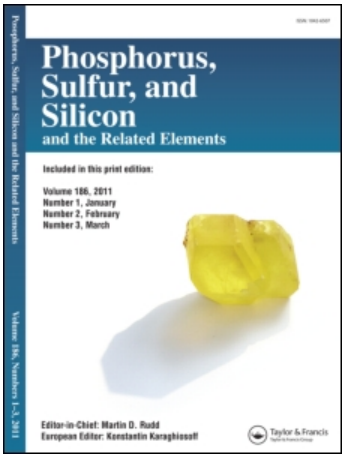

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Synthesis of New Polyfused Thienopyrimidine, Thienopyridine, Thienothiazine, Thienoxazine, and Thienodiazepine Derivatives

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SYNTHESIS OF NEW POLYFUSED THIENOPYRIMIDINE, THIENOPYRIDINE, THIENOTHIAZINE, THIENOXAZINE, AND THIENODIAZEPINE DERIVATIVES

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3,4-Diamino-2-carbethoxy-5-cyanothieno(2,3-b)thiophene (1) was treated with ethylenediamine to afford 3,4-diamino-2,5-bi[2-(4,5-dihydro-1H-imidazole-2-yl]-thieno(2,3-b)thiophene ***2****, which in turn was treated with chloroacety chloride to give bis[imidazolothieno diazepine] derivative* ***3*** *and with each of p-chlorobenzaldehyde, triethyl orthoformate, and Lawesson's reagent (LR) to yield bis[imidazolothienopyrimidine] derivatives* ***4–6****. Compound* ***1*** *was subjected to Mannich reaction to afford Mannich bases* ***7*** *and* ***8a,b****. The later products (****8a,b****) were treated with malononitrile yielding* ***9a*** *and* ***9b****. Treatment of compound 1 with* CS_2*, NaOH and* CH_3I *produced compounds* ***10*** *and* ***11****. The reaction of compound* ***10*** *with each of o-aminothiphenal, o-phenylenediamen, hydrazine hydrate, and phenylhydrazine afforded compounds* ***12a,b****,* ***13a,b****. Compound* ***1*** *was allowed to react with* CS_2*, phenyl (benzoyl)isothiocyanate and phenylisocyanate to get the described products* ***14–19****, respectively. On reacting compound* ***1*** *with ethylcyanoacetate thieno(2,3-b)pyridine derivative* ***21*** *was obtained through the intermediate* ***20****. Finally, compound* ***1*** *was treated with malononitrile to yield compound* ***22****.*

Keywords: Thieno(2,3-b)thiophene; thienoimidazolino(1,4)diazepine; thienoimidazolinopyrimidine; thienopyridine; PTC

Reviewing literature showed that thiophenes are of interest for medicinal chemistry. Many thiophenes and polyfused thiophene derivatives have biological and farmacological activities.[1–6] Since 1950 several synthetic methods for thieno[2,3-d]thiophenes have been investigated and developed.[7–11] These compounds have been studied for different purposes in the pharmaceutical field and tested as potential antiviral,[12]

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antibiotic,[13] antiglaucoma,[14] analgesic, and antipyretic drugs.[15] Regarding with the growing interest of thieno[2,3-b] thiophenes, so this work aims to prepare a new series of these compounds starting with 3,4-dimino-2-carbethoxy-5-cyano(2,3-b) thiophene.[9]

RESULTS AND DISCUSSION

The target compound 3,4-diamino-2-carbethoxy-5-cyanothieno(2,3-b)thiophene[9] (**1**) was treated with ethylene diamine[16,17] in 1:5 molar ratio of CS_2/DMF mixtuer to yield 3,4-diamino-2,5-bi[2-(4,5-dihydro-1H-imidazole-2-yl]thieno-(2,3-b)thiophene (**2**). The reaction mechanism was postutaled to proceed through a nucleophilic attack of the ethylene diamene's NH_2 groups at each of the olefinic CN group[16,17] with the elimination of NH_3 molecule and at the carbethoxy carbonyl group with elimination of H_2O and EtOH molecules to form compound **2**. Treatment of this compound with chloroacetyl chloride yielded bi[4,5-dihydroimidazolo(2,3-d)1,4-diazepino]thieno(2,3-b)thiophene derivative **3**. Bis-[4,5-dihydroimidazolo-(2,3-c)pyrimidino]thieno(2,3-b)thiophene derivatives **4** and **5** were obtained by cyclizing compound **2** either with p-chlorobenzaldehyde in refluxing DMF through the elimination of H_2O molecules or with triethylorthoformate in boiling acetic acid via the elimination of EtOH molecules, respectively (Scheme 1, Table I).

