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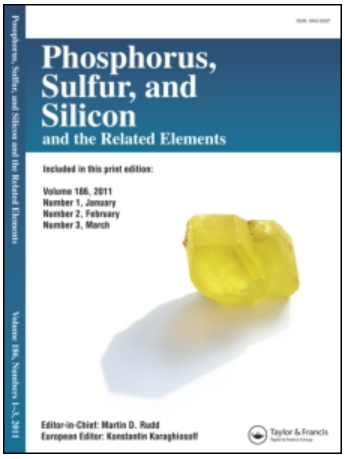

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Recent Advances in 1,2,3-Dithiazole Chemistry

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The reactions of 5-arylimino-4-chloro-5*H*-1,2,3-dithiazoles **1** with primary and sterically less bulky secondary alkylamines in CH_2Cl_2 at 25°C gave (arylimino)-cyanomethyl alkylamino disufides and *N'*-(aryl)-*N*-alkylcyanoformamidines. However, **1** reacted with excess bulky dialkylamines to give 5-(arylimino)-4-(dialkylamino)-5*H*-1,2,3-dithiazoles, which reacted with hydroxide base in aqueous EtOH to give *N'*-arylthiocarbamoyl-*N,N'*-dialkyamidines, excellent starting materials for various heterocyclic compounds. However, the reactions of 4-chloro-5*H*-1,2,3-dithiazol-5-one **2** and its analog, -5-thione **3** with primary and secondary alkylamines gave *N*-alkyl- and *N,N*-dialkylcyanothioformamides and *N*-alkyl- and *N,N*-dialkyl-5-cyanoformyl sulfenamides, respectively, depending on the alkylamines.

KEY WORD
5-(Arylimino)-4-(dialkylamino)-5*H*-1,2,3-dithiazoles, (Arylimino)cyanomethyl Alkylamino Disulfides, *N*-Alkyl *S*-Cyanoformyl Sulfenamides, *N'*-Arylthiocarbamoyl-*N,N*-dialkylamidines.

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INTRODUCTION

4,5-Dichloro-5*H*-1,2,3-dithiazolium chloride (Appel salt) has been utilized for the synthesis of 5-arylimino-4-chloro-5*H*-1,2,3-dithiazoles **1**, 4-chloro-5*H*-1,2,3-dithiazol-5-one **2**, and 4-chloro-5*H*-1,2,3-dithiazole-5-thione **3**.[1] Compounds **1** have been known as interesting compounds with their biological activities as fungicides, ovicides, insecticides, herbicides and pharmaceuticals,[2] and also their potential utility as synthetic intermediates.[1,3-4] However, little is known about the chemistry of compounds **2** and **3**.

Synthesis of *N*-Alkyl-, *N,N*-Dialkyl-, and *N*-Arylcyanothioformamides

Hydrolysis of **1** in a mixture of aqueous NH_3 and EtOH was reported to give *N*-arylcyanothioformamides **4** in 14 - 86% yields.[2] We had some difficulties to separate

the reaction mixtures by chromatography. We developed a facile method for the synthesis of **4**. That is, a heterogeneous reduction of hydrochloride salt of **1** with $NaBH_3CN$ gave good to excellent yields of **4**.[5] Yields and melting points are summarized in Table 1.

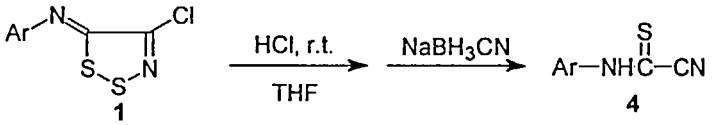

TABLE 1

Yields and melting points of *N*-arylcyanothioformamides **4**

Compounds	Ar	Yield [a](%)	mp (°C)
4a	4-$O_2NC_6H_4$	84	128 -130[c] (lit[6] 128 - 130)
4b	3-$O_2NC_6H_4$	88	103 -104[d] (lit[6] 99 - 102)
4c	2-Me(3-O_2N)C_6H_3	78	97 - 98[d]
4d	2-ClC_6H_4	75	106 -108[c] (lit[7] 108 - 110)
4e	2-O_2N(4-Ph)C_6H_3	90	146 - 147[d]
4f	2-$EtO_2CC_6H_4$	63[b]	89-90[f]
4g	4-H_2N(3-Ph)C_6H_3	68	148-150[e]
4h	4-H_2N(3-Ph)(5-Ph)C_6H_2	51	138-139[d]
4i	3-H_2N(2-Ph)(4-Ph)C_6H_2	49	172-176[e]
4j	3-H_2N(2-Me)(4-Ph)C_6H_2	86	152-155[d]
4k	4-H_2N(2-Me)(5-Ph)C_6H_2	74	118-119[d]
4l	2-Carbazolyl	100	158 - 159[e]

[a] Isolated yields. [b] *N*-(2-Carbethoxyphenyl)dithiooxamide was obtained in 5% yield. Solvent for the recrystallization : [c] $CHCl_3$ - *n*-hexane; [d] pertoleum ether (bp 40 - 60 °C) - Et_2O; [e] CH_2Cl_2 - *n*-hexane; [f] *n*-hexane.

This method has the advantage over the reported method in yields and ease of isolation of the products. In addition , this is the first examples (**4g - k**) for the preparation of compounds **4** having an amino group on *N*-aryl substituents.

The mechanism of the formation of **4** may be rationalized by a nucleophilic attack of a hydride ion to S-2 of hydrochloride salt of **1**, followed by elimination of sulfur atom along with hydrogen chloride to give **4** (Scheme 1).

