H, d, J = 8.79 Hz, 2,6-H or 3,5-H).

Anal. Calcd. for $C_{14}H_{13}N_4S_2$: C, 52.83; H, 4.43; N, 17.60; S, 20.11. Found: C, 52.73; H, 4.48; N, 17.63; S, 19.90.

3-Benzyl-4,6-bis(methylthio)pyrazolo[3,4-*d*]pyrimidine (**14d**).

This compound (0.91 g, 3 mmoles) was synthesized in 60% yield from **10h** (0.99 g, 5 mmoles), carbon disulfide (0.76 g, 10 mmoles) and methyl iodide (2.13 g, 15 mmoles) in a manner similar to that described for the preparation of **14a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 176°; ir (potassium bromide): ν max cm^{-1} 3185 (NH), 1762, 1634, 1597, 1527; uv (ethanol): λ max nm (log ϵ) 218 (4.26, shoulder), 256 (4.55, shoulder), 262 (4.57), 305 (3.93); ^1H nmr (deuteriochloroform): δ 2.60 (3H, s, SMe), 2.63 (3H, s, SMe), 4.37 (2H, s, $-CH_2-$), 7.25 (5H, s, phenyl-H), 8.55 (1H, s, NH).

Anal. Calcd. for $C_{14}H_{14}N_4S_2$: C, 55.60; H, 4.67; N, 18.53; S, 21.20. Found: C, 55.69; H, 4.68; N, 18.55; S, 21.23.

4,6-Dihydroxy-3-phenylpyrazolo[3,4-*d*]pyrimidine (**15a**).

A solution of 0.865 g (3 mmoles) of **14a**, 10 ml of 30% hydrogen peroxide in 30 ml of acetic acid was heated at 70° for 5 hours. After evaporation of the solvent, the residue was washed with 10 ml of water, the product was dried in air and recrystallized from methanol to give 0.602 g (2.6 mmoles) of **15a** as colorless needles, mp >384° [lit, [44], mp >370°], in 88% yield; ir (potassium bromide): ν max cm^{-1} 3495, 3195, 3075 (OH or NH), 1750, 1661 (CO); ^1H nmr (deuteriodimethyl sulfoxide): δ 7.44-7.56 (3H, m, phenyl-H), 8.05-8.19 (2H, m, phenyl-H), 10.57 (1H, bs, NH or OH), 11.32 (1H, bs, NH or OH); ms: m/z 228 (M^+, 77), 195 (11), 42 (100).

4,6-Dihydroxy-3-(2-methoxyphenyl)pyrazolo[3,4-*d*]pyrimidine (**15b**).

This compound (0.689 g, 2.7 mmoles) was synthesized in 89% yield from **14b** (0.954 g, 3 mmoles) and 30% hydrogen peroxide (10 ml) in a manner similar to that described for the preparation of **15a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 323°; ir (potassium bromide): ν max cm^{-1} 3410, 3235, 3080 (OH or NH), 1718, 1670, 1605 (CO); ^1H nmr (deuteriodimethyl sulfoxide): δ 3.82 (3H, s, SMe), 7.03 (1H, dt, J = 1.1, 7.2 Hz, 5'-H), 7.14 (1H, d, J = 7.0 Hz, 3'-H), 7.45 (1H, m, 4'-H), 7.84 (1H, d, J = 7.5 Hz, 6'-H), 10.43 (1H, bs, NH or OH), 11.20 (1H, bs, NH or OH), 13.06 (1H, bs, NH or OH); ms: m/z 258 (M^+, 77), 229 (11), 215 (17), 197 (30), 42 (100).

Anal. Calcd. for $C_{12}H_{10}N_4O_3$: C, 55.81; H, 3.50; N, 21.70. Found: C, 55.67; H, 3.49; N, 21.45.

4,6-Dihydroxy-3-(4-methoxyphenyl)pyrazolo[3,4-*d*]pyrimidine (**15c**).

