Synthesis of Isomeric 5-(Phenylsulphonyl)pyrimidines

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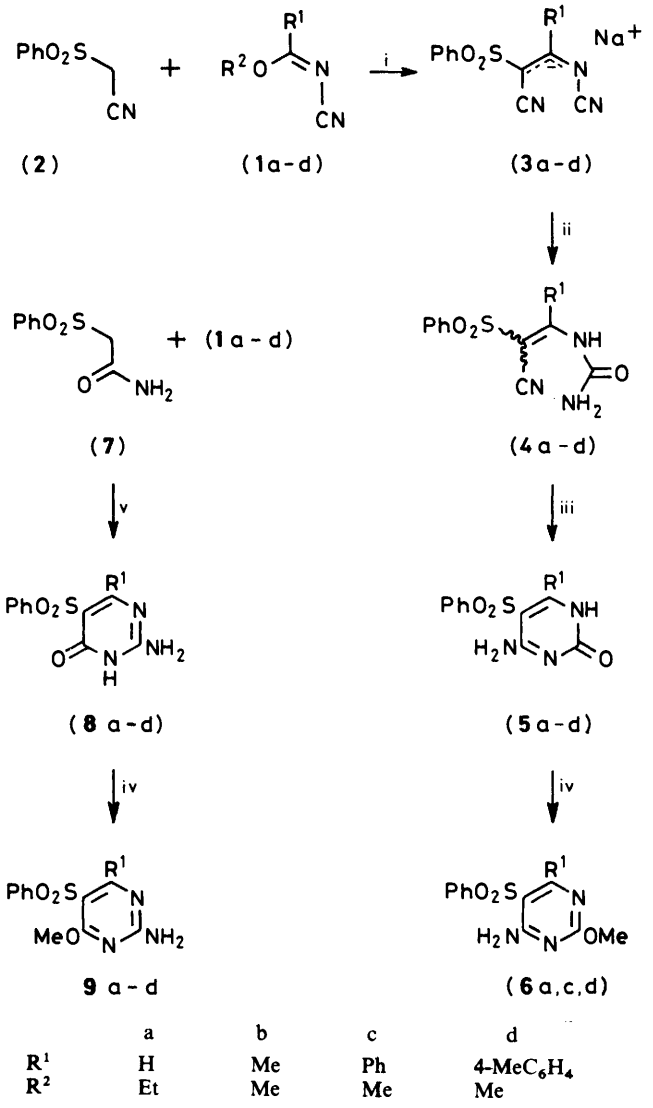
The reaction of alkyl *N*-cyanoimidates (**1a—d**) with (phenylsulphonyl)acetonitrile (**2**) and sodium methoxide afforded intermediate salts (**3a—d**), which were characterized as their conjugate acids (**10b,c**). Acidic hydrolysis of salts (**3a—d**) yielded 3-[(aminocarbonyl)amino]propenenitriles (**4a—d**), which cyclized to pyrimidin-2-ones (**5a—d**) upon dissolution in 2M-sodium hydroxide. These, in turn, were methylated to pyrimidin-4-amines (**6a,c,d**). The isomeric pyrimidin-4-ones (**8a—d**) were prepared unambiguously from the imidates (**1a—d**) and 2-(phenylsulphonyl)acetamide (**7**) and were methylated to pyrimidin-2-amines (**9a—d**). Hydrogen chloride induced a selective cyclization of the dicarbonitriles (**10b,c**) to 2-chloro- (**11**) or 4-chloro-pyrimidine (**12**). Several representatives of pyrimidinamines (**6**) and (**9**) were obtained alternatively by selective cyclizations of the salts (**3**).

Carbon–carbon double bonds bearing electron-withdrawing substituents and a leaving group undergo addition of nucleophiles followed by elimination.[1] Stable intermediates obtained in such way were cyclized to pyrimidines.[2,3] The activated carbon–nitrogen double bond of alkyl *N*-acylimidates added suitable nucleophiles leading to intermediates which cyclized intramolecularly to aromatic heterocycles.[4,5] Alkyl *N*-cyanoimidates are useful starting materials for the preparation of aromatic heterocycles through nucleophilic substitution.[6–11] We now report a simple synthesis of new 5-(phenylsulphonyl)pyrimidines from alkyl *N*-cyanoimidates.