According to our previous work in (LR) ring closure reactions with substrates containing different functional groups[18] as well as

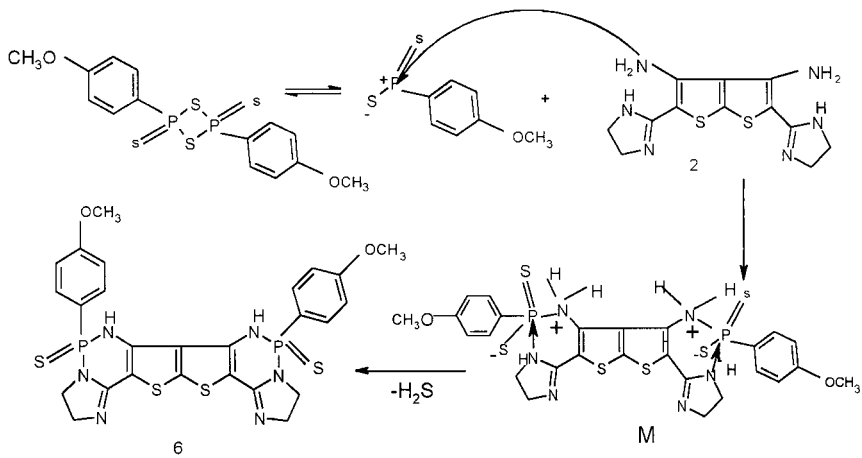
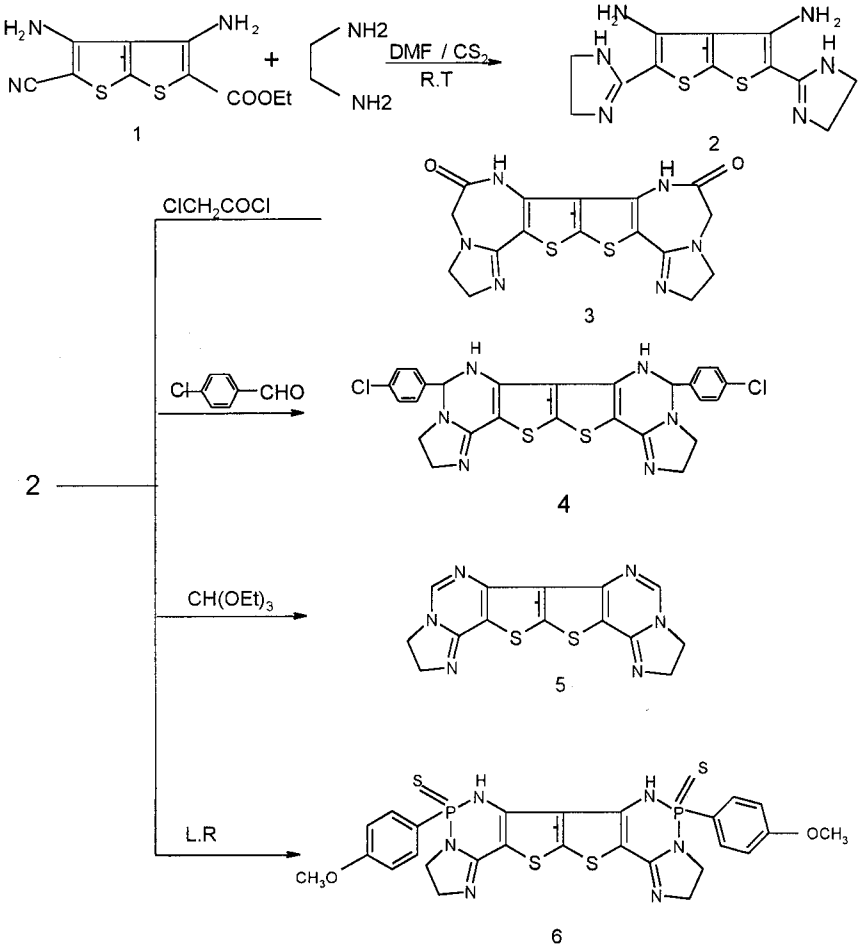