This compound (0.759 g, 2.9 mmoles) was synthesized in 98% yield from **14c** (0.954 g, 3 mmoles) and 30% hydrogen peroxide (10 ml) in a manner similar to that described for the preparation of **15a**. An analytical sample was recrystallized from methanol to give colorless needles, mp >390°; ir (potassium bromide): ν max cm^{-1} 3450, 3180, 3070 (OH or NH), 1751, 1650 (CO); ^1H nmr (deuteriodimethyl sulfoxide): δ 3.82 (3H, s, OMe), 7.05 (2H, d, J = 9.0 Hz, phenyl-H), 8.13 (2H, d, J = 9.0 Hz, phenyl-H), 10.52 (1H, bs, NH or OH), 11.26 (1H, bs, NH or OH); ms: m/z 258 (M^+, 9), 240 (12), 214 (13), 60 (31), 43 (100).

Anal. Calcd. for $C_{12}H_{10}N_4O_3$: C, 55.81; H, 3.90; N, 21.70. Found: C, 55.44; H, 3.94; N, 21.37.

4-Benzylamino-6-methylthio-3-phenylpyrazolo[3,4-*d*]pyrimidine (**16a**).

A mixture of 0.864 g (3 mmoles) of **14a** and 0.643 g (6 mmoles) of benzylamine was heated at 150° for 2 hours. After cooling, the product was recrystallized from methanol to give 0.608 g (1.7 mmoles) of **16a** as colorless needles, mp 195°, in 58% yield; ir (potassium bromide): ν cm^{-1} 3420 (NH); uv (ethanol): λ max nm (log ϵ) 252 (4.52), 290 (4.13, shoulder).

Anal. Calcd. for $C_{19}H_{17}N_5S$: C, 65.68; H, 4.93; N, 20.16; S, 9.23. Found: C, 65.70; H, 5.07; N, 19.92; S, 8.90.

4-Benzylamino-3-(2-methoxyphenyl)-6-methylthiopyrazolo[3,4-*d*]-pyrimidine (**16b**).

This compound (0.643 g, 1.7 mmoles) was synthesized in 66% yield from **14b** (0.954 g, 3 mmoles) and benzylamine (0.643 g, 6 mmoles) in a similar manner to that described for the preparation of **16a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 193°, ir (potassium bromide): ν max cm^{-1} 3410 (NH), 1575; uv (ethanol): λ max nm (log ϵ) 249 (4.51), 286 (4.28); ^1H nmr (deuteriochloroform): δ 2.58 (3H, s, SMe), 3.49 (3H, s, OMe), 4.69 (2H, d, J = 6.0 Hz, $-CH_2-$), 5.71 (1H, bs, NH), 7.22 (5H, s, phenyl-H).

Anal. Calcd. for $C_{20}H_{19}N_5OS$: C, 63.64; H, 5.07; N, 18.55; S, 8.49. Found: C, 63.40; H, 5.02; N, 18.54; S, 8.70.

Methyl 2-Pyrrolyldithiocarboxylate (**17**).