Results and discussion

By allowing the reaction of equimolar amounts of alkyl *N*-cyanoimidates (**1a—d**), (phenylsulphonyl)acetonitrile (**2**), and sodium methoxide in dry methanol at room temperature, the stable intermediate sodium salts (**3a—d**) were formed. The complete disappearance of the reactants after 1—4 h was monitored by t.l.c. The salts (**3b,c**) were characterized as their conjugate acids (**10b,c**) (see later). Acidification of the reaction mixtures with 2M-hydrochloric acid at room temperature resulted in selective hydrolysis of the *N*-bonded carbonitrile affording 3-[(aminocarbonyl)amino]propenenitriles (**4a—d**) (Table 1). The lability of *N*-bonded carbonitriles in related salts[3,8,10] or in *N*-cyanoamidines[12] has been reported. On the basis of spectroscopic evidence the enamino tautomer is preferred to the imino form in compounds (**4a—d**). The carbonitrile stretching bands around 2 220s cm^{-1} are characteristic for enaminonitriles and not compatible with a carbonitrile bonded to a saturated carbon.[13] The signal in the range 10.5—11.1 p.p.m. in the ^1H n.m.r. spectra is in accord with the nitrogen-bonded proton of the enamino form but too far downfield for a proton bonded to carbon in an imino tautomer. Double-bond stereoisomerism is possible in these propenenitriles (**4a—d**) and was detected in one instance. In the ^1H n.m.r. spectrum of (**4a**) in hexadeuterodimethyl sulphoxide two signals at 8.33 and 8.13 p.p.m. (relative intensities 7:5) were recorded for the proton at position 3, which coalesced to a sharp singlet at 8.24 p.p.m. upon addition of deuterium oxide. This indicates the presence of a mixture of (*E*),(*Z*)-isomers of the acidic compound (**4a**) which undergo rapid prototropic equilibration on addition of a protic solvent.

Dissolution of the propenenitriles (**4a—d**) in 2M-sodium hydroxide gave the pyrimidin-2-ones (**5a—d**) and these were

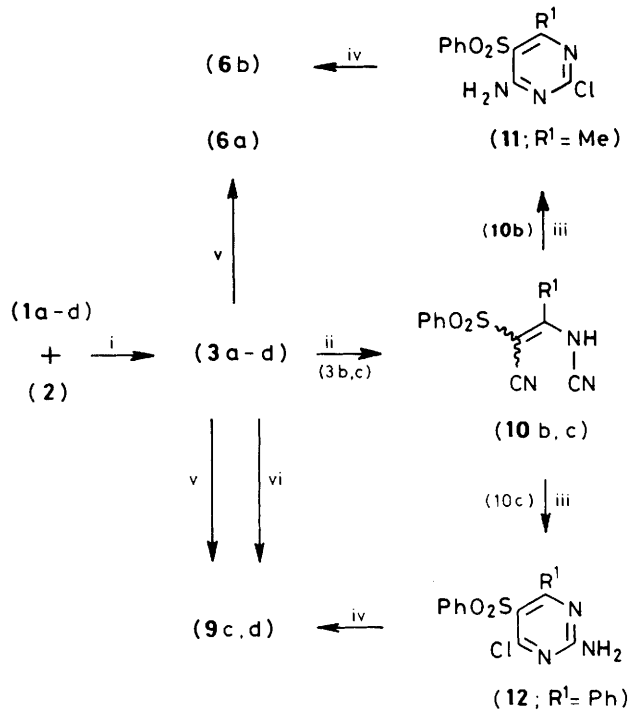


	a	b	c	d
R^1	H	Me	Ph	4-MeC_6H_4
R^2	Et	Me	Me	Me

Scheme 1. *Reagents:* i, 1 equiv. NaOMe, MeOH, room temp.; ii, 2M-HCl, room temp.; iii, 2M-NaOH, room temp.; iv, Me_2SO_4, $NaHCO_3$, dioxane–water; v, $NaOPr^i$, Pr^iOH, reflux