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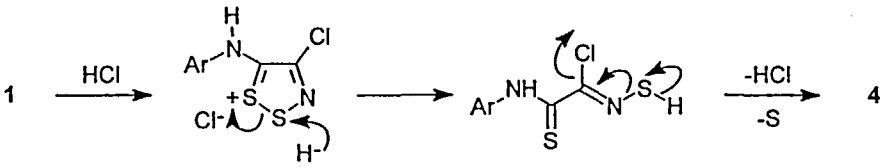
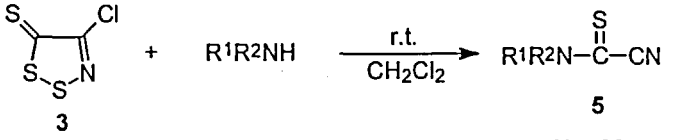


Scheme 1

In the meantime, treatment of compound **3** with a variety of primary and secondary alkylamines in CH_2Cl_2 at room temperature afforded *N*-alkyl- and *N,N*-dialkylcyanothioformamides **5**.[8]



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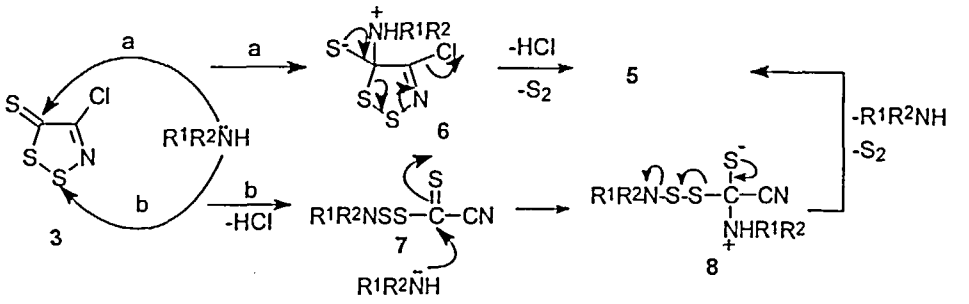
There have been several methods for the preparation of *N*-aryl- **4**[12-14] and N-alkylcyanothioformamides **5**[15-17] which have been exclusively prepared by the reactions of aryl- and alkylisothiocyanates with cyanides, respectively. Synthesis of *N,N*-dialkylcyanothioformamides **5** have been mainly achieved by either a nucleophilic displacement of *C*-sulfonylthioformamide by cyanide[11] or the reaction of sodium cyanodithioformate with *N,N*-dialkylamines.[10] Treatment of nitroacetamides with Lawesson's reagent gave **5** depending on the number of alkyl groups on nitrogen atom of the amides.[18] It is conceived that the present method utilizing compound **3** has the advantage over the reported methods with respect to the versatility, yields, and ease of work-up.

The formation of **5** can be rationalized by a nucleophilic attack of alkylamine at C-5 to give an intermediate **6** which loses HCl and S_2 to yield **5**. Alternatively a nucleophilic attack of alkylamine at S-2 with the concomitant displacement of chlorine atom can lead to an intermediate **7**, which is attacked by the second molecule of alkylamine to give **5** via an intermediate **8** (Scheme 2).

Synthesis of 4*H*-3,1-Benzothiazines 12 and 4*H*-3,1-Benzoxazines 13[19]

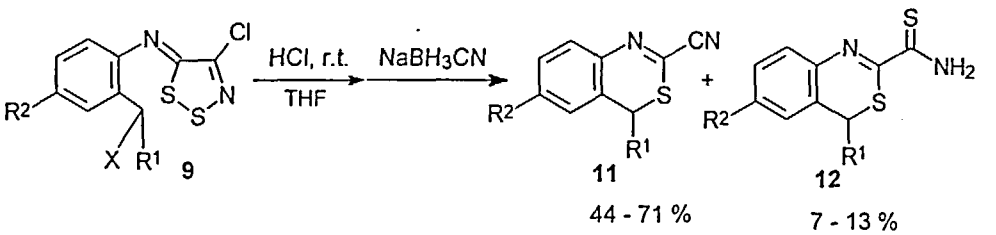
4-Chloro-5-(*o*-halomethylarylimino)-5*H*-1,2,3-dithiazoles **9** are readily converted into compounds **11** by treatment with hydrogen chloride gas, folowed by slightly excessive



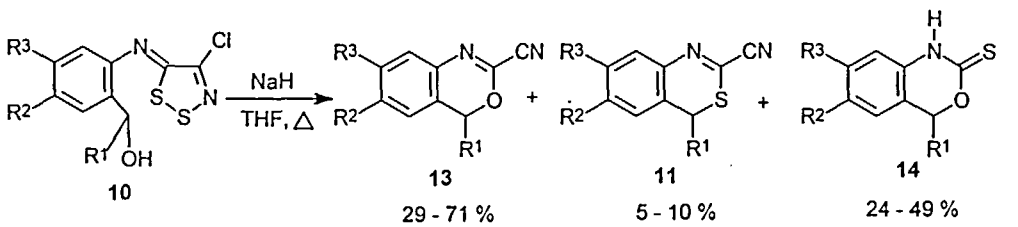
Scheme 2

molar amounts of $NaBH_3CN$.

The formation of **11** can be explained on the basis of an intramolecular nucleophilic displacement of halogen atom by sulfur atom of cyanothioamide functionality as shown in Scheme 1.



On the other hand, refluxing of O-hydroxymethyl analogs **10** with NaH in THF led to compounds **13**, **11** and 1*H*, 4*H*-3,1-benzoxazine-2-thione **14**.