A 500 ml round-bottomed three-necked flask was equipped with a mechanical stirrer with a suitable seal, an efficient reflux condensor protected from moisture in the air by a drying tube. The flask was surrounded by an ice bath. Approximately 20 ml of dry ether and 6.03 g (0.26 g-atom) of magnesium were placed in the flask and cooled to about 0°. Ethyl bromide (21.8 g, 0.20 mole) was slowly added to the above stirred mixture of ether and magnesium. The reaction mixture was then warmed until the reaction of ethyl bromide and magnesium was under way. A crystal of iodine may be added if the reaction does not start readily. The ethyl bromide was then allowed to distil into reaction mixture during a period of about 1 hour. The reaction mixture and the tube containing the ethyl bromide were cooled if the refluxing of the reaction mixture becomes so vigorous that the reflux condenser does not condense the ethyl bromide. After all the ethyl bromide has been added, the reaction mixture was warmed for one hour so that there was a gentle reflux. After cooling at 0°, a solution of 13.4 g (0.20 mole) of freshly distilled pyrrole in 20 ml of dry ether was added dropwise while the reaction mixture was stirred vigorously and cooled. The reaction mixture was stirred for 1 hour at room temperature. At this time, pyrrolylmagnesium bromide was prepared. Carbon disulfide (15.3 g, 0.20 mmole) was slowly added to the above Grignard reagent under stirring at 0° over a period of 20 minutes and stirring was continued for 1 hour at room temperature. To a Grignard reaction product (magnesium 2-pyrrolyldithiocarboxylate), 57.0 g (0.40 mole) of methyl iodide was slowly added dropwise while the reaction mixture was stirred vigorously at room temperature. After stirring for 3 hours, the reaction mixture was decomposed by adding 20 ml of a saturated ammonium chloride solution dropwise, with vigorous stirring, to the thoroughly cooled reaction. After the reaction mixture has been allowed to stand for one hour, the ether solution was poured off and the precipitate washed by decantation with two 200 ml portions of ether. After drying over sodium sulfate, the ether was removed by distillation, and the residual methyl 2-pyrrolyl-dithiocarboxylate was distilled. This product could be also purified by alumina column chromatography using hexane as an eluent to give a yellow oil. The yield of methyl 2-pyrrolyldithiocarboxylate, a yellow liquid boiling at 59°/13 mm Hg, was 14.7 g, (47%) [65]; ^1H nmr (deuteriochloroform): δ (3H, s, SMe), 6.20-6.43 (1H, m, 3-H), 6.96-7.20 (2H, m, 4, 5-H), 8.90 (1H, m, NH).

2-Cyano-3-methylthio-3-pyrrol-2-ylacrylonitrile (**18**).

To a solution of 3.15 g (20 mmoles) of methyl 2-pyrrolyldithiocarboxylate (**17**) in 30 ml of benzene, 3.46 g (24 mmoles) of fresh tetracyanoethylene oxide (**9**) was slowly added in small portions under stirring at 0°. Stirring was continued for 2 hours at room temperature. After removal of the solvent under reduced pressure. The residue was chromatographed over by column using benzene as an eluent to give 3.33 g (17.6 mmoles) of yellow needles, mp 112° [lit [62] mp 112°], in 88% yield.

Dimethyl 4-Cyano-3-methylthio-5-aza[2.2.3]cyclazine-6,7-dicarboxylate (**20**).

A mixture of 0.946 g (5 mmoles) of **18** and 5 ml of triethylamine was refluxed for 1 hour. After removal of the excess of triethylamine, the product was heated at 150° for 1 hour to give the cyclized product. 2,6-Lutidine can also be used as catalyst of cyclization of **18** instead of triethylamine. This material was used in the next step without purification. A mixture of the above crude imino, 1.066 g (7.5 mmoles) of dimethyl acetylenedicarboxylate, 0.90 g of 5% of palladium-on-charcoal (Pd-C), and 30 ml of toluene was refluxed for 20 hours. After removal of the solvent and Pd-C, the residue was chromatographed on an alumina column using benzene as an eluent to give orange needles. This compound was recrystallized from methanol to give 0.378 g (1.15 mmoles) of **20** as orange needles, mp 212°, in 23% yield; ir (potassium bromide): ν max cm^{-1} 2210 (CN), 1740, 1715 (CO); uv (ethanol): λ max nm (log ϵ) 239 (4.45), 278 (4.28), 302 (4.26), 376 (4.32), 440 (3.61); ^1H nmr (deuteriochloroform): δ 3.03 (3H, s, SMe), 4.08 (3H, s, OMe), 4.10 (3H, s, OMe), 7.62 (1H, d, J = 4.5 Hz, 2-H), 7.86 (1H, d, J = 4.5 Hz, 1-H); ms: (m/z) 329 (M^+, 100), 298 (44), 270 (17), 240 (11), 213 (48).

Anal. Calcd. for $C_{14}H_{11}N_3O_4S$: C, 54.71; H, 3.37; N, 12.76; S, 9.74. Found: C, 54.52; H, 3.44; N, 12.70; S, 9.53.

2-Cyano-3-morpholino-3-pyrrol-2-ylacrylonitrile (**21a**).

