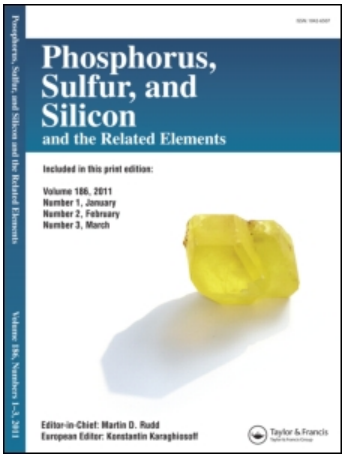

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Zohdi, Hussein F. , Rateb, Nora M. and Abdelhamid, Abdou O.(1998) 'REACTIONS WITH HYDRAZONOYL HALIDES XIX[1]: SYNTHESIS OF SOME PYRAZOLE AND 5-ARYLAZOTHIAZOLE DERIVATIVES', Phosphorus, Sulfur, and Silicon and the Related Elements, 133: 1, 103 — 117
To link to this Article: DOI: 10.1080/10426509808032458
URL: http://dx.doi.org/10.1080/10426509808032458

Phosphorus, Sulfur and Silicon, Vol. 133, pp. 103-117
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REACTIONS WITH HYDRAZONOYL HALIDES XIX[1]: SYNTHESIS OF SOME PYRAZOLE AND 5-ARYLAZOTHIAZOLE DERIVATIVES

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(Received 27 August, 1997; In final form 23 March, 1998)

Hydrazonoyl chlorides **1** reacted with 2-aryl-1-cyano-1-thiazol-2-ylethenes **2** in presence of triethylamine to give the cycloadducts **4**. which were converted to the corresponding pyrazoles **5** by the action of sodium methoxide. The reaction of hydrazonoyl halides **1** and **6** with each of 2-arylidene-2-cyanoethanethioamides **7** and 2-arylhydrazono-2-cyanoethanethioamides **14** in ethanolic triethylamine or ethanolic sodium hydroxide solutions, has been investigated. Structures of all the products were established on the basis of their spectral data and alternative synthesis.

Keywords: Hydrazonoyl halides; thiazoles; 2-arylidene-2-cyanoethanethioamides; arylhydrazono-2-cyanoethanethioamides; pyrazoles

INTRODUCTION

A large number of thiazole derivatives have been found to exhibit pharmacological activity[2–4], specifically as antituberculous[5], bacteriostatic[6] and fungistatic[7] agents. Many thiazoles are frequently present in the tuberculostically active drugs[8] and utilized in the synthesis of cyanine and merocyanine drugs[9,10],in addition to the use to protect light sensitive photographic films from harmful effect of UV radiation[11]. In continuation of our earlier work on the synthesis of thiazoles[12], the results of the reaction of hydrazonoyl halides with 2-aryl-1-cyano-1-thiazol-2-ylethenes, 2-arylidene-2-cyanoethanethioamides and 2-arylhydrazono-2-cyanoethanethioamides are reported,

The reaction of hydrazonoyl chorides **1a-c** with the appropriate **2a-f**, in toluene-triethylamine at room temperature, gave one of two possible regioisomers **3** or **4**, as evidenced by TLC (*cf.* Scheme 1). Structure **4** was assigned to the iso-

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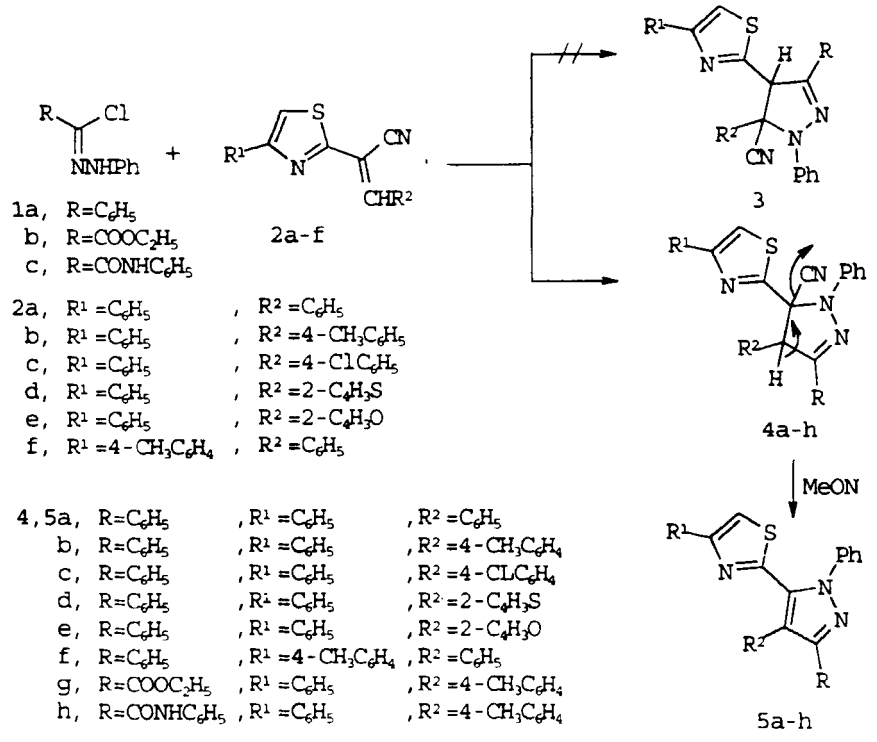
lated cycloadducts on the basis of spectral data. The **IR** spectra of all the products revealed the absence of nitrile absorption, similar to those reported for nitriles activated by oxygen or nitrogen atoms in the α-position[13,14], such as 5-cyano-4,5-dihydropyrazoles. Their ^{1}**H NMR** spectra showed, in each case, a singlet in the region of δ 5.37–5.41. These values seem to be more compatible with the regioisomeric structure **4** rather than **3**, since they are very close to those reported[15,16] for pyrazoline H-4 chemical shifts, δ 5.15–5.3. The chemical shift value for pyrazoline H-5 was reported[17] at δ 6.00 ppm. The products **4a-h** were readily converted into the corresponding pyrazole derivatives **5a-f** upon boiling in sodium methoxide solution. The products were assigned structute **5** which is compatible with their elemental analyses and spectral data. ^{1}**H NMR** spectra of all the products revealed the absence, in each case, of the characteristic signal due to pyrazoline H-4 moiety.