The formation of **13** can be rationalized by an nucleophilic attack of alkoxide ion at imino carbon, followed by extrusion of S_2 (Scheme 3). On the other hand, nucleophilic attack of hydride ion at S-2, leading to bond cleavage between S-1 and S-2, followed by dehydrocyanation gives isothiocyanate **15**, which undergoes an intramolecular cyclization to give **14**.

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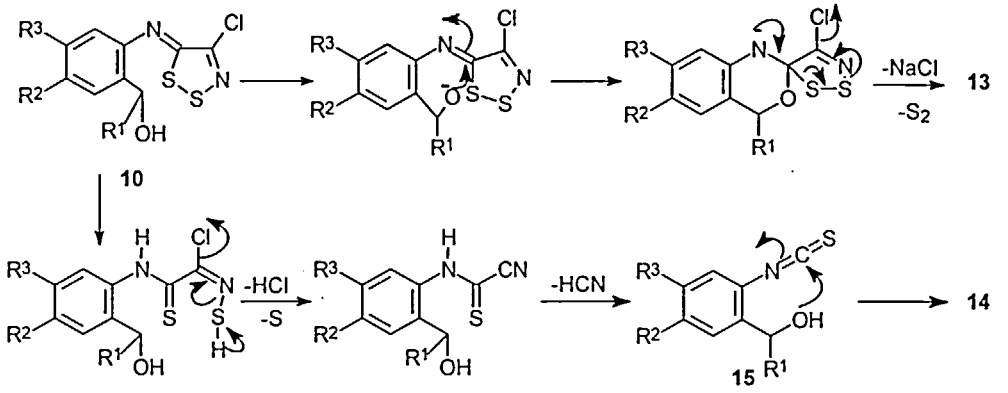
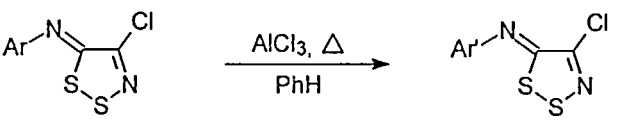


Scheme 3

Reactions of 1 with Anhydrous Aluminum Chloride

4-Chloro-5-(4-nitrophenylimino)-5*H*-1,2,3-dithiazole **1a** in anhydrous benzene was heated in the presence of anhydrous $AlCl_3$ at reflux[20] to give two compounds **16a** and **16b** which have an amino group on arylimino group at C-5 of compound **1a**. Yields of **16a** and **16b** were variable depending on the molar ratio between **1a** and $AlCl_3$.



The highest yields of **16a** and **16b** were obtained when **14** equivalents of $AlCl_3$ were used. The results obtained from the reactions of compounds **1** having a nitro group on arylimino group at C-5 with $AlCl_3$ are summarized in Table 2.

The structures of compounds **16** were determined on the basis of the spectroscopic[21] and mass spectral data and elemental analyses in addition to the synthesis of the authentic samples.

Reactions of 4-Chloro-5-(4-toluenesulfonylimino)-5*H*-1,2,3-dithiazole 17 with Primary and Secondary Alkylamines[22]

Reactions of 4-chloro-5-(4-toluenesulfonylimino)-5*H*-1,2,3-dithiazole **17** with primary and secondary alkylamines gave *N*'-(4-toluenesulfonyl)-*N*-alkyl- and *N*,*N*-dialkylcyano-

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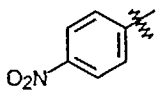
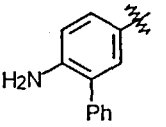
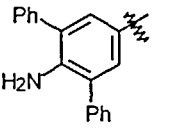
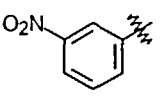
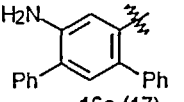
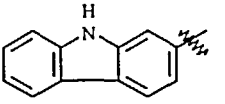
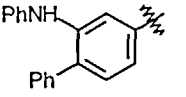
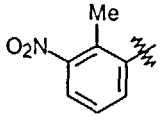
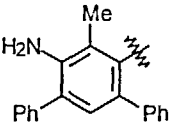
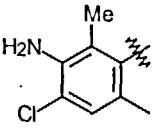
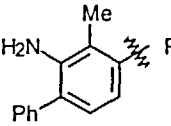
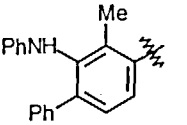
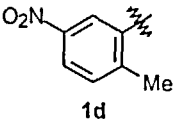
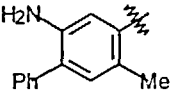
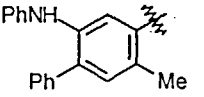
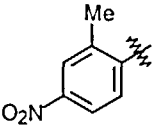
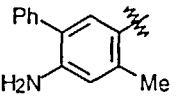
TABLE 2

Reactions of 4-chloro-5-(nitroarylimino)-5*H*-1,2,3-dithiazoles (**1a - e**) with benzene in the presence of $AlCl_3$ (14 equiv)

Ar	Ar'[a](%)				
 **1a**	 **16a (35)**	 **16b (17)**			
 **1b**	 **16c (17)**	 **16d (8)**	 **16e (6)**		
 **1c**	 **16f (11) (4)[b]**	 **16g (10) (8)[b]**	 **16h (8) (16)[b]**	 **16i (12) (o)[b]**	
 **1d**	 **16j (16)**	 **16k (4)**			
 **1e**	 **16l (14)[c]**				

[a] Isolated yield. [b] Yields when $AlCl_3$ (7 equiv) was used. Unreacted **1c** (40 %) was recovered. [c] Unreacted **1e** (28 %) was recovered.

formamidines **18**, which reacted further to give 1,3-dialkyl-2-(4-toluenesulfonyl)-guanidines **19**. The results are summarized in Table 3.