FIGURE 1



SCHEME 1

others[19], compound **2** was cyclized with lewesson's reagent (LR) in refluxing DMF through the elimination of H_2S molecules to afford bi[4,5-dihydro-imidazolo(1,2-c)(1,3,2)diazaphosphinino]thieno(2,3-b)thiophene (**6**) (Scheme 1, Table I). The suggested mechanism for this reaction is a nucleophilic attack by the NH_2 group at LR to give the intermediate M, which underwent interamolecular cyclization via the elimination of H_2S molecules to give compound **6** Figure 1.

When compound **1** was subjected to the Mannich reaction by using p-nitroaniline, morpholine, or piperidine in presence of formaline, the corresponding Mannich bases **7–8a**,**b** were obtained. Each of the two

TABLE I Analytical and Spectral Data of the Prepared Compounds

Compound no.	m.p.[a] (crys. solvent)	Yield (%)	$M_F/(M_w)$	Analytical data calc. (found)[b] (%) C	H	N	S	IR (KBr) ν (cm^{-1})[c]	δ(ppm) ^{1}H-NMR (DMSO-d_6)[d]
2	250 Dioxane	80	$C_{12}H_{14}N_6S_2$ (242.38)	59.46 59.37	5.82 5.70	8.26 8.32	26.45 26.31	3425, 3353,3300, 3274, 3172 ($2NH_2$, 2NH); 2979 (CH); 1610 (C═N)	7.50-6.90 (br, 2H, 2NH); 6.70-6.00 (br, 4H, $2NH_2$); 2.65-2.30 (t, 4H, $2CH_2N$═), 1.30-0.90 (t, 4H, $2CH_2N$)
3	251 DMF/H_2O	76	$C_{16}H_{14}N_6S_2O_2$ (306.35)	62.73 62.84	4.61 4.74	27.43 27.31	20.93 20.88	3360 (2NH); 2924 (CH); 1654 (2C═O), 1600 (C═N)	6.20 (s, 2H, 2NH); 2.70 (s, 4H, $2CH_2$); 1.65-1.40 (t, 4H, $2CH_2$); 1.38-1.10 (t, 4H, $2CH_2$)
4	204 DMF/H_2O	65	$C_{26}H_2ON_6S_2Cl_2$ (551.62)	56.61 56.80	3.65 3.54	15.23 15.12	11.63 11.48	3350 (2NH); 3166, 2950 (CH); 1600 (C═N), 836 (C-Cl)	8.35 (s, 2H, 2NH); 7.75-6.50 (m, 8H, arom.); 2.75-2.35 (t, 4H, $2CH_2$), 1.70-1.30 (t, 4H, $2CH_2$); 3.2 (s, 2H, 2CH)