Table 1. Propenenitriles (**4a—d**) and (**10b,c**)

Compd.	Yield (%)	M.p. (°C)	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
(**4a**)	40	220—222	MeOH	47.8	3.9	16.8	$C_{10}H_9N_3O_3S$	47.8	3.6	16.7
(**4b**)	61	114—115	MeOH	49.5	4.3	16.1	$C_{11}H_{11}N_3O_3S$	49.8	4.2	15.8
(**4c**)	74	99—100	MeOH	58.5	3.7	13.1	$C_{16}H_{13}N_3O_3S$	58.7	4.0	12.8
(**4d**)	80	76—78	AcOEt	59.6	4.2	12.0	$C_{17}H_{15}N_3O_3S$	59.8	4.4	12.3
(**10b**)	53	133—134	Toluene	53.5	3.6	17.2	$C_{11}H_9N_3O_2S$	53.4	3.7	17.0
(**10c**)	69	97—98	MeOH	62.2	3.6	13.3	$C_{16}H_{11}N_3O_2S$	62.1	3.6	13.6



Scheme 2. *Reagents:* i, 1 equiv. NaOMe, MeOH, room temp.; ii, 18M-H_2SO_4; iii, HCl, dry Et_2O; iv, NaOMe, MeOH, room temp.; v, HCl, dry MeOH; vi, 1 equiv. NaOMe, MeOH, reflux

isolated in good yield after acidification of the reaction mixture. The sodium salts of the pyrimidin-2-ones (**5a,c,d**) were *O*-methylated with dimethyl sulphate to the pyrimidin-4-amines (**6a,c,d**) (Method A). The relatively hard electrophile dimethyl sulphate proved to be very convenient for the methylation at the hard site of the ambident nucleophile.

The isomeric pyrimidin-4-ones (**8a—d**) were prepared unambiguously in 60—94% yield by refluxing equimolar amounts of the imidates (**1a—d**) and 2-(phenylsulphonyl)acetamide (**7**) with an excess of sodium isopropoxide in dry isopropyl alcohol. The pyrimidin-4-ones (**8—d**) were refluxed in aqueous dioxane with sodium hydrogen carbonate and dimethyl sulphate to afford the pyrimidin-2-amines (**9a—d**) (Method A).

Acidification of methanolic solutions of the sodium salts (**3b,c**) with concentrated sulphuric acid allowed the isolation of their conjugate acids (**10b,c**) (Table 1). The 3-(cyanoamino)propenenitrile tautomer of compounds (**10b,c**) depicted in Scheme 2 is suggested by spectroscopic evidence. Carbonitrile stretching bands at 2 260s and 2 220m cm^{-1} are found in both compounds and tentatively assigned to the cyanoamino group and the enaminonitrile, respectively. Bands at 2 260m and 2 220s cm^{-1} are reported for *N,N'*-dicyanoguanidine,[14] whereas alkyl *N*-cyanoimidates show a characteristic carbonitrile band at 2 220 cm^{-1}.[11] Although a *C*-bonded proton was not detected at the region expected in ^1H n.m.r. spectra, a rapidly equilibrating imino tautomer or a mixture of (*E*),(*Z*)-diastereoisomers cannot be excluded.

By suspending the propenenitrile (**10b**) in dry diethyl ether and bubbling dry hydrogen chloride through it, the 2-chloropyrimidin-4-amine (**11**) was obtained in excellent yield. However, (**10c**) afforded the 4-chloropyrimidin-2-amine (**12**) under the same conditions. The structures of (**11**) and (**12**) were established by their transformation by means of a nucleophilic substitution with sodium methoxide into (**6b**) and (**9c**), respectively (Method B).

Alternatively, when hydrogen chloride was bubbled through a methanolic solution of the salts (**3a,c,d**) the pyrimidin-4-amine (**6a**) or the pyrimidin-2-amines (**9c,d**) were obtained in 52—88% yields (Method C). By refluxing the salts (**9c,d**) with one further molar equivalent of sodium methoxide, the pyrimidin-2-amines (**9c,d**) were formed exclusively (Method D).