Interestingly, better yields of **19** can be obtained when sterically less hindered amine between two different amines to be involved in the conversion of **17** to **19** via the formation of **18** is used for the second step.

The mechanism of the formation of **18** and **19** are proposed as follows: One might envisage the direct nuclophilic attack of an amine on the imino carbon atom of **17**

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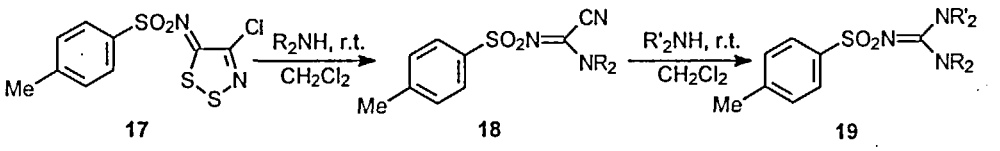

17 18 19

TABLE 3

Synthses of *N'*-(4-toluenesulfonyl)-*N*-alkyl- and *N,N*-dialkylcyanoformamidines **18** and 1,3-dialkyl-2-(4-toluenesulfonyl)guanidines **19**

R_2NH	R'_2NH	Yield [a] (%)	mp (°C)	Yield [a] (%)	mp (°C)
		18		**19**	
		**a** 79	126 - 127	**a** 81 (65)[b]	144 - 145.5
				**b** 99	179 - 180
				**c** 50	103 - 104
	Et_2NH			**d** 51	63 - 64
		**b** 77	128 - 129.5	**e** 83 (53)[b]	106 - 107
				**f** 40	116 - 117.5
Et_2NH		**c** 53 (18)[b]	100 - 101	**g** 57	48 - 49
		**d** 63	97 - 97.5	**f** 70	
i-$PrNH_2$		**e** 55	105 - 109		
t-$BuNH_2$		**f** 68	132 - 133		
n- $pentNH_2$		**g** 74	43 - 44		

[a] Isolated yield. Solvent for the recrystallization : *n*-hexane - CH_2Cl_2 for **18**, **19a**, and **19e** ; *n*-hexane - EtOAc for **19b-d**, and **19f-g** [b] Numbers in the parentheses represent yield from the treatment of **17** in morpholine (10 mL), pyrrolidine (10 mL), and Et_2NH (10 mL), respectively without using the solvent.

(Scheme 5, path a) followed by elimination of S_2 along with hydrogen chloride to give **18**. On the other hand, nucleophilic attack of an amine on S-2 to give (4-tolunesulfonylimino)cyanomethyl alkylamino disulfides (Scheme 5, path b), followed

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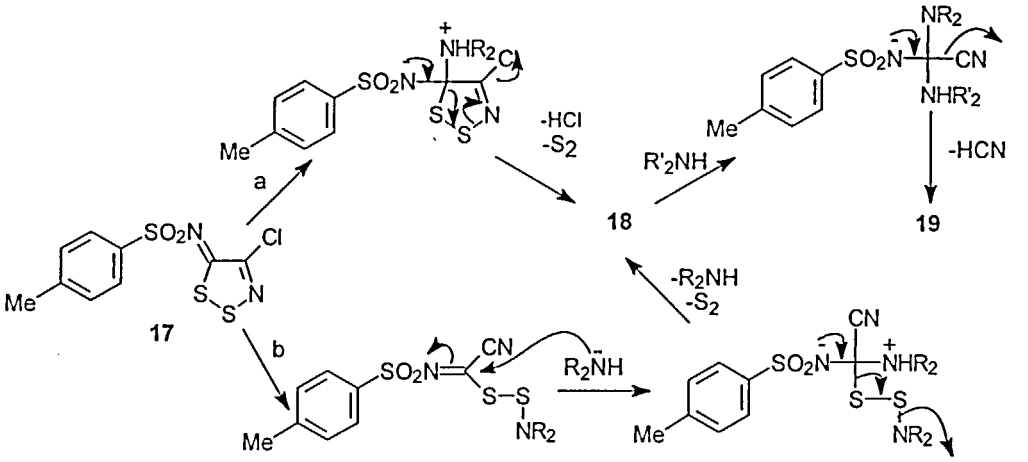
by nucleophilic attack of another molecule of the amine at imino carbon might also give **18**.



Scheme 5

The formation of **19** can be explained by nuclophilic addition of amine to the imino double bond of **18**, followed by elimination of cyano group.