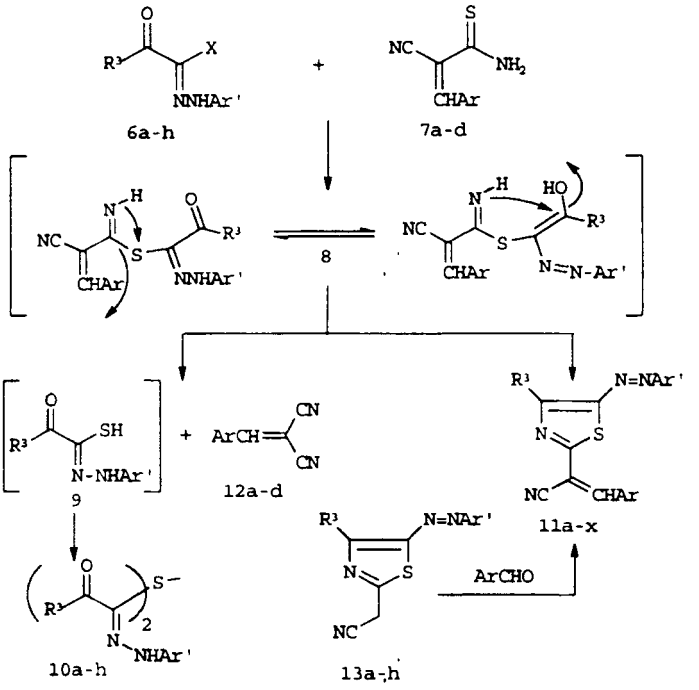


SCHEME 1

As an extension of our work[18] toward the synthesis of thiazole derivatives utilizing the reaction of hydrazonoyl halides with 2-cyanoethanethioamide deriva-

tives, we report herein that the products of such reactions depend on the nature of the base and the type of hydrazonoyl halides used. Treatment of **6a** with **7a** in ethanolic sodium hydroxide (triethylamine) solution afforded a mixture of three products according to TLC (*cf.* Scheme 2). Elemental analyses indicated the products to have molecular formulas $C_{18}H_{18}N_4O_2S$, $C_{20}H_{16}N_4S$ and $C_{11}H_8N_2$, respectively. Mass spectra of the products showed the expected molecular ions at *m/z* 354, 344 and 168, respectively. **IR** (cm^{-1}) spectrum of the first product showed bands at 3150 (NH), 1650 (CO) and 1610 (C=N), while its **^{1}H NMR** (δ) spectrum revealed signals at 2.4(s, 6H, 2 $\underline{CH_3}CO$), 7.1–7.6 (m, 10H, ArH's) and 11.2(s, br, 2H, 2NH). Accordingly the product was assigned structure **10**. Unequivocal support of structure **10** was achieved by the independent synthesis[18] of **10a**. **^{1}H NMR** (δ) spectrum of the second product revealed signals at 2.37(s, 3H, 4-$CH_3C_6H_4$), 2.41(s, 3H, CH_3 -thiazole C-4), 6.90–7.42(m, 9H, ArH's) and 8.88(s, 1H, -$\underline{CH}$=). Its **IR** (cm^{-1}) spectrum showed absorption bands at 2219 (CN), 1601(C=N) and no carbonyl absorption was observed. This product was authentically prepared *via* the reaction of 4-methyl-5-phenylazothiazol-2-yl-acetonitrile (**13a**)[18]with *p*-tolualdehyde in boiling acetic acid – sodium acetate solution (*cf.* Scheme 2). From the above data, this fraction was formulated as 1-(4-methyl-5-phenylazo)thiazole-2'-yl-2-tolylacrylonitrile **(11a)** **^{1}H NMR**(δ) spectrum of the third product **12a** revealed signals at 2.38(s, 3H, CH_3), 7.48–8.14(m. 4H, ArH's) and 8.17(s, 1H, vinyl H). Its **IR** (cm^{-1}) spectrum showed absorption bands at 2240 (CN), 1588 (C=N) and no depression was observed in its mixed melting with l, l-dicyano-2-(4-methylphenyl)ethene (**12a**)[19]. The initial step is believed to involve the formation of the mixed hydrazonoyl imidoyl sulfide **8**, which may arise either from displacement of the hydrazonoyl halogen atom by the thioamide anion or by the thioamide itself (to give a protonated form of the mixed sulfide). Intermediate **8** may lose a molecule of **12a** to give the non-isolable thiohydrazide **9**, which may react with **6a** to afford the hydrazonoyl sulfide **10a**. On the other hand, **8** may lose a molecule of water to afford the thiazole derivative **11a**. Similarly, the hydrazonoyl halides **6b-h** reacted with the appropriate 2-arylidene-1-cyanoethanethioamide derivatives **7a-d**, in ethanolic sodium hydroxide solution, to give, in each case, a mixture of the corresponding hydrazonoyl sulfides **10**, 5-arylazo-4-substituted-thiazoles **11** and 2-aryl-1,1-dicyanoethenes **12**.