5	>300 Acetic acid	61	$C_{14}H_{10}N_6S_2$ (326.40)	51.52 51.62	3.09 3.00	25.75 25.68	19.65 19.71	2980, 2878 (CH); 1600 (C═N)	3.42-2.80 (t, 4H, $2CH_2$); 2.67-2.30 (t, 4H, $2CH_2$), 1.80 (s, 2H, 2CH)
6	185 DMF/H_2O	69	$C_{26}H_{24}N_6S_4O_2P_2$ (642.72)	48.59 48.68	3.76 3.83	13.06 13.00	19.96 20.10	3323 (2NH); 3145, 2960 (CH), 1135 (2C═S)	7.71-6.30 (m, 8H, arom.); 6.10 (s, 2H, 2HN); 3.9 (s, 6H, $2CH_3$); 2.80-2.62 (t, 4H, $2CH_2$); 1.55-1.20 (t, 4H, $2CH_2$)
7	180 DMF/H_2O	85	$C_{24}H_{21}N_7S_2O_6$ (567.61)	50.97 50.88	3.73 3.84	17.27 17.15	11.30 11.21	3340, 3250 (4NH); 3100, 2955 (CH), 2200 (CN), 1670 (C═O); 1520, 1340 (NO_2)	7.52-6.68 (m, 4H, arom.); 6.50-5.75 (m, 4H, arom.); 4.68-4.32 (q, 2H, CH_2 ester); 4.15 (s, 2H, CH_2); 3.80-3.00 (br, 4H, 4NH); 2.30 (s, 2H, CH_2); 1.38-1.00 (t, 3H, CH_3)
8a	200 DMF/H_2O	79	$C_{20}H_{27}N_5S_2O_4$ (465.60)	51.59 51.67	5.85 5.93	15.04 15.00	13.77 13.86	3349 (2NH); 2967 (CH); 2194 (CN); 1652 (C═O)	4.80-4.35 (q, 2H, CH_2-aster), 4.25 (s, 4H, $2CH_2$), 4.10-3.65 (t, 8H, $2CH_2OCH_2$); 3.30-2.80 (t, 8H, $2CH_2NCH_2$); 2.3 (S, 2H, 2NH); 1.32 (t,3H, CH_3)
8b	230 DMF/H_2O	73	$C_{22}H_{31}N_5S_2O_2$ (461.65)	57.24 57.35	6.77 6.28	15.17 15.26	13.89 13.79	3317, 3171 (2NH); 2204 (CN); 1671 (C═O)	7.35-6.85 (br, 1H, NH); 6.32-6.00 (br, 1H, NH); 4.88-4.25 (m, 12H, $6CH_2$); 4.10-3.68 (q, 2H, CH_2 ester); 3.61-3.00 (t,8H,$2CH_2NCH_2$); 2.50 (s, 4H, $2CH_2$); 1.85-0.90 (t, 3H, CH_3)
9a	>300 DMF/H_2O	70	$C_{24}H_{25}N_9S_2O_3$ (551.65)	52.26 52.39	4.57 4.60	22.85 22.94	11.63 11.60	3424, 3321,3280, 3128, 3028 ($2NH_2$, NH); 2851 (CH); 2197 (CN); 1669 (C═O)	7.32 (S, 1H═NH); 5.10-4.22 (br, 4H, $2NH_2$); 3.85-3.31 (t, 8H, $2CH_2OCH_2$); 2.40 (s, 4H, $2CH_2$); 2.13-1.81 (t, 8H, 2 CH_2NCH_2)