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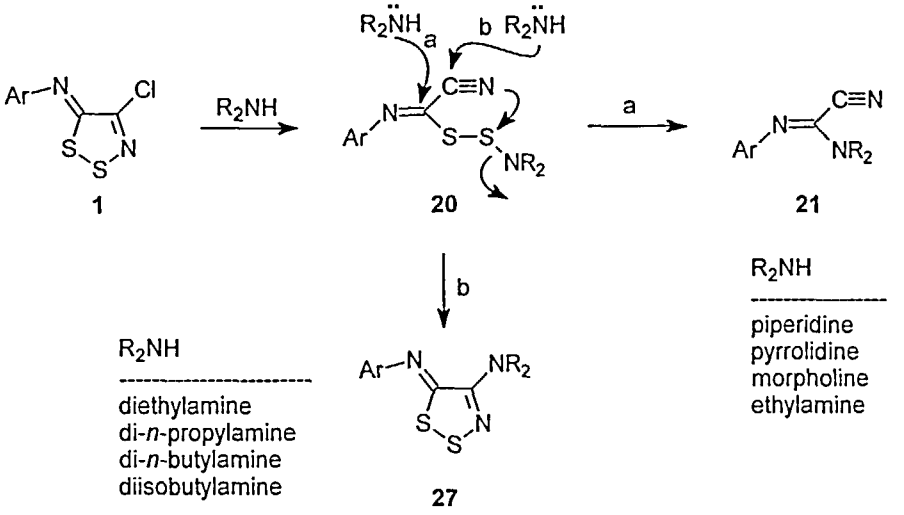
Reactions of 1 with Primary and Sterically Less Bulky Secondary Alkylamines[23]

The reactions of 5-(4-tolylimino)-4-chloro-5*H*-1,2,3-dithiazole **1f** (Ar = 4-MeC_6H_4) with piperidine (2.4 equiv) in CH_2Cl_2 at room temperature afforded amino disulfide **20a** (Ar = 4-MeC_6H_4, R_2 = -$CH_2(CH_2)_3CH_2$-) and cyanoformamidine **21a** (Ar = 4-MeC_6H_4, R_2 = -$CH_2(CH_2)_3CH_2$-) in 64 and 49% yields, respectively in addition to 9% yield of thiourea derivatives **22** (Scheme 6). The results obtained from the reactions of **1f** with other alkylamines are summarized in Table 4.

Amino disulfide **20d** (Ar = 4-$MeOC_6H_4$, R_2 = -$CH_2(CH_2)_3CH_2$-) was treated with pyrrolidine (7 equiv) and isopropylamine (8 equiv) in CH_2Cl_2 at room and reflux temperatures to give compounds **21d** (Ar = 4-$MeOC_6H_4$, R_2 = -$CH_2(CH_2)_2CH_2$-) and **21e** (Ar = 4-$MeOC_6H_4$, R_2 = -$CH_2(CH_2)_3CH_2$-) in 97% and 26% yields, respectively. The results indicate that the amino iminomethyl disulfides of the type **20** can act as intermediates in the course of the formation of cyanoformamidines. The mechanism of the reaction of **1** with alkylamines are outlined in Scheme 7.



Scheme 6

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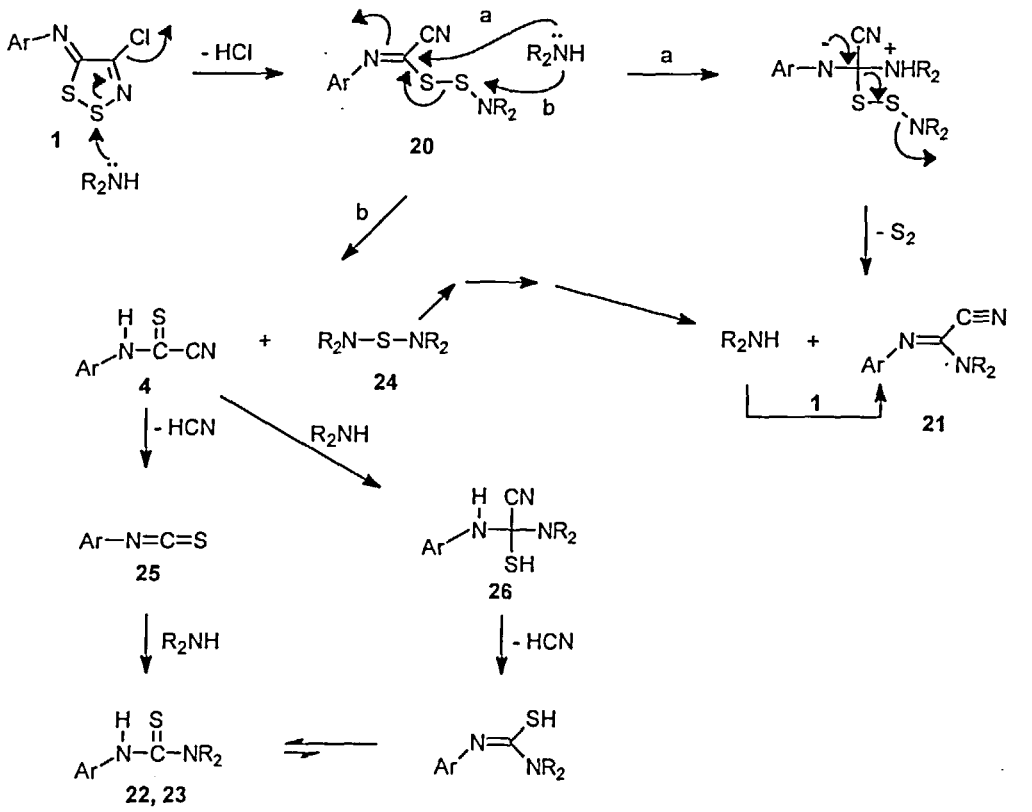
TABLE 4

Reactions of 4-chloro-5-(4-tolylimino)-5*H*-1,2,3-dithiazole **1f** with primary and secondary alkylamines

Entry	**1f** (mM)	Amine (mM)	Time (h)	**1f**	Yield[a] (%) disulfide		amidine	
a	1.08	piperidine (2.4)	1.0		**20a**	64		
b	2.06	piperidine (6.1)	1.0				**21a**	49[b]
c	0.869	pyrrolidine (1.8)	1.5	8	**20b**	56	**21b**	18
d	2.07	pyrrolidine (6.0)	0.5				**21b**	84[c]
e	1.31	isopropylamine (2.9)	1.5	49	**20c**	23		
f	2.31	morpholine (6.8)	2.5				**21c**	77

[a]Isolated yield. [b]*N,N*-(Pentane-1,5-diyl)-*N'*-(4-tolyl)thiourea (**22**)(9%) and an unknown compound were isolated. [c] *N,N*-(butane-1,4-diyl)-*N'*-(4-tolyl)thiourea (**23**)(12%) was isolated.