In these selective cyclizations to pyrimidinamines other isomers possible were not detected by spectroscopic means or by t.l.c., although specimens of the latter were available for comparison. This selectivity can be interpreted as follows. The mechanism of dicarbonitrile cyclization probably involves intermediate formation of imidates or imidoyl chlorides.[15,16] Under basic conditions good yields of imidates are formed only when electron-withdrawing substituents are present.[17] Imidate formation under acidic conditions is favoured by electron-donating substituents.[18] In 3-cyanoamino-2-cyanopropenenitrile salts of structure related to (**3**) the C-bonded carbonitriles are attacked under basic conditions,[2] whereas N-bonded carbonitriles undergo addition under acidic conditions.[2,8] In the absence of strong steric hindrance and under the acidic conditions used, the unsubstituted or methyl substituted salts (**3a,b**) and (**10b**) led exclusively to products arising from intermediate imidate or imidoyl chloride formation at the N-bonded carbonitrile. However, a strong steric hindrance is present in the (**E**)-configuration of the aryl substituted salts (**3c,d**) and in (**10c**) as observed in molecular models. They should adopt a (*Z*)-configuration with the phenylsulphonyl group located as far as possible from the aryl group. Low rotation barriers around the double bond are found for push-pull alkenes.[19,20] (*E*),(*Z*)-Isomerization should be possible in salts (**3**). Such isomerizations of activated alkenes have been also observed in addition of nucleophiles.[1] The (*Z*)-configuration would place the C-bonded carbonitrile out of reach of an imidate formed reversibly in the N-bonded carbonitrile. However, imidate formation in the C-bonded carbonitrile would increase the size of this group considerably and favour an (*E*)-configuration appropriate for intramolecular cyclization. This tentative explanation accounts for exclusive formation of pyrimidin-2-amines from aryl substituted salts (**3c,d**) under basic or acidic conditions.

Experimental

I.r. spectra were obtained as KBr pellets on a Perkin-Elmer 257 spectrophotometer. ^{1}H N.m.r. spectra were recorded on a Varian T-60A spectrometer with $SiMe_4$ as an internal standard in the solvents as indicated. Melting points were determined on a Buchi melting-point apparatus or a Bühler metal block (>260 °C) and are uncorrected. Analytical t.l.c. was performed on silica gel using toluene–ethyl acetate (4:1) or ethyl acetate as the eluant. The alkyl *N*-cyanoimidates (**1a—d**) were prepared as reported.[11]

Preparation of 3-[(*Aminocarbonyl*)*amino*]-2-(*phenylsulphonyl*)*propenenitriles* (**4a—d**).—A mixture of sodium methoxide (6 mmol), (phenylsulphonyl)acetonitrile (**2**) (0.91 g, 5 mmol), and alkyl *N*-cyanoimidate (**1a—d**) (5 mmol) in dry methanol (25 ml) was stirred for 4 h at room temperature. 2M-Hydrochloric acid (15 ml) was added and the mixture was stirred for 2 h at room temperature. The precipitate thus formed was collected and recrystallized to yield the following propenenitriles (**4a—d**) (Table 1). 3-[(*Aminocarbonyl*)*amino*]-2-(*phenylsulphonyl*)*propenenitrile* (**4a**), $\nu_{max.}$ 3 440, 3 310, and 3 190 (NH), 2 220 (conj. CN), and 1 695 cm^{-1} (CO); $\delta_H[(CD_3)_2SO]$ 6.9 (2 H, br s, NH_2, exchangeable), 7.5—7.9 (5 H, m, ArH), 8.13 and 8.33 (1 H, 2 s, relative intensities 5:7, 3-H), and 10.5 (1 H, br s, NH, exchangeable). 3-*Methyl*- (**4b**), $\nu_{max.}$ 3 460, 3 300, and 3 220 (NH), 2 215 (conj. CN), and 1 695 cm^{-1} (CO); $\delta_H[(CD_3)_2SO]$ 2.15 (3 H, s, Me), 6.4 (2 H, br s, NH_2, exchangeable), 7.5—8.0 (5 H, m, ArH), and 10.9 (1 H, br s, NH, exchangeable). 3-*Phenyl*- (**4c**), $\nu_{max.}$ 3 410, 3 315, and 3 190 (NH), 2 220 (conj. CN), and 1 690 (CO); $\delta_H[(CD_3)_2SO]$ 7.1 (2 H, br s, NH_2, exchangeable), 7.3—8.0 (10 H, m, ArH), and 11.1 (1 H, br s, NH, exchangeable). 3-(p-*Tolyl*)- (**4d**), $\nu_{max.}$ 3 465 and 3 195 (NH), 2 220 (conj. CN), and 1 665 cm^{-1} (CO); $\delta_H(CDCl_3)$ 2.40 (3 H, s, Me), 6.6 (2 H, br s, NH_2, exchangeable), 7.2—7.8 (9 H, m, ArH), and 10.6 (1 H, br s, NH, exchangeable).