Treatment of hydrazonoyl chloride **6a** with 2-phenylhydrazono-2-cyanoethanethioamide **14a**, in ethanolic sodium hydroxide (triethylamine) solution at room temperature, afforded three products which analyzed correctly for $C_{18}H_{18}N_4O_2S$, $C_{18}H_{14}N_6S$ and $C_9H_6N_4$. These products were identified as hydrazonoyl sulfide **10a**, [4-methyl-5-phenylazothiazol-2-yl]phenyl-hydrazonoacetonitrile **16a** and dicyanomethane phenylhydrazone **17a**, respectively (*cf.*



6,10,13

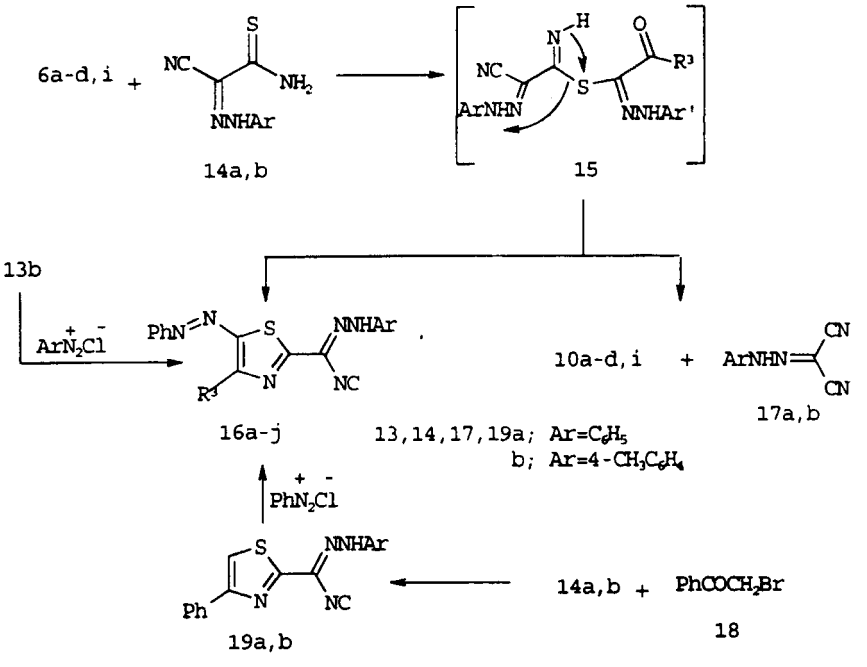
a; R^3 = CH_3 , Ar' = C_6H_5
b; R^3 = C_6H_5 , Ar' = C_6H_5
c; R^3 = 2-C_4H_3S , Ar' = C_6H_5
d; R^3 = 2-$C_{10}H_7$, Ar' = C_6H_5
e; R^3 = CH_3 , Ar' = 4-$CH_3C_6H_4$
f; R^3 = C_6H_5 , Ar' = 4-$CH_3C_6H_4$
g; R^3 = 2-C_4H_3S , Ar' = 4-$CH_3C_6H_4$
h; R^3 = 2-$C_{10}H_7$, Ar' = 4-$CH_3C_6H_4$
i; R^3 = 2-C_4H_3O , Ar' = C_6H_5
j; R^3 = 2-C_4H_3O , Ar' = 4-$CH_3C_6H_4$

7,12a; Ar = 4-$CH_3C_6H_4$
b; Ar = 4-ClC_6H_4
c; Ar = 2-C_4H_3S
d; Ar = 2-C_4H_3O

11a; R^3 = CH_3 , Ar' = C_6H_5 , Ar = 4-CH_3C_6H
b; R^3 = CH_3 , Ar' = C_6H_5 , Ar = 4-ClC_6H_4
c; R^3 = CH_3 , Ar' = C_6H_5 , Ar = 2-C_4H_3S
d; R^3 = CH_3 , Ar' = C_6H_5 , Ar = 2-C_4H_3O
e; R^3 = C_6H_5 , Ar' = C_6H_5 , Ar = 4-CH_3C_6H
f; R^3 = C_6H_5 , Ar' = C_6H_5 , Ar = 4-ClC_6H_4
g; R^3 = C_6H_5 , Ar' = C_6H_5 , Ar = 2-C_4H_3S
h; R^3 = C_6H_5 , AR' = C_6H_5 , Ar = 2-C_4H_3O
i; R^3 = 2-C_4H_3S , Ar' = C_6H_5 , Ar = 4-CH_3C_6H
j; R^3 = 2-C_4H_3S , Ar' = C_6H_5 , Ar = 2-C_4H_3S
k; R^3 = 2-$C_{10}H_7$, Ar' = C_6H_5 , Ar = 4-CH_3C_6H
l; R^3 = 2-$C_{10}H_7$, Ar' = C_6H_5 , Ar = 2-C_4H_3S
m; R^3 = 2-$C_{10}H_7$, Ar' = C_6H_5 , Ar = 2-C_4H_3O
n; R^3 = CH_3 , Ar' = 4-$CH_3C_6H_4$, Ar = 4-CH_3C_6H
o; R^3 = CH_3 , Ar' = 4-$CH_3C_6H_4$, Ar = 4-ClC_6H_4
p; R^3 = CH_3 , Ar' = 4-$CH_3C_6H_4$, Ar = 2-C_4H_3S
q; R^3 = CH_3 , Ar' = 4-$CH_3C_6H_4$, Ar = 2-C_4H_3O
r; R^3 = C_6H_5 , Ar' = 4-$CH_3C_6H_4$, Ar = 4-CH_3C_6H
s; R^3 = C_6H_5 , Ar' = 4-$CH_3C_6H_4$, Ar = 2-C_4H_3S
t; R^3 = C_6H_5 , Ar' = 4-$CH_3C_6H_4$, Ar = 2-C_4H_3O
u; R^3 = 2-C_4H_3S , Ar' = 4-$CH_3C_6H_4$, Ar = 4-CH_3C_6H
v; R^3 = 2-$C_{10}H_7$, Ar' = 4-$CH_3C_6H_4$, Ar = 4-CH_3C_6H
w; R^3 = 2-$C_{10}H_7$, Ar' = 4-$CH_3C_6H_4$, Ar = 2-C_4H_3S
x; R^3 = 2-$C_{10}H_7$, Ar' = 4-$CH_3C_6H_4$, Ar = 2-C_4H_3O

SCHEME 2

Scheme 3). Structure **16** was established on the basis ofelemental analysis and spectral data. Thus, 1**H NMR** (δ), spectrum of **16a** showed signals at 2.90(s, 3H, CH_3), 7.18–7,90(m, 10H, ArH's) and 12.32(s, br, 1H, NH), while its **IR** (cm^{-1}) spectrum revealed absorption bands at 3247 (NH), 2206 (CN), 1601 (C=N) and the carbonyl absorption band was absent.