9b	282 Dioxane	67	$C_{26}H_{29}N_9S_2O$ (547.71)	57.02 57.21	5.34 5.23	23.02 23.10	11.71 11.84	3423, 3317, 3290, 3195, 3171 ($2NH_2$, NH); 2880, 2920 (CH); 2200 (CN); 1671 (C═O)	6.52-5.90 (m, 12H,6CH_2); 2.90-2.40 (br, 4H, 2NH_2.); 2.20 (S, 4H, 2CH_2); 1.66 (s, 1H, NH); 1.50-1.15 (t, 8H.2CH_2NCH_2)
10	300 DMF	80	$C_{16}H_{17}N_3S_6O_2$ (475.72)	40.40 40.52	3.60 8.51	8.83 8.74	40.44 40.60	2975, 2914 (CH); 2200 (CN); 1664 (C═O) 1602 (C═N)	4.15-3.70 (q, 2H, CH_2); 2.85 (s, 12H, 4CH_3); 1.45-1.00 (t, 3H, CH_3eter)
11	>300 DMF/H_2O	20	$C_{14}H_{14}N_2S_6O_4$ (466.66)	36.03 36.14	3.02 3.00	6.00 6.13	41.22 41.30	3486, 3370 (2OH); 1664 (2C═O); 1602 (C═N)	7.50 (S, 2H, 2H); 2.90 (s, 12H, 4CH_3)
12a	225 DMF/H_2O	71	$C_{24}H_{15}N_5S_4O_2$ (553.68)	54.02 54.10	2.83 2.89	13.12 13.05	24.03 24.14	3356, 3200 (2NH); 3100, 2974 (CH); 2190 (CN); 1700 (C═O); 1633 (C═N)	7.48-6.00 (m, 8H, arom), 5.90 (s, 2H, 2NH); 4.00-3.81 (q, 2H, CH_2); 2.50-2.31 (t, 3H, CH_3)
12b	184 DMF/H_2O	65	$C_{24}H_{17}N_7S_2O_2$ (499.58)	57.70 57.85	3.43 3.51	19.63 19.54	12.84 12.90	3361, 3310 (2NH); 3100, 2923 (CH); 2191 (CN); 1700 (C═O) 1665, (C═N)	8.60-7.63 (m, 4H, arom.), 7.30-6.42 (m, 4H, arom.); 5.71 (s, 2H, 2NH); 4.94 (s, 2H, 2NH); 4.00-3.31 (q, 2H, CH_2); 1.30-1.05 (t, 3H, CH_3)
13a	265 Dioxane	60	$C_{12}H_{11}N_7S_4O$ (397.52)	36.26 36.15	2.79 2.70	24.66 24.75	32.26 32.35	3442, 3340, 3310, 3280, 3185 ($2NH_2$, NH); 2992 (CH); 1650 (C═O); 1600 (C═N)	4.00-3.31 (br, 4H, 2NH_2); 2.68 (s, 3H, CH_3); 2.51 (s, 3H, CH_3); 2.32 (s, 1H, NH)
13b	210 DMF/H_2O	54	$C_{24}H_{19}N_7S_4O$ (549.72)	52.44 52.39	3.48 3.41	17.84 17.91	23.33 23.42	3447, 3300, 3140 (3NH); 3060, 2919 (CH); 1650 (C═O)	7.32-6.40 (m, 10H, arom.); 3.85 (s, 2H, 2NH); 3.72 (s, 1H, NH); 3.35 (s, 3H, CH_3); 2.90 (s, 3H, CH_3)
14	145 Dioxane	36	$C_{12}H_9N_3S_6O_2$ (419.61)	34.35 34.41	2.16 2.21	10.01 10.10	45.85 45.72	3434 (2NH); 2949 (CH); 2580 (2SH); 2192(CN); 1655 (C═O); 1150 (2C═S)	4.25-3.72 (q,2H,CH_2); 3.19-2.82 (s, 2H, 2SH); 2.45 (s, 1H, NH); 2.09 (s, 1H, NH); 1.71-1.10 (t, 3H, CH_3)
15	242 DMF/H_2O	49	$C_{10}H_3N_3S_6O$ (373.54)	32.61 32.09	0.81 0.79	11.25 11.35	51.50 51.59	3410, 3380 (3NH); 1629 (C═O); 1159 (2C═S)	4.00 (s, 1H, ═NH), 3.49-3.00 (br, 2H, 2NH)
16	280 DMF/H_2O	68	$C_{22}H_{13}N_5S_4$ O (491.64)	53.75 53.67	2.66 2.73	14.24 14.33	26.09 26.15	3446, 3380 (3NH); 3150 (CH), 1640 (C═O); 1148 (2C═S)	8.10 (═NH); 7.81-6.00 (m, 10H, arom); 2.20 (s, 1H, NH); 1.98 (s, 1H, NH)
17a	180 DMF/H_2O	70	$C_{26}H_{19}N_5S_4O_4$ (593.73)	52.60 52.71	3.23 3.32	11.79 11.86	21.60 21.50	3416, 3215 (4NH); 3010, 2930 (CH); 2199 (CN); 1700 (COester), 1641 (2C═O); 1130, 1100 (2C═S)	7.65-6.31 (m, 10H, arom.); 6.15 (s, 2H, 2NH). 4.22-3.65 (q, 2H, CH_2); 2.91 (s, 1H, NH); 2.32 (s, 1H, NH); 1.67-1.15 (t,3H,CH_3)
17b	154 DMF/H_2O	59	$C_{24}H_{19}N_5S_2O_4$ (505.58)	57.02 57.10	3.79 3.71	13.85 13.92	12.68 12.75	3428, 3350, 3290 (4NH); 2982 (CH); 2186(CN); 1700 (COester); 1645 (2C═O)	8.20 (s, 1H, NH), 8.11 (s, 1H, NH); 7.10-6.06 (m, 10H, arom.); 4.15-4.00 (q, 2H, CH_2); 3.12 (s, 1H, NH); 1.98 (s, 1H, NH); 1.65-1.11 (t, 3H, CH_3)