Cyclic amines with a pair of protruded electrons follow the path a to give cyanoformamidine **21**, whereas the sterically hindered amine might attack at the sulfur atom α to the nitrogen atom of the amino group to give *N*-arylcyanothioformamides **4** and bisaminosulfides **24**, which decompose to generate amine (path b). The amine



Scheme 7

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generated by path b is in turn involved in the formation of **21**. The assumption that the compounds **4** are involved as intermediates was proved by the reaction of **4a** with pyrrolidine in which compound **21f** (Ar = 4-$O_2NC_6H_4$, R_2 = -$CH_2(CH_2)_2CH_2$-) and *N,N*-(butane-1,4-diyl)-*N'*-(4-nitrophenyl)thiourea were isolated in 14 and 29% yields, respectively.

The reactions of **1** with excess amounts (6 equiv) of bulky secondary alkylamines in CH_2Cl_2 (30 mL) at room temperature gave 5-(arylimino)-4-(dialkylamino)-5*H*-1,2,3-dithiazoles **27**[24] (Scheme 6). The results are summarized in Table 5.

The structures of **27** were determined on the spectroscopic data and elemental analyses in addition to *X*-ray single crystallographic analysis of **27b**. The mechanism of the formation of **27** via the the intermediacy of disulfide **20** was proved by UV absorption spectroscopy.

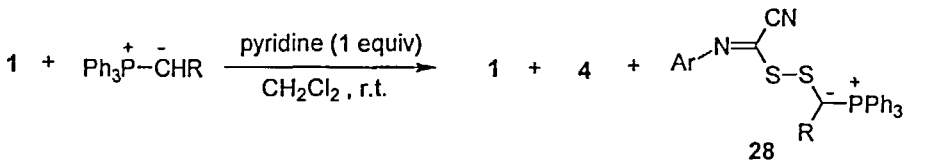
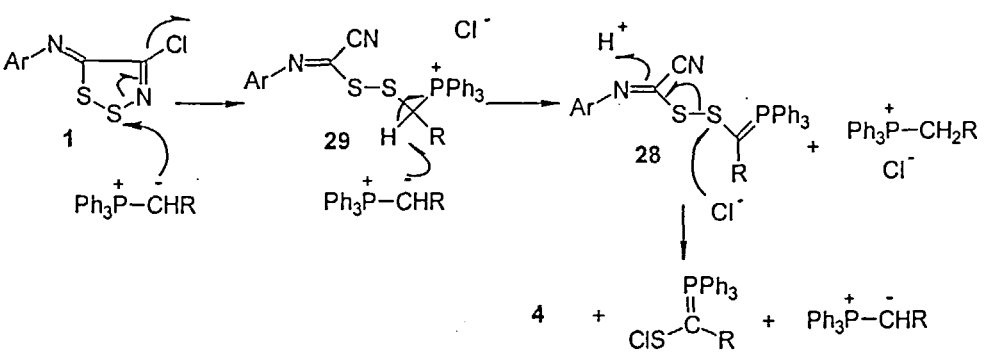


TABLE 6

Reactions of **1** with Some Stable Phosphoranes

Ar	R						
			Yield,[a] (%)				
4-$MeOC_6H_4$	CO_2Et	**1f**	7	**4f**	11	**28a**	69
4-MeC_6H_4	CO_2Et	**1g**	8(11)	**4g**	7 (32)	**28b**	81 (38)
4-BrC_6H_4	CO_2Et	**1h**	7	**4h**	7	**28c**	78
4-$O_2NC_6H_4$	CO_2Et	**1a**	15(17)	**4a**	8 (38)	**28d**	70 (32)
4-$MeOC_6H_4$	COMe	**1f**	7 (6)	**4f**	9 (38)	**28e**	79 (39)
4-MeC_6H_4	COMe	**1g**	8	**4g**	7	**28f**	77
4-BrC_6H_4	COMe	**1h**	5	**4h**	7	**28g**	80
2-NCC_6H_4	COMe	**2i**	8	**4i**	8	**28h**	68
4-$O_2NC_6H_4$	COMe	**1a**	9	**4a**	9	**28i**	76
2-MeC_6H_4	4-ClC_6H_4CO	**1j**	16	**4g**	11	**28j**	48
4-$MeOC_6H_4$	CN	**1f**	15	**4f**	16	**28k**	53
2-MeC_6H_4	CN	**1j**	14	**4g**	20	**28l**	58

[a] Isolated yield. Number in the parenthesis represents the yield in the absence of pyridine.