Preparation of 4-*Amino*-5-*phenylsulphonylpyrimidin*-2(1H)-*ones* (**5a—d**).—A solution of the appropriate propenenitrile (**4a—d**) (3 mmol) in 2M-sodium hydroxide (20 ml) was stirred for 5 h at room temperature and then acidified with concentrated sulphuric acid. The precipitate was collected, washed with water, and recrystallized to yield the following pyrimidin-2(1*H*)-ones (**5a—d**) (Table 2). 4-*Amino*-5-*phenylsulphonylpyrimidin*-2(1H)-*one* (**5a**), $\nu_{max.}$ 3 420, 3 300, and 3 240 (NH), and 1 670 cm^{-1} (CO); $\delta_H[(CD_3)_2SO]$ 7.6—8.0 (5 H, m, ArH), 8.16 (2 H, br s, NH_2, exchangeable), and 8.31 (1 H, s, 6-H). 6-*Methyl*- (**5b**), $\nu_{max.}$ 3 440, 3 300, and 3 210 (NH), and 1 650 cm^{-1} (CO); $\delta_H[(CD_3)_2SO]$ 2.10 (3 H, s, Me), 7.4—7.6 (3 H, m, *m*,*p*-ArH), and 7.7—8.1 (4 H, m, *o*-ArH + NH_2 exchangeable). 6-*Phenyl*- (**5c**), $\nu_{max.}$ 3 420 and 3 300—2 500 (NH + OH), 1 650 (CO), and 1 600 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 7.1—7.2 (6 H, m, ArH) and 7.4—7.7 (6 H, m, ArH + NH_2 exchangeable). 6-(p-*Tolyl*)- (**5d**), $\nu_{max.}$ 3 500—2 600 (NH + OH), 1 650 (CO), and 1 600 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 2.36 (3 H, s, Me), 7.2—7.6 (6 H, m, ArH + NH_2 exchangeable), 7.8—8.3 (5 H, m, ArH), and 12.1 (1 H, br s, NH + OH, exchangeable).