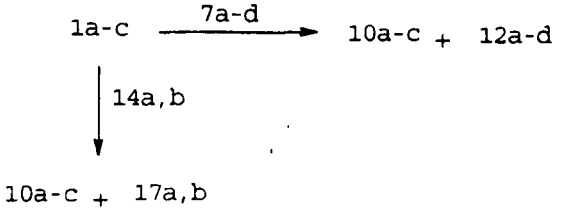
16a, R^3 = CH_3, Ar = C_6H_5
b, R^3 = C_6H_5, Ar = C_6H_5
c, R^3 = 2-C_4H_3S, Ar = C_6H_5
d, R^3 = 2-C_4H_3O, Ar = C_6H_5
e, R^3 = 2-$C_{10}H_7$, Ar = C_6H_5
16f, R^3 = CH_3, Ar = 4-$CH_3C_6H_4$
g, R^3 = C_6H_5, Ar = 4-$CH_3C_6H_4$
h, R^3 = 2-C_4H_3S, Ar = 4-$CH_3C_6H_4$
i, R^3 = 2-C_4H_3O, Ar = 4-$CH_3C_6H_4$
j, R^3 = 2-$C_{10}H_7$, Ar = 4-$CH_3C_6H_4$

SCHEME 3

Compound **16a** was readily obtained by treatment of [4-methyl-5-phenylazothiazol-2-yl]acetonitrile **13a** with benzenediazonium chloride in ethanolic sodium hydroxide solution or [4-methylthiazol-2-yl] phenylhydrazonoacetonitrile[20,21] **19a** with benzenediazonium chloride in ethanolic sodium hydroxide solution. Similarly, treatment of **6b-d,i** with the appropriate 2-arylhydrazono-2-cyanoethanethioamide **14a,b,** in ethanolic sodium hydroxide (triethylamine) solution, afforded, in each case, a mixture of the corre-

sponding hydrazonoyl sulfide **10**, 5-arylazo-4-substitutedthiazoles **16** and dicyanomethane arylhydrazone **17** (*cf.* Scheme 3).

In contrast to the above results, tratment of the hydrazonoyl chlorides **1a-c** with 2-arylidene-2-cyanoethanethioamides **7a-d** or 2-phenylhydrazono-2-cyanoethanethioamides **14a,b,** in ethanolic triethylamine solution or ethanolic sodium hydroxide solution afforded the hydrazonoyl sulfides **10a-c** (*cf.* Scheme 4).



SCHEME 4

It is worth mentioning that the reaction of hydrazonoyl chlorides **1a-c** with each of 2-arylidene-2-cyanoethanethioamides **7a-d** or 2-arylhydrazono-2-cyanoethanethioamides **14a,b,** in ethanolic triethylamine or sodium hydroxide solution afforded the hydrazonoyl sulfides only in good yields. In case of the reaction of α-ketohydrazonoyl halides **6a-h** with **7a-d** or **14a,b**, the yield of the products depends on the base used. Thus, in case of triethylamine as a base, the major products was the hydrazonoyl sulfide (70–75%) with the thiazole derivative as the minor products (15–20%). Using sodium hydroxide as a base gave the thiazole derivatives as the major products (70–80%) and hydrazonoyl sulfides as the minor products (10–15%).

EXPERIMENTAL

All melting points were uncorrected. IR spectra were recorded (KBr) on a Shimadzu FT-IR 8201 PC spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer and chemical shifts were expressed in δ units using TMS as internal reference. Ms spectra were recorded on a GC-MS QP1000 EX Shimadzu, Japan. Elemental analyses were carried out at the Microanalytical Center of the University of Cairo, Giza, Egypt. Compounds **2a**[20], **10a,b**[18], **13a**[18],**b**[18],**c**[22],**e**[18] and **19a**[20,21] were prepared as previously described.

Synthesis of 2-aryl-1-cyano-1-thiazol-2-ylethene 2b-f

To a stirred mixture of 4-phenylthiazol-2-yl-acetonitrile[20] (lg, 5 mmol) and the appropriate aldehyde (5 mmol) in ethanol (20 ml), few drops of sodium ethoxide solution were added at room temperature. Stirring was continued for 1h. The resulting solid was collected, washed with water and recrystallized. The mp and spectral data for compounds **2b-f** are listed in Table I.

TABLE I Characterization and Spectroscopic data of the newly synthesized compounds