A solution of 0.189 g (1 mmole) of **18** and 0.174 g (2 mmoles) of morpholine in 10 ml of methanol was refluxed for 4 hours. After removal of the solvent, the residue was recrystallized from methanol to give 0.137 g (0.6 mmoles) of yellow needles, mp 164°, in 60% yield; ir (potassium bromide): ν max cm^{-1} 3280 (NH), 2200 (CN); uv (ethanol): λ max nm (log ϵ) 244 (4.13, shoulder), 248 (4.14), 295 (4.30, shoulder), 303 (4.33), 314 (4.20, shoulder), 410 (3.64); ^1H nmr (deuteriochloroform): δ 3.94 (8H, s, N-CH_2-CH_2)$_2$-O), 6.27-6.40 (2H, m, 3,4-H), 7.40 (1H, dd, J = 1.1, 2.6 Hz, 5-H), 7.83 (1H, bs, 1-H); ms: (m/z) 228 (M^+, 100), 171 (16), 170 (14), 116 (17), 57 (12).

Anal. Calcd. for $C_{12}H_{12}N_4O$: C, 63.15; H, 5.30; N, 24.55. Found: C, 62.99; H, 5.41; N, 24.27.

2-Cyano-3-piperidino-3-pyrrol-2-ylacrylonitrile (**21b**).

This compound (0.145 g, 0.64 mmole) was synthesized in 64% yield from **18** (0.189 g, 1 mmole) and piperidine (0.170 g, 2 mmoles) in a manner similar to that described for the preparation of **21a**. An analytical sample was recrystallized from methanol to give yellow needles, mp 181°; ir (potassium bromide): ν max cm^{-1} 3270 (NH), 2190 (CN); uv (ethanol): λ max nm (log ϵ) 243 (4.14, shoulder), 249 (4.17), 292 (4.32, shoulder), 303 (4.36), 314 (4.22, shoulder), 4.04 (3.64); ^1H nmr (deuteriochloroform): δ 1.79 (6H, s, 3,4,5-H), 3.86 (4H, s, 2,6-H), 6.26-6.41 (2H, m, 3,4-H), 7.39 (1H, dd, J = 0.99, 2.75 Hz, 5-H), 7.78 (1H, bs, 1-H); ms: (m/z) 226 (M^+, 100), 197 (17), 84 (13).

Anal. Calcd. for $C_{13}H_{14}N_4$: C, 69.00; H, 6.24; N, 24.76. Found: C, 69.21; H, 6.52; N, 24.87.

2-Cyano-3-pyrrolidino-3-pyrrol-2-ylacrylonitrile (**21c**).

This compound (0.161 g, 0.76 mmole) was synthesized in 76% yield from **18** (0.189 g, 1 mmole) and pyrrolidine (0.142 g, 2 mmoles) in a manner similar to that described for the preparation of **21a**. An analytical sample was recrystallized from methanol to give yellow needles, mp 190°; ir (potassium bromide): ν max cm^{-1} 3270 (NH), 2208 (CN); uv (ethanol): λ max nm (log ϵ) 242 (4.18, shoulder), 249 (4.23), 290 (4.33, shoulder), 300 (4.37), 312 (4.20, shoulder), 405 (3.65); ^1H nmr (deuteriochloroform): δ 2.03-2.25 (4H, m, 3,4-H), 3.70-3.98 (4H, m, 2,5-H), 6.25-6.32 (2H, m, 3,4-H), 7.39 (1H, s, 5-H), 7.73 (1H, s, 1-H); ms: (m/z) 212 (M^+, 100), 184 (27), 157 (11), 116 (12), 70 (16).

Anal. Calcd. for $C_{12}H_{12}N_4$: C, 67.91; H, 5.70; N, 26.40. Found: C, 67.87; H, 5.82; N, 26.08.

Dimethyl 4-Cyano-3-morpholino-5-aza[2.2.3]cyclazine-6,7-dicarboxylate (**23a**).