Preparation of 2-*Amino*-5-*phenylsulphonylpyrimidin*-4(1H)-*ones* (**8a—d**).—To a solution of sodium (0.46 g, 20 mg-atom) in dry isopropyl alcohol (25 ml), 2-(phenylsulphonyl)acetamide (1.0 g, 5 mmol) and the appropriate alkyl *N*-cyanoimidate (**1a—d**) were added. The mixture was heated under reflux for 2 d. The reaction mixture at room temperature was acidified with concentrated (*ca.* 18 molar) sulphuric acid (0.9 ml, *ca.* 16 mmol) and diluted with water. The precipitate was collected, washed with water, and recrystallized to yield the following pyrimidin-4(1*H*)-ones (**8a—d**) (Table 2). 2-*Amino*-5-*phenylsulphonylpyrimidin*-4-(1H)-*one* (**8a**), $\nu_{max.}$ 3 500—2 500 (NH + OH), 1 700 (CO), and 1 625 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 7.4—7.6 (3 H, m, *m*,*p*-ArH), 7.8—8.1 (4 H, m, *o*-ArH + NH_2 exchangeable), and 8.47 (1 H, s, 6-H). 6-*Methyl*- (**8b**), $\nu_{max.}$ 3 420 and 3 300—2 500 (NH + OH), 1 650 (CO), and 1 600 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 2.17 (3 H, s, Me), 7.4—7.5 (3 H, m, *m*,*p*-ArH), 7.7—8.0 (4 H, m, *o*-ArH + NH_2 exchangeable), and 11.6 (1 H, br s, NH, exchangeable). 6-*Phenyl*- (**8c**), $\nu_{max.}$ 3 420 and 3 300—2 600 (NH + OH), 1 650 (CO), and 1 600 cm^{-1}); $\delta_H[CD_3)_2SO]$ 7.3—7.5 (6 H, m, ArH) and 7.7—7.9 (6 H, m, ArH + NH_2 exchangeable). 6-(p-*Tolyl*)- (**8d**), $\nu_{max.}$ 3 420 and 3 500—2 500 (NH + OH), 1 640 (CO), and 1 600 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 2.40 (3 H, s, Me), 7.1—7.7 (6 H, m, ArH + NH_2 exchangeable), 7.8—8.2 (5 H, m, ArH), and 12.0 (1 H, br s, NH).

General Methods for the Preparation of Pyrimidinamines (**6**) *or* (**9**).—(a) *Method A.* A mixture of the pyrimidinone (**5**) or (**8**) (2 mmol), sodium hydrogen carbonate (1.5 g), dimethyl sulphate (3 ml), dioxane (10 ml), and water (2 ml) was refluxed for 12 h. The reaction mixture was then cooled to room temperature and diluted with water (100 ml). The precipitate was collected and recrystallized to yield the pyrimidinamine (**6**) or (**9**).

(b) *Method B.* A mixture of chloropyrimidine (**11**) or (**12**) (1.4 mmol) and sodium methoxide (1.5 mmol) in dry methanol (25 ml) was stirred for 1 h at room temperature. The solvent was evaporated and the residue was diluted with water. The precipitate was collected and recrystallized to yield the pyrimidinamine (**6b**) or (**9c**).

(c) *Method C.* A solution of sodium methoxide (6 mmol), (phenylsulphonyl)acetonitrile (**2**) (0.91 g, 5 mmol), and alkyl *N*-cyanoimidate (**1**) (5 mmol) in dry methanol (25 ml) was stirred for 4 h at room temperature. Dry hydrogen chloride was then bubbled through it for 10 min. The precipitate thus formed was collected and recrystallized to yield the pyrimidinamine (**6**) or (**9**).

(d) *Method D.* A solution of sodium methoxide (20 mmol), phenylsulphonylacetonitrile (**2**) (1.81 g, 10 mmol), and methyl

Table 2. Pyrimidin-2-ones (**5a—d**) and pyrimidin-4-ones (**8a—d**)

Compd.	Yield (%)	M.p. (°C)	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
(**5a**)	92	296—297	MeOH	45.4	3.9	17.6	$C_9H_9N_3O_3S$	45.2	3.8	17.6
(**5b**)	50	301—303	EtOH	49.4	4.1	16.0	$C_{11}H_{11}N_3O_3S$	49.8	4.2	15.8
(**5c**)	47	350	MeOH	59.0	3.8	12.5	$C_{16}H_{13}N_3O_3S$	58.7	4.0	12.8
(**5d**)	60	316—317	EtOH	60.1	4.6	12.6	$C_{17}H_{15}N_3O_3S$	59.8	4.4	12.3
(**8a**)	78	290—291	MeOH	44.9	3.6	17.4	$C_9H_9N_3O_3S$	45.2	3.8	17.6
(**8b**)	80	318—319	EtOH	49.8	4.3	15.5	$C_{11}H_{11}N_3O_3S$	49.8	4.2	15.8
(**8c**)	60	>350	MeOH	55.8	4.1	12.8	$C_{16}H_{13}N_3O_3S$	58.7	4.0	12.8
(**8d**)	94	324—325	EtOH	59.6	4.4	12.0	$C_{17}H_{15}N_3O_3S$	59.8	4.4	12.3