Compd.	*M.P°C*	δ
2b	135–6[a]	2.34(s, 3H, CH_3) and 7.26–7.89(m, 10H, ArH's and thiazole H-5)
2c	123–5[h]	7,18–7.78(m, ArH's and thiazole H-5)
2d	145–6[a]	7.03–7.64(m, ArH's, thiophene H's and thiazole H-5)
2e	165–6[a]	6.30–7.62(m, ArH's, furan H's and thiazole H-5)
2f	145[c]	2.31(s, 3H, CH_3) and 7.24–7.91(m, 10H, ArH's and thiazole H-5)
4a	88–90[a]	5.40(s, 1H, pyrazoline H-4) and 7.13–7.99(m, 21H, ArH's and thiazole H-5)
4b	88–89[a]	2.35(s, 3H, CH_3); 5.35(s, 1H, pyrazoline H-4) and 7.03–7.96(m, 20H, ArH's and thiazole H-5)
4c	86–88[a]	5.41(s, 1H, pyrazoline H-4) and 7.25–7.90(m, 20H, ArH's and thiazole H-5)
4d	125–7[a]	5.38(s, 1H, pyrazoline H-4) and 7.05–7.90(m, 19H, ArH's, thiophene H's and thiazole H-5)
4e	110–12[a]	5.37(s, 1H, pyrazoline H-4) and 6.52–7.90(m, 19H, ArH's, furan H's and thiazole H-5)
4f	100–102[a]	2.36(s, 3H, CH_3); 5.37(s, 1H, pyrazoline H-4) and 7.23–7.97(m, 20H, ArH's and thiazole H-5)
4g	88–90[a]	1.17(t, 3H, CH_2-$\underline{CH_3}$) ; 2.32(s, 3H, CH_3), 4.11(q, 2H, $\underline{CH_2}$-CH_3) ; 5.41(s, 1H, pyrazoline H-4) and 7.28–7.99(m, 15H, ArH's and thiazole H-5)
4h	106–108[a]	2.36(s, 3H, CH_3) ; 5.42(s, 1H, pyrazoline H-4); 7.22–7.93(m, 20H, ArH's and thiazole H-5) and 8.55(s, br, 1H, NH)
5a	194–5[c]	7.18–7.79(m, ArH's and thiazole H-5)
5b	201–3[c]	2.40(s, 3H, CH_3) and 7.03–7.96(m, 20H, ArH's and thiazole H-5)
5c	199–200[c]	7.25–7.90(m, ArH's and thiazole H-5)
5d	180–2[c]	7.0–7.69(m, ArH's, thiophene H's and thiazole H-5)
5e	151–2[c]	6.32–7.70(m, ArH's, furan H's and thiazole H-5)
5f	205–6[c]	2.40(s, 3H, CH_3) and 7.17–7.64(m, 20H, ArH's and thiazole H-5)
5g	192–4[c]	1.19(t, 3H, CH_2-$\underline{CH_3}$); 2.38(s, 3H, CH_3); 4.17(q, 2H, $\underline{CH_2}$-CH_3) and 7.31–8.05(m, 15H, ArH's and thiazole H-5)
5h	253–4[c]	2.43(s, 3H, CH_3) ; 7.26–7.99(m, 20H, ArH's and thiazole H-5) and 8.25(s, br, 1H, NH)

Compd.	*M.P°C*	δ
10c	200–202[c]	7.11–8.15(m, 16H, thiophene and ArH's) and 12.14(s, br, 2H, NH)
10d	231–3[a]	6.62–7.77(m, 16H, furan and ArH's) and 12.09(s, br, 2H, NH)
10e	240–2[d]	7.19–8.31(m, 24H, ArH's) and 12.26 (s, br, 2H, NH)
10f	207–9[e]	2.34(s, 6H, $2CH_3$); 2.53(s, 6H, $2CH_3CO$); 7.18,7.35(2d, *J* 8Hz, 8H, ArH's) and 11.55(s, br, 2H, NH)
10g	212–4[c]	2.33(s, 6H, $2CH_3$); 7.14,7.95(m, 18H, ArH's) and 12.15(s, br, 2H, NH)
10h	215–17[c]	2.36(s, 6H, $2CH_3$); 7.14–8.20(m, 14H, thiophene and ArH's) and 12.12(s, br, 2H, NH)
10i	167–8[b]	2.35(s, 6H, $2CH_3$); 6.59–7.72(m, 14H, furan and ArH's) and 12.06(s, br, 2H, NH)
10j	221–2[c]	2.33(s, 6H, $2CH_3$); 7.14–8.55(m, 22H, ArH's) and 12.30 (s, br, 2H, NH)
11a	223–5[b]	2.37(s, 3H, CH_3); 2.41(s, 3H, thiazole4-CH_3); 7.15–7.89(m, 9H, ArH's) and 8.88(s, 1H, CH)
11b	203–5[b]	2.43(s, 3H, thiazole 4-CH_3); 7.21–7.83(m, 9H, ArH's) and 8.86(s, 1H, CH)
11c	173–5[a]	2.46(s, 3H, thiazole 4-CH_3) ; 7.01–7.90(m, 8H, thiophene and ArH's) and 8.82(s, 1H, CH)
11d	230–2[a]	2.40(s, 3H, thiazole 4-CH_3); 6.48–7.71(m, 8H, furan and ArH's) and 8.76(s, 1H, CH)
11e	150–2[a]	2.33(s, 3H, CH_3); 7.23–7.86(m, 14H, ArH's) and 8.80(s, 1H, CH)
11f	153–5[a]	7.20–7.90(m, 14H, ArH's) and 8.27(s, 1H, CH)
11g	175–7[a]	7.06–7.88(m, 13H, thiophene and ArH's) and 8.92(s, 1H, CH)
11h	200–202[a]	6.37–7.80(m, 13H, furan and ArH's) and 8.79(s, 1H, CH)
11i	190–2[a]	2.31(s, 3H, CH_3) ; 7.10–7.93(m, 12H, thiophene and ArH's) and 8.87(s, 1H, CH)
11j	185–7[a]	7.01–7.71(m, 11H, thiophene and ArH's) and 8.90(s, 1H, CH)
11k	150–1[c]	2.34(s, 3H, CH_3), 7.33–7.96(m, 16H, ArH's) and 8.89(s, 1H, CH)
11l	190–1[a]	7.02–7.79(m, 15H, thiophene and ArH's) and 8.91(s, 1H, CH)
11m	185–6[a]	6.46–7.66(m, 15H, furan and ArH's) and 8.76(s, 1H, CH)
11n	170–1[a]	2.34,2.38(2s, 6H, $2CH_3$); 2.45(s, 3H, thiazole 4-CH3); 7.16–7.93 (m, 8H, ArH's) and 8.77(s, 1H, CH)
11o	165–7[a]	2.33(s, 3H, CH_3); 2.41(s, 3H, thiazole 4-CH_3); 7.19–7.78 (m, 8H, ArH's) and 8.78(s, 1H, CH)
11p	193–5[a]	2.41(s, 3H, CH_3); 2.44(s, 3H, thiazole 4-CH_3); 7.08–7.91(m, 8H, thiophene and ArH's) and 8.82(s, 1H, CH)
11q	263–5[a]	2.42(s, 3H, CH_3); 2.49(s, 3H, thiazole 4-CH_3); 6.39–7.69(m, 8H, furan and ArH's) and 8.84(s, 1H, CH)
11r	148–50[a]	2.36,2.44(2s, 6H, $2CH_3$); 7.14–7.96 (m, 13H, ArH's) and 8.85(s, 1H, CH)
11s	228–30[a]	2.44(s, 3H, CH_3); 7.15–7.89(m, 12H, thiophene and ArH's) and 8.75(s, 1H, CH)
11t	195–7[a]	2.46(s, 3H, CH_3); 6.51–7.83(m, 12H, furan and ArH's) and 8.79(s, 1H, CH)