(Continued on next page)

TABLE I Analytical and Spectral Data of the Prepared Compounds *(Continued)*

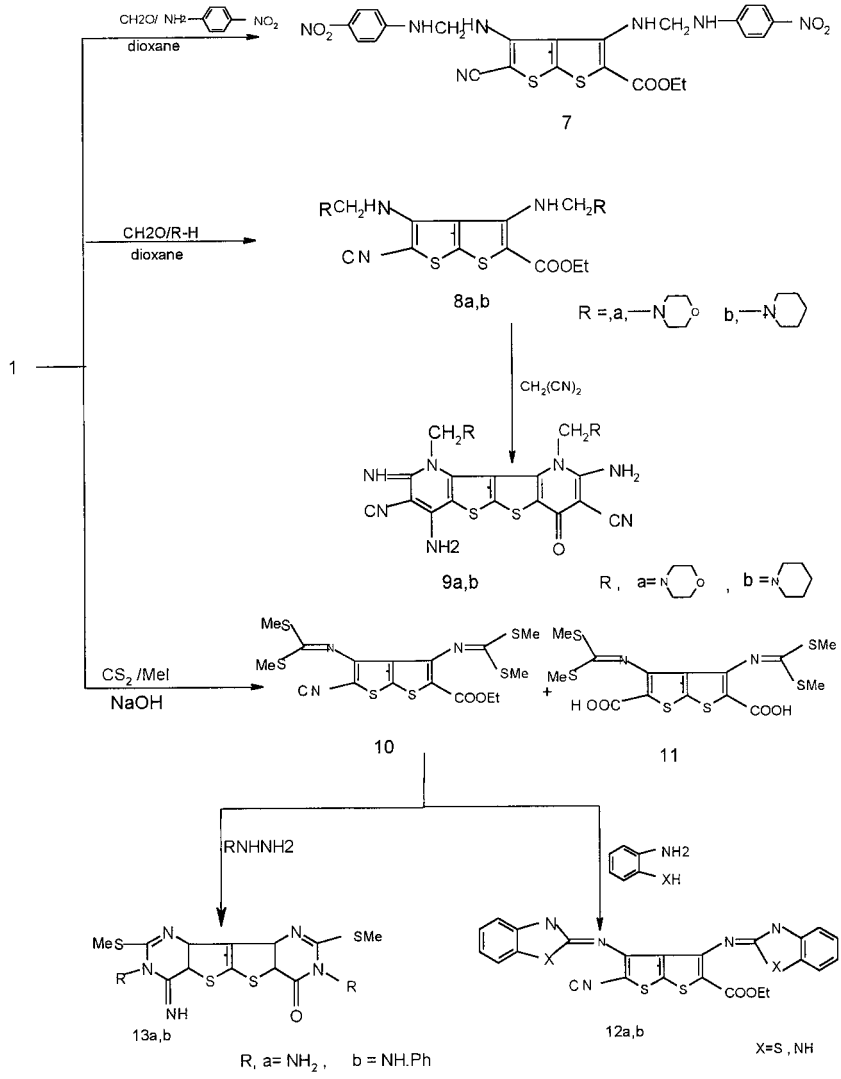
Compound no.	m.p.[a] (crys. solvent)	Yield (%)	$M_F/(M_w)$	Analytical data calc. (found)[b] (%) C	H	N	S	IR (KBr) ν (cm^{-1})[c]	δ(ppm) ^{1}H-NMR (DMSO-d_6)[d]
18	140 Dioxane	67	$C_{24}H_{13}N_5S_4O_3$ (547.66)	52.64 52.70	2.39 2.44	12.79 12.70	23.42 23.34	3410, 3352, 3210 (3NH); 3040 (CH); 2190 (CN); 1662 (C═O), 1645 (2C═O); 1600 (C═N)	6.35 (s, 1H, NH); 6.28-4.91 (m, 10H, arom); 2.26-1.52 (br, 2H, 2NH)
19	285 DMF/H_2O	48	$C_{22}H_{13}N_5S_2O_3$ (459.51)	57.51 57.60	2.85 2.92	15.24 15.15	13.96 13.88	3424, 3200, 3163 (3NH); 1705 (C═O); 1610 (C═N)	7.25 (s, 1H, NH); 7.10-6.21 (m, 10H, arom); 4.15-3.31 (br, 2H, 2NH)
20	230 DMF/H_2O	71	$C_{16}H_{11}N_5S_2O_4$ (401.42)	47.87 48.00	2.76 2.60	17.45 17.60	15.98 16.11	3350, 3215, 3150 (NH_2, 2NH); 2910 (CH); 2191 (CN); 1710 (COester), 1650, 1628 (2C═O)	6.41 (s, 1H, NH), 6.32 (s, 2H, 2NH); 6.19–5.98 (br, 2H, NH_2); 4.10-3.58 (q, 2H, CH_2); 1.62-0.80 (t, 3H, —CH_3); 2.51 (s, 2H, —CH_2)
21	>300 DMF/H_2O	69	$C_{14}H_5N_5S_2O_3$ (355.36)	47.32 47.39	1.42 1.50	19.71 19.63	18.05 18.15	3520, 3445 (2OH); 3415, 3317 (NH_2); 2910 (CH); 2191 (2CN); 1660 (C═O)	7.31 (s, 1H, CH); 4.16-3.43 (br, 2H, NH_2); 2.80 (s, 1H, 0H); 2.68 (s, 1H, 0H)
22	>300 Dioxane	52	$C_{14}H_7N_7S_2O$ (353.39)	47.58 47.49	1.99 1.93	27.75 27.69	18.15 18.26	3437, 3346, 3247, 3120 (5NH); 2971 (CH); 2191; 2120 (2CN); 1646 (C═O)	7.22 (s, 2H, 2CH); 6.43 (s, 1H, NH); 6.03 (s, 1H, NH); 2.98 (s, 3H, 3NH)