Scheme 8

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TABLE 5

Preparation of 5-(arylimino)-4-(dialkylamino)-5*H*-1,2,3-dithiazoles **27**

Ar	R	Time (h)	Yield[a] (%)	
4-$O_2NC_6H_4$	Et	48	**27a**	26
5-O_2N(2-Cl)C_6H_3	Et	6	**27b**	32
3-O_2N(4-Cl)C_6H_3	*n*-Pr	48	**27c**	75
4-$O_2NC_6H_4$	*n*-Pr	48	**27d**	60
4-BrC_6H_4	*n*-Pr	48	**27e**	50
4-$MeOC_6H_4$	*n*-Pr	48	**27f**	23
4-$O_2NC_6H_4$	*n*-Bu	24	**27g**	63
4-BrC_6H_4	*n*-Bu	48	**27h**	59
4-$O_2NC_6H_4$	*i*-Bu	72	**27i**	7
4-MeC_6H_4	-$CH_2(CH_2)_3CH_2$-	1	**27j**	14[b]
4-MeC_6H_4	-$CMeH(CH_2)_3CH_2$-	48	**27k**	15

[a] Isolated yield by either chromatography or HPLC. [b] Cyanoformamidine **21** (Ar = 4-MeC_6H_4, R_2 = -$CH_2(CH_2)_3CH_2$- and thiourea derivative **22** were isolated in 50 and 10% yields, respectively.

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Reactions of 1 with Stable Phosphoranes

The reactions of **1** with stable phosphoranes such as carboethoxymethylene-, acetylmethylene-, 4-chlorobenzoylmethylene-, and cyanomethylenetriphenylphosphoranes in the presence of pyridine in CH_2Cl_2 at room temperature gave a new type of the corresponding phosphoranes **28** with aryliminocyanomethyldithio moiety as a major product.[25] The results are summarized in Table 6.

The mechanism of the formations of compounds **4** and **28** can be rationalized by a nucleophilic attack of phosphorane to S-2 to form a phosphonium chloride **29**, which loses a hydrogen chloride in the presence of another molecule of phosphorane to form a dithiomethylenephosphorane **28**. Compounds **28** react with hydrogen chloride to form cyanothioformamides **4** (Scheme 8).

Synthesis of *N*-Alkyl and *N,N*-Dialkyl *S*-Cyanoformyl Sulfenamides

Compound **2** was treated with primary and secondary alkylamines in CH_2Cl_2 at room temperature to give *N*-alkyl (**30a-f**) and *N,N*-dialkyl *S*-cyanoformyl sulfenamides (**30g - i**). Reaction times and yields of compounds **30** are summarized in Table 7.

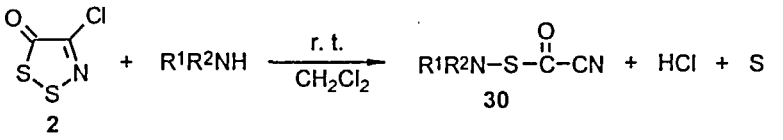

TABLE 7

Reaction times and yields of *N*-alkyl and *N,N*-dialkyl *S*-cyanoformyl sulfenamides **30**

Compound	R^1	R^2	Time (h)	Yield[a] (%)	mp (°C)
30a	*i*-Pr	H	15	78	191-193
30b	*t*-Bu	H	14	99	190 (sublime)
30c	*n*-Pent	H	13	93	87-89
30d	*n*-Hex	H	14	66	74-77
30e	Bn	H	5	79	168-169
30f	Piperonyl	H	7	75	162-164
30g	Allyl	Allyl	15	41	liquid
30h	Et	Et	17	37	liquid
30i	*n*-Pr	*n*-Pr	40	50	liquid

[a] Isolated yields. Solvent for the recrystallization : EtOAc - *n*-hexane.

The formation of **30** can be rationalized on the basis of a nucleophilic attack of alkylamine to S-1 or S-2 atoms. The nucleophilic attack to S-1 (path a) gives **30** along with the extrusion of S and HCl. On the other hand, the nucleophilic attack to S-2 (path b) gives disulfide **31** as an intermediate with the concomitant formation of HCl. The intermediate **31** reacts with the second molecule of alkylamine to give **30**, S and alkylamine. However, since no intermediate **31** is detected, we prefer the path a (Scheme 9).

Synthesis of *N'*-Arylthiocarbamoyl-*N,N*-Dialkylamidines 32

Treatment of compounds **27** with hydroxide base in aqueous EtOH solution gave *N'*-

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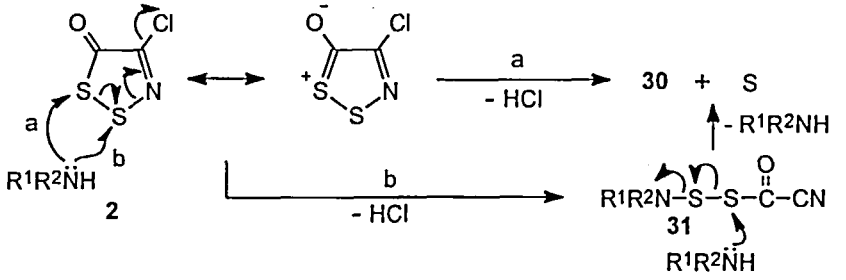

Scheme 9

arylthiocarbamoyl-*N,N*-dialkylamidines **32** which reacted with various electrophiles to give new heterocyclic compounds.[26] Yields of **32** are summarized in Table 8.