Compd.	*M.P°C*	δ
11u	190–1[a]	2.36, 2.44(2s, 6H, $2CH_3$); 7.09–7.94(m, 11H, thiophene and ArH's) and 8.93(s, 1H, CH)
11v	180–2[a]	2.34, 2.41(2s, 6H, $2CH_3$); 7.25–7.84(m, 15H, ArH's) and 8.86(s, 1H, CH)
11w	165–7[a]	2.46(s, 3H, CH_3); 7.12–7.70(m, 14H, thiophene and ArH's) and 8.77(s, 1H, CH)
11x	155–7[a]	2.42(s, 3H, CH_3); 6.33–7.78(m, 14H, furan and ArH's) and 8.75(s, 1H, CH)
13d	170–2[c]	3.61(s, 2H, CH_2); 7.22–7.95(m, 12H, ArH's)
13f	210–2[c]	2.41(s, 3H, CH_3); 3.60(s, 2H, CH_2); 7.20–7.87(m, 9H, ArH's)
13g	240–2[c]	2.45(s, 3H, CH_3); 3.63(s, 2H, CH_2); and 7.03–7.76(m, 7H, thiophene and ArH's)
13h	180–1[c]	2.44(s, 3H, CH_3); 3.62(s, 2H, CH_2); and 7.29–7.86(m, 11H, ArH's)
13i	168–70[c]	3.59(s, 2H, CH_2); and 6.43–7.75(m, 8H, furan and ArH's)
13j	208–210[c]	2.40(s, 3H, CH_3); 3.58(s, 2H, CH_2); and 6.41–7.69(m, 7H, furan and ArH's)
16a	225–6[e]	2.90(s, 3H, thiazole 4-CH_3); 7.18–7.90(m, 10H, ArH's) and 12.32(s, br, 1H, NH)
16b	235–6[b]	7.15–7.80(m, 15H, ArH's) and 12.18(s, br, 1H, NH)
16c	220–2[b]	7.09–7.76(m, 13H, thiophene and ArH's) and 12.04(s, br, 1H, NH)
16d	195–7[b]	6.63–7.85(m, 13H, furan and ArH's) and 12.09(s, br, 1H, NH)
16e	225–7[e]	7.13–7.91(m, 17H, ArH's) and 12.11(s, br, 1H, NH)
16f	235–6[e]	2.36(s, 3H, CH_3); 2.90(s, 3H, thiazole 4-CH_3); 7.18–7.90(m, 9H, ArH's) and 12.10(s, br, 1H, NH)
16g	252–3[e]	2.39(s, 3H, CH_3); 7.20–7.88(m, 14H, ArH's) and 12.17(s, br, 1H, NH)
16h	220–3[a]	2.37(s, 3H, CH_3); 7.13–7.74(m, 12H, thiophene and ArH's) and 12.14(s, br, 1H, NH)
16i	225–7[e]	2.38(s, 3H, CH_3); 6.70–7.94(m, 12H, furan and ArH's) and 12.16(s, br, 1H, NH)
16j	205–7[a]	2.40(s, 3H, CH_3); 7.23–7.98(m, 16H, ArH's) and 12.08(s, br, 1H, NH)
19b	165–6[a]	2.41(s, 3H, CH_3); 7.23–7.81(m, 10H, ArH's and thiazole H-5) and 12.16(s, br, 1H, NH)

Solvent of Crystallization: [a] EtOH, [b] EtoH/Dioxane, [c] HOAc, [d] DMF, [e] Dioxane
Microanalytical data are satisfactory : ± 0.2 %.

Synthesis of the pyrazoline derivatives 4a-h

To a stirred mixture of the thiazole derivatives **2a-f** (5 mmol) and the appropriate hydrazonoyl chlorides **1a-c** (5 mmol) in dry toluene (25 ml), at room temperature, was added triethylamine (0.7 ml, 5 mmol). Stirring was continued for 4 h, the formed triethylamine hydrochloride was filtered off and the reaction mixture was evaporated till dryness. The semisolid material was triturated with petroleum

ether (40–60°) and the resulting solid was collected and recrystallized from ethanol to give compounds **4a-h** in 60–80% yields.

Synthesis of the pyrazole derivatives 5a-h

To a boiling solution of the appropriate **4a-h** (5 mmol) in methanol (20 ml) was added NaOMe (5 mmol) dropwise. A color discharge occurs and a white precipitate was immediately formed which was collected and recrystallized from acetic acid to give compounds **5a-h** in almost quantitative yields.

Reaction of hydrazonoyl halides 6a-h with 7a-d and 14a,b

To a stirred mixture of eqimolar amounts of each of the hydrazonoyl halides **6a-h**(10 mmol) and the appropriate 2-arylidene-2-cyanoethanethioamides **7a-d** or 2-arylhydrazono-2-cyanoethane-thioamides **14a,b** (10 mmol) in ethanol (30 ml) was added triethylamine (1.4 ml, 10 mmol) or aqueous sodium hydroxide solution (0.4g NaOH in 5 ml of H_2O) at room temperature. A yellowish solid was formed within 15 min., which was collected, washed with water and recrystallized to give **10a-i** (70–75% in case of TEA and 10–15% in case of NaOH). The remaining reaction mixture was further stirred for 2 h where a solid was formed, collected, washed with water and recrystallized to afford **11a-x** and **16a-j** (15–20% in case of TEA and 60–80% in case of NaOH). Dilution of the mother liquor with cold water gave a solid which upon crystallization afforded the corresponding 2-aryl-1, I-dicyanoethene **12a-d** (in case of the reaction with **7a-d**) and 1.1-dicyanomethane arylhydrazone **17a,b** (in case of the reaction with **14a-d**). The analytical and spectral data for compounds **10a-i**, **11a-x** and **16a-j** are listed in Table I.