Table 3. Pyrimidin-4-amines (**6a—d**) and pyrimidin-2-amines (**9a—d**)

Compd.	Method	Yield (%)	M.p. (°C)	Solvent	Found (%) C	H	N	S	Formula	Required (%) C	H	N	S
(**6g**)	A	67	306—307	*a*									
	C	52	306—308	*a*	50.0	4.4	15.9		$C_{11}H_{11}N_3O_3S$	49.8	4.2	15.8	
(**6b**)	B	95	168—169	MeOH	51.8	4.5	15.3		$C_{12}H_{13}N_3O_3S$	51.6	4.7	15.0	
(**6c**)	A	42	131—133	MeOH	59.7	4.5	12.6		$C_{17}H_{15}N_3O_3S$	59.8	4.4	12.3	
(**6d**)	A	43	142—143	MeOH	60.7	4.9	12.0		$C_{18}H_{17}N_3O_3S$	60.8	4.8	11.8	
(**9a**)	A	51	311—312	*a*	49.7	4.4	15.7		$C_{11}H_{11}N_3O_3S$	49.8	4.2	15.8	
(**9b**)	A	47	156—157	MeOH	51.3	4.7	15.2		$C_{12}H_{13}N_3O_3S$	51.6	4.7	15.0	
(**9c**)	A	86	145—147	EtOH									
	B	88	144—145	EtOH									
	C	88	145—146	EtOH									
	D	59	145—146	EtOH	60.1	4.5	12.6	9.6	$C_{17}H_{15}N_3O_3S$	59.8	4.4	12.3	9.4
(**9d**)	A	55	135—136	MeOH									
	C	60	136—137	MeOH									
	D	55	135—137	MeOH	70.0	4.6	11.9		$C_{18}H_{17}N_3O_3S$	60.8	4.8	11.8	

[a] Insoluble in common solvents. The analysis was performed without recrystallization.

N-cyanoimidate (**1c,d**) (10 mmol) was refluxed for 12 h. The reaction mixture at room temperature was diluted with water (200 ml). The precipitate was collected and recrystallized to afford the pyrimidin-2-amine (**9c,d**).

Preparation of 2-Methoxy-5-phenylsulphonylpyrimidin-4-amines (**6a—d**).—Using the general methods A—C described above, the following pyrimidin-4-amines (**6a—d**) were prepared (Table 3). *2-Methoxy-5-phenylsulphonylpyrimidin-4-amine* (**6a**), $\nu_{max.}$ 3 430, 3 290, and 3 150 (NH), and 1 640 cm^{-1}. *6-Methyl-* (**6b**) $\nu_{max.}$ 3 490, 3 470, and 3 360 (NH), and 1 610 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 2.40 (3 H, s, Me), 3.77 (3 H, s, MeO), and 7.4—7.9 (7 H, m, ArH + NH_2 exchangeable). *6-Phenyl-* (**6c**), $\nu_{max.}$ 3 440, 3 290, and 3 150 (NH), and 1 630 cm^{-1}; $\delta_H(CDCl_3)$ 3.98(3 H, s, MeO) and 6.8—7.4 (12 H, m, ArH + NH_2 exchangeable). *6-(p-Tolyl)-* (**6d**), $\nu_{max.}$ 3 420, 3 360, and 3 300 (NH), and 1 600 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 2.35 (3 H, s, Me), 3.81 (3 H, s, MeO), 6.9—7.1 (7 H, m, ArH + NH_2 exchangeable), and 7.2—7.4 (4 H, m, ArH).