TABLE 8

Yields of *N'*-arylthiocarbamoyl-*N,N*-dialkylamidines **32**

Compound	Ar	R	Yield [a] (%)	mp (°C)
32a	4-$O_2NC_6H_4$	Et	70	229-231[b]
32b	4-$O_2NC_6H_4$	n-Pr	99	210-213[c]
32c	4-$O_2NC_6H_4$	n-Bu	83	209-210[d]
32d	4-$O_2NC_6H_4$	Allyl	99	200-203[e]
32e	4-ClC_6H_4	n-Pr	77	200-203[d]
32f	4-BrC_6H_4	n-Pr	82	205-207[d]
32g	4-MeC_6H_4	n-Pr	77	242-243[d]
32h	4-$MeOC_6H_4$	n-Bu	79	164-166[e]

[a] Isolated yield. Solvent for the recrystallization: [b] acetone - EtOAc; [c] MeOH; [d] $CHCl_3$ - acetone; [e] $CHCl_3$

^{13}C NMR spectrum of compound **32c** shows six peaks at 122.51, 124.17, 139.63, 158.92, 164.15, and 175.95 ppm in addition to eight peaks due to two butyl groups. Although the last two peaks, i.e. 175.95 and 164.15 ppm may be assignable to thione and imino carbons, respectively, in view of the literature values,[27-29] one cannot rule out the possibility of an equilibrium mixture of two tautomeric forms.

The formation of compounds **32** might be explained by a nucleophilic attack of hydroxide ion to S-2 to cleave a bond between S-1 and S-2 rather than S-2 and nitrogen atom, giving an intermediate **33** (Scheme 10).

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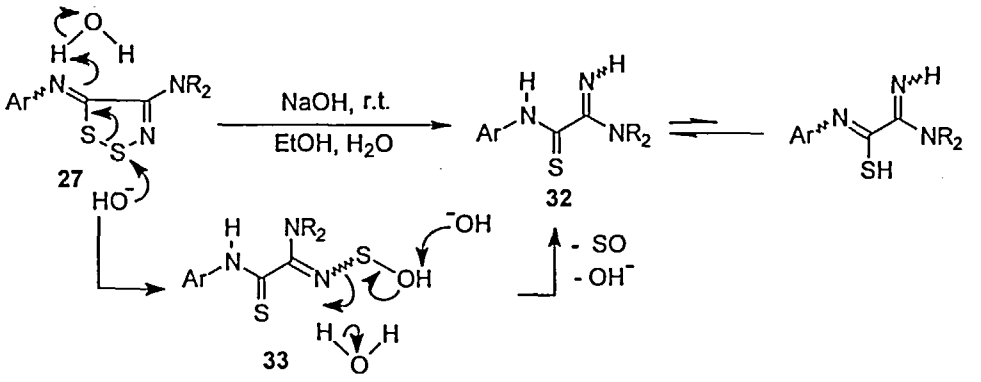

Scheme 10

The synthetic potentialities of **32** are demonstrated in the reactions with various electrophiles as exemplified in Scheme 11.

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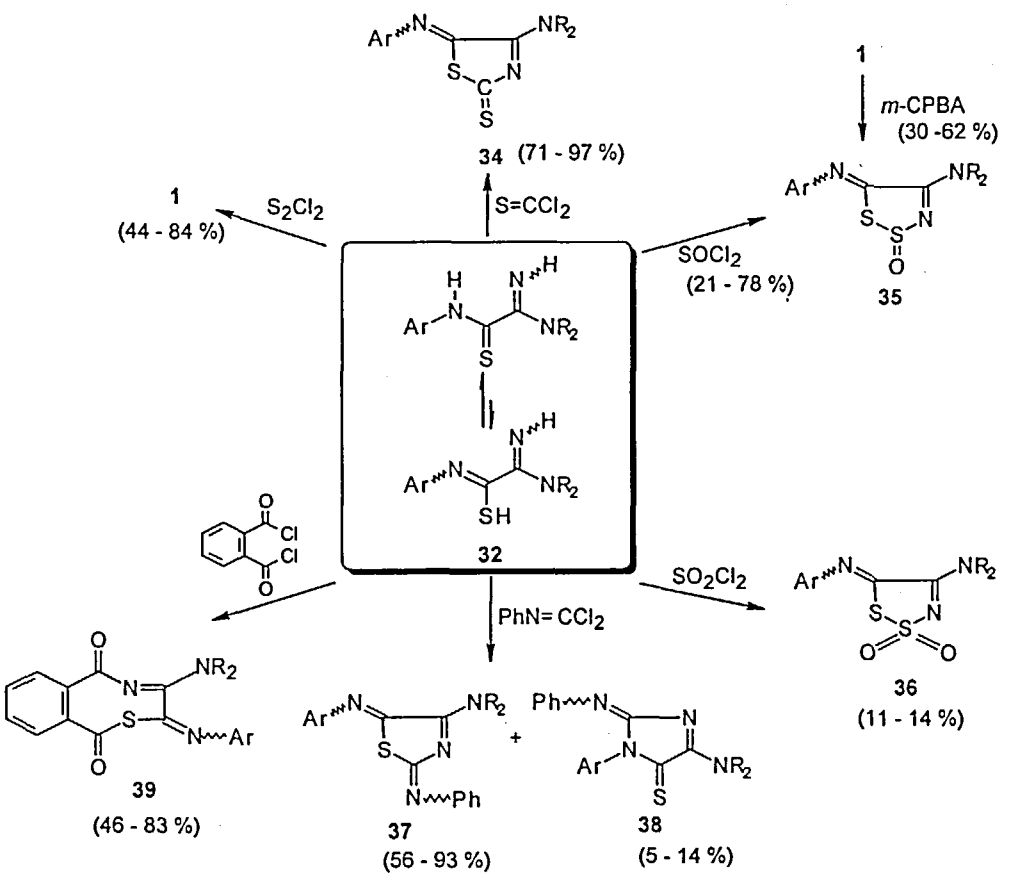

Scheme 11

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