Synthesis of 1-(5-arylazo-4-substituted) thizole-2'-yl-2-substitutedacrylonitrile derivatives 11a-x; Alternative method

A solution of **13a-h** (5 mmol) and the appropriate aldehyde (5 mmol) in glacial acetic acid (30 ml) containing fused sodium acetate (0.4g, 5 mmol) was heated under reflux for 2 h. The reaction mixture was cooled, poured onto ice and the resulting solid (obtained in almost quantitative yields) was collected and crystallized from ethanol to give products (**11a-x**) identical to those obtained above.

Synthesis of 5-arylazo4-substituted-thiazol-2-yl-acetonitrile derivatives 13a-h

To a stirred solution of the appropriate hydrazonoyl halides **6a-h** (5 mmol) and 2-cyanoethanethioamide (0.5g, 5 mmol) in ethanol (20 ml) was added an aqueous sodium hydroxide solution (0.2g NaOH in 5 ml of H_2O) at room temperature. Stirring was continued for 2 h, the formed solid was collected, washed with water and crystallized from acetic acid to give **13a-h** in 55–75% yields (*cf.* Table I).

Synthesis of [4-aryl-5-phenylazothiazol-2-yl]arylhydrazonoacetonitrile; 16b,g Alternative methods

Method A

An aqueous solution of aryldiazonium chloride (5 mmol) was added dropwise to a stirred solution of **13a** (1.5g, 5 mmol) in ethanolic sodium acetate solution (0.8g, 10 mmol / 20 ml) at 0°C. The formed solid was collected, washed with water and crystallized to give **16b,g**, (in 68 and 75% yields).

Method B

An aqueous solution of benzenediazonium chloride (5 mmol) was added dropwise to a stirred solution of **19a,b** (5 mmol) in ethanolic sodium hydroxide (0.2g, 5 mmol / 20 ml) at 0°C. The formed solid was collected, washed with water and crystallized from acetic acid to give **16b,g**, (in 53 and 55% yields) respectively.

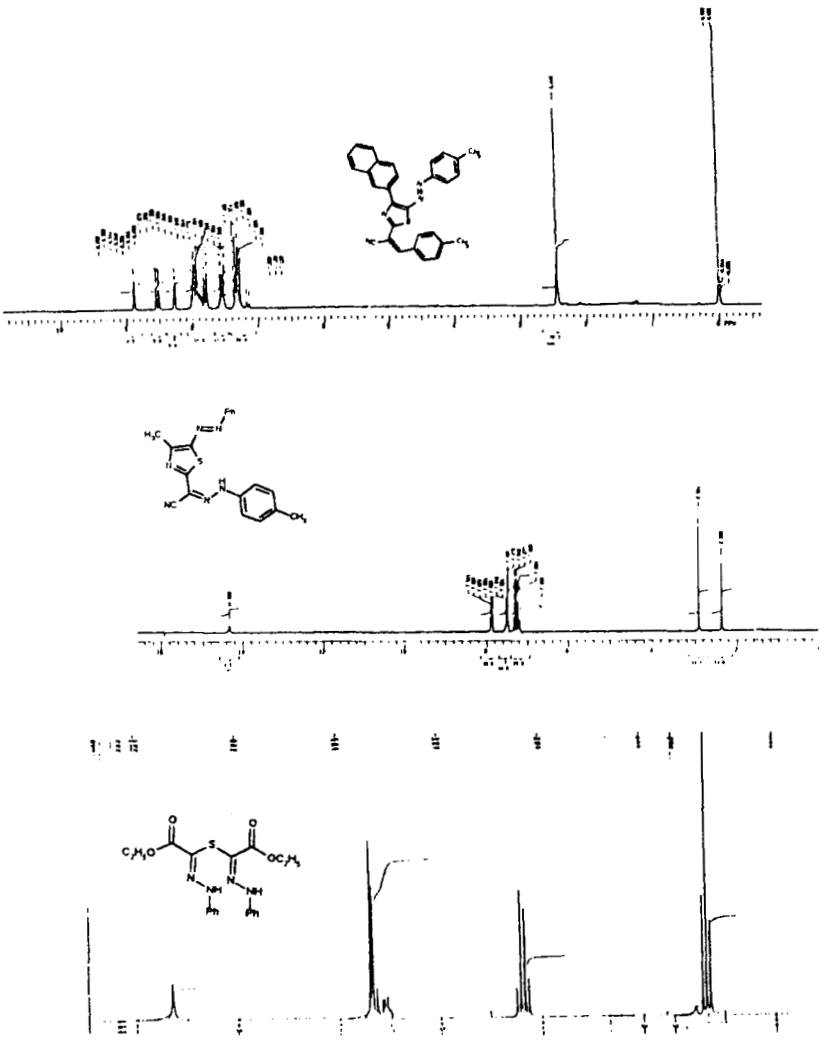
Synthesis of [4-phenylthiazol-2-yl]arylhydrazonoacetonitrile derivatives; 19a,b