Preparation of 4-Methoxy-5-phenylsulphonylpyrimidin-2-amines (**9a—d**).—Using the general methods A—D described above, the following pyrimidin-2-amines (**9a—d**) were prepared (Table 3). *4-Methoxy-5-phenylsuphonylpyrimidin-2-amine* (**9a**), $\nu_{max.}$ 3 420, 3 295, and 3 200 (NH), and 1 640 cm^{-1}, *6-Methyl-* (**9b**), $\nu_{max.}$ 3 400 and 3 100 (NH), and 1 615 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 2.43 (3 H, s, Me), 3.56 (3 H, s, MeO), and 7.5—8.0 (7 H, m, ArH + NH_2 exchangeable). *6-Phenyl-* (**9c**), $\nu_{max.}$ 3 420, 3 290, and 3 190 (NH), and 1 635 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 3.83 (3 H, s, MeO) and 7.3—7.8 (12 H, m, ArH + NH_2 exchangeable). *6-(p-Tolyl)-* (**9d**), $\nu_{max.}$ 3 425, 3 350, and 3 300 (NH), and 1 615 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 2.36 (3 H, s, Me), 3.82 (3 H, s, MeO), 6.8—7.2 (7 H, m, ArH + NH_2 exchangeable), and 7.3—7.6 (4 H, m, ArH).

Preparation of 3-(Cyanoamino)-2-phenylsulphonylpropenenitriles (**10b,c**)—A solution of sodium methoxide (30 mmol), phenylsulphonylacetonitrile (**2**) (5.43 g, 30 mmol), and *N*-cyanoimidate (**1b,c**) (30 mmol) in dry methanol (40 ml) was stirred for 2 h at room temperature. Concentrated (*ca.* 18 molar) sulphuric acid (1.4 ml, *ca.* 25 mmol) was added and the solvent was evaporated. The residue was diluted with water. The precipitate was collected, washed with water, and recrystallized to yield the following propenenitriles (**10b,c**) (Table 1). *3-Cyanoamino-3-methyl-2-phenylsulphonylpropenenitrile* (**10b**), $\nu_{max.}$ 3 205 (NH), 2 260 and 2 220 (CN), and 1 600 cm^{-1}; $\delta_H(CDCl_3)$ 2.50 (3 H, s, Me) and 7.4—7.9 (6 H, m, ArH + NH_2 exchangeable). *3-(Cyanoamino)-3-phenyl-2-phenylsulphonylpropenenitrile* (**10c**), $\nu_{max.}$ 3 190 (NH), 2 260 and 2 220 (CN); $\delta_H[(CD_3)_2SO]$ 7.0—7.8 (m, ArH + NH).

Preparation of 2-Chloro-6-methyl-5-phenylsulphonylpyrimidin-4-amine (**11**).—Through a suspension of propenenitrile (**10b**) (1 g, 4 mmol) in dry diethyl ether (25 ml), dry hydrogen chloride was bubbled for 15 min. The precipitate was collected, washed with diethyl ether, and recrystallized from methanol to yield *2-chloropyrimidin-4-amine* (**11**) (1.26 g, 98%), m.p. 184—185 °C (Found: C, 46.7; H, 3.3; N, 14.7. $C_{11}H_{10}ClN_3O_2S$ requires C, 46.6; H, 3.6; N, 14.8%); $\nu_{max.}$ 3 410 and 3 340 (NH), and 1 610 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 2.40 (3 H, s, Me), 7.3—7.8 (5 H, m, ArH), and 8.10 (2 H, s, NH_2, exchangeable).

Preparation of 4-Chloro-6-phenyl-5-phenylsulphonylpyrimidin-2-amine (**12**).—Through a suspension of the propenenitrile (**10c**) (1.24 g, 4 mmol) in dry diethyl ether (25 ml), dry hydrogen chloride was bubbled for 15 min. The precipitate was collected, washed with diethyl ether, and recrystallized from ethanol to yield *4-chloropyrimidin-2-amine* (**12**) (0.96 g, 70%), m.p. 200—201 °C (Found: C, 55.3; H, 3.4; N, 12.2. $C_{16}H_{12}ClN_3O_2S$ requires C, 55.6; H, 3.5; N, 12.2); $\nu_{max.}$ 3 440 and 3 340 (NH), and 1 630 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 6.8—7.4 (m, ArH + NH_2 exchangeable).

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