[a]Uncorrected.

[b]Satisfactory microanalysis obtained C, ±0.35; H, ±0.4; N, ±0.2; S, ±0.32.

[c]Measured by Nicolet FT-IR 720 Spectrophotometer.

[d]Measured by a varian EM360L spectrometer at 60 MHz using TMS as internal standard and DMSO as a solvent.



SCHEME 2

compounds **8a**,**b** was allowed to react with double molarity of malononitrile in refluxing DMF to give bi[thieno(3,2-b)pyridine] derivatives **9a**,**b**, in excellent yield (Scheme 2, Table I). The reaction mechanism was postulated to proceed through a nucleophilic attack of Mannich bases NH groups at the cyano group of malononitrile followed by a nucleophilic attack of the active CH_2 group at the ethoxycarbonyl group,

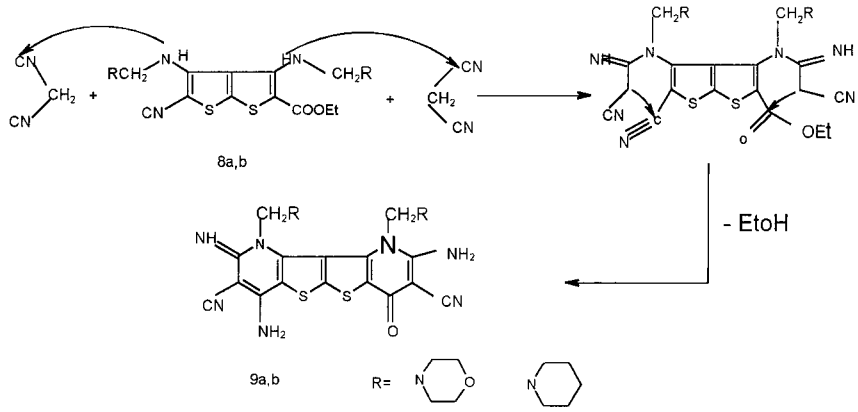