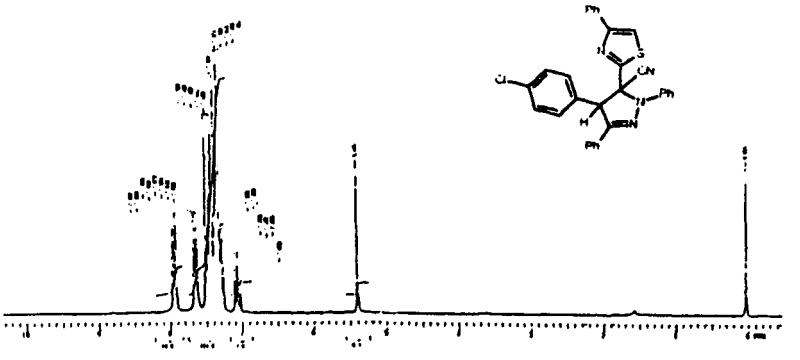
Method A

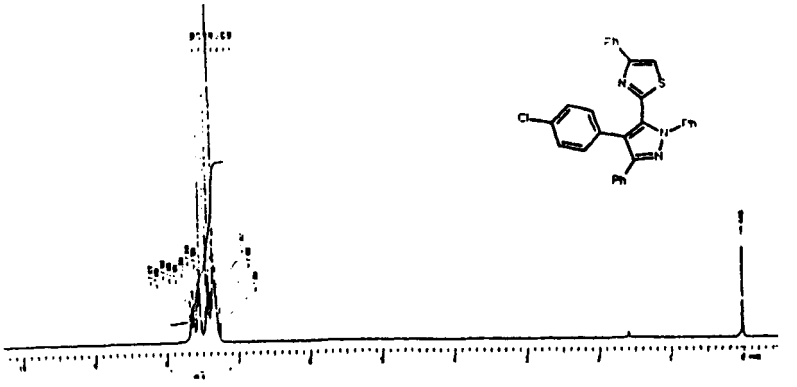
A mixture of ω-bromoacetophenone (1g, 5 mmol) and the appropriate 2–arylhydrazono-2-cyanoethanethioamide **14a,b** (5 mmo) in ethanol (25 ml) was heated under reflux for 30 min. and then allowed to cool. The reaction mixture was poured over ice and few drops of ammonium hydroxide were added. The so formed solid was collected, washed with water and recrysrallized from ethanol to give **19a,b**, in 72 and 70% yields, respectively.

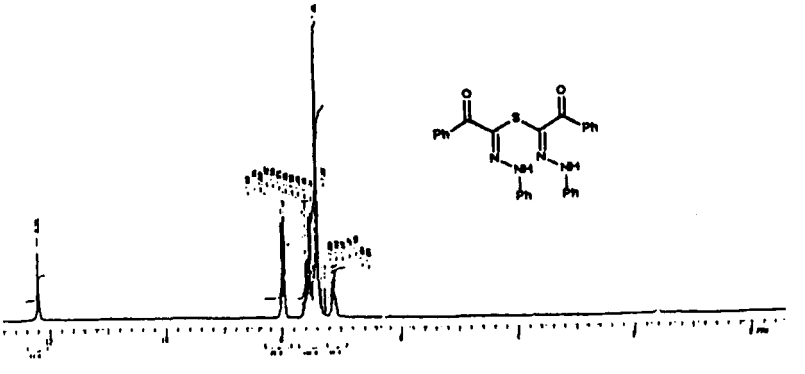
Method B

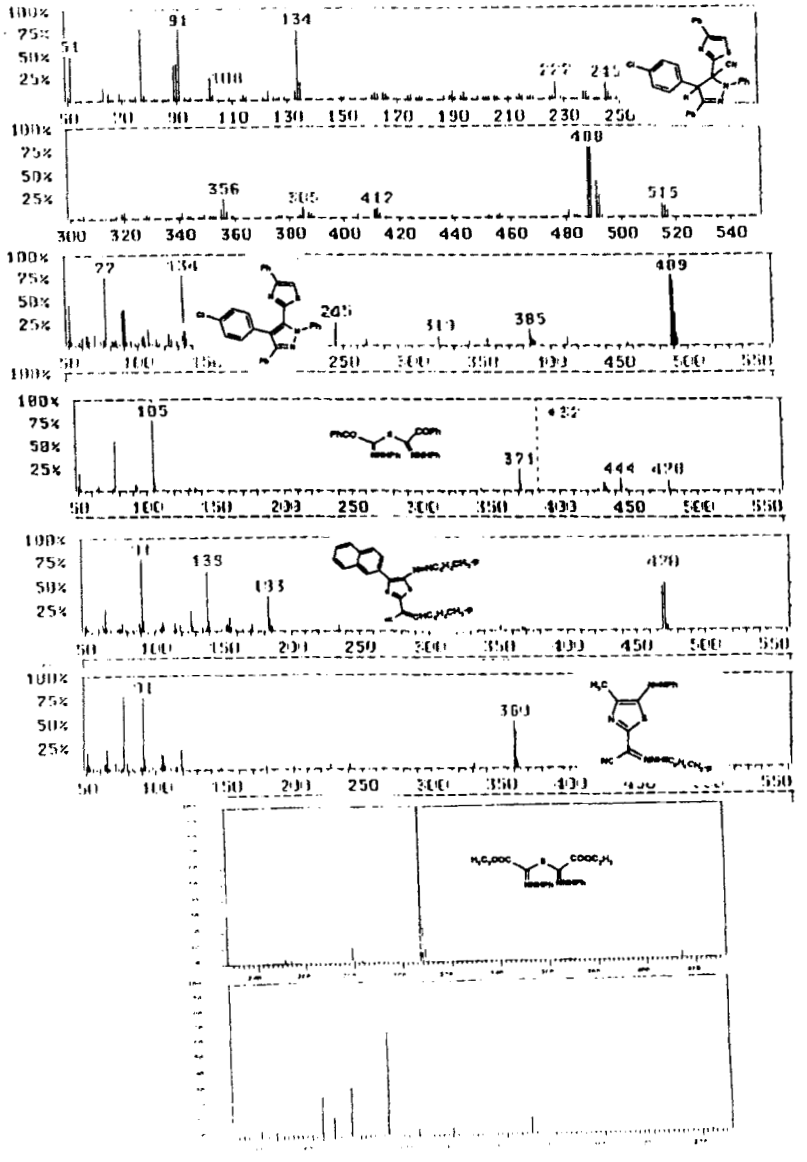
An aqueous solution of benzenediazonium chloride or *p*-toluidinediazonium chloride (5 mmol) was added dropwise to a stirred solution of (4-phenylthiazol-2-yl)acetonitrile (1g, 5 mmol) in ethanolic sodium acetate (0.8g, 10 mmol / 20 ml) at 0°C. The formed solid was collected, washed with water and crystallized from ethanol to give identical products to **19a,b**, in 65 and 72% yields, respectively.











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