This compound (0.083 g, 0.23 mmole) was synthesized in 45% yield from **21a** (0.114 g, 0.5 mmole) and dimethyl acetylenedicarboxylate (0.107 g, 0.75 mmole) in a manner similar to that described for the preparation of **20**. An analytical sample was recrystallized from methanol to give yellow leaflets, mp 271°; ir (potassium bromide): ν max cm^{-1} 2240 (CN), 1738, 1725 (CO); uv (ethanol): λ max nm (log ϵ) 222 (4.46), 244 (4.17), 267 (4.26), 273 (4.26, shoulder), 297 (4.23), 324 (4.03, shoulder), 381 (4.33); ^1H nmr (deuteriochloroform): δ 4.03 (3H, s, OMe), 4.06 (3H, s, OMe), 3.90-4.04 (8H, m, N-(CH_2-CH_2)$_2$-O), 7.33 (1H, d, J = 4.2 Hz, 2-H), 7.54 (1H, d, J = 4.2 Hz, 1-H); ms: (m/z) 368 (M^+, 100), 337 (21), 252 (26), 149 (21), 81 (31), 71 (21), 69 (57), 57 (50), 55 (27).

Anal. Calcd. for $C_{18}H_{16}N_4O_5$: C, 58.69; H, 4.38; N, 15.21. Found: C, 58.26; H, 4.46; N, 14.96.

Dimethyl 4-Cyano-3-piperidino-5-aza[2.2.3]cyclazine-6,7-dicarboxylate (**23b**).

This compound (0.132 g, 0.36 mmole) was synthesized in 72% yield from **21b** (0.113 g, 0.5 mmole) and dimethyl acetylenedicarboxylate (0.107 g, 0.75 mmole) in a similar manner to that described for the preparation of **20**. An analytical sample was recrystallized from methanol to give yellow needles, mp 253°; ir (potassium bromide): ν max cm^{-1} 2205 (CN), 1742, 1721 (CO); uv (ethanol): λ max nm (log ϵ) 223 (4.40), 242 (4.09, shoulder), 267 (4.25), 272 (4.24, shoulder), 297 (4.21), 377 (4.31); ^1H nmr (deuteriochloroform): δ 1.87 (6H, m, 3,4,5-H), 4.02 (4H, m, N-CH_2-), 4.05 (6H, s, OMe), 7.25 (1H, d, J = 4.2 Hz, 2-H), 7.50 (1H, d, J = 4.2 Hz, 1-H); ms: (m/z) 366 (M^+, 100), 309 (58), 250 (32), 81 (21), 69 (35).

Anal. Calcd. for $C_{19}H_{18}N_4O_4$: C, 62.29; H, 4.95; N, 15.29. Found: C, 61.93; H, 5.07; N, 14.99.

Dimethyl 4-Cyano-3-pyrrolidino-5-aza[2.2.3]cyclazine-6,7-dicarboxylate (**23c**).

This compound (0.078 g, 0.22 mmole) was synthesized in 44% yield from **21c** (0.106 g, 0.5 mmole) and dimethyl aceytlenedicarboxylate (0.107 g, 0.75 mmole) in a manner similar to that described for the preparation of **20**. An analytical sample was recrystallized from methanol to give yellow needles, mp 236°; ir (potassium bromide): ν max cm^{-1} 2205 (CN), 1742, 1721 (CO); uv (ethanol): λ max nm (log ϵ) 222 (4.46), 244 (4.15), 265 (4.25), 271 (4.24), 297 (4.24), 325 (3.99), 378 (4.32); ^1H nmr (deuteriochloroform): δ 2.18-2.33 (4H, m, -CH_2-CH_2), 4.02 (3H, s, OMe), 4.06 (3H, s, OMe), 3.80-4.20 (4H, m, N-CH_2-), 7.16 (1H, d, J = 4.2 Hz, 2-H), 7.41 (1H, d, J = 4.2 Hz, 1-H); ms: (m/z) 352 (M^+, 19), 236 (5), 144 (22), 69 (28), 57 (33), 44 (79), 43 (100).

Anal. Calcd. for $C_{18}H_{16}N_4O_4$: C, 61.36; H, 4.58; N, 15.90. Found: C, 61.10; H, 4.67; N, 15.77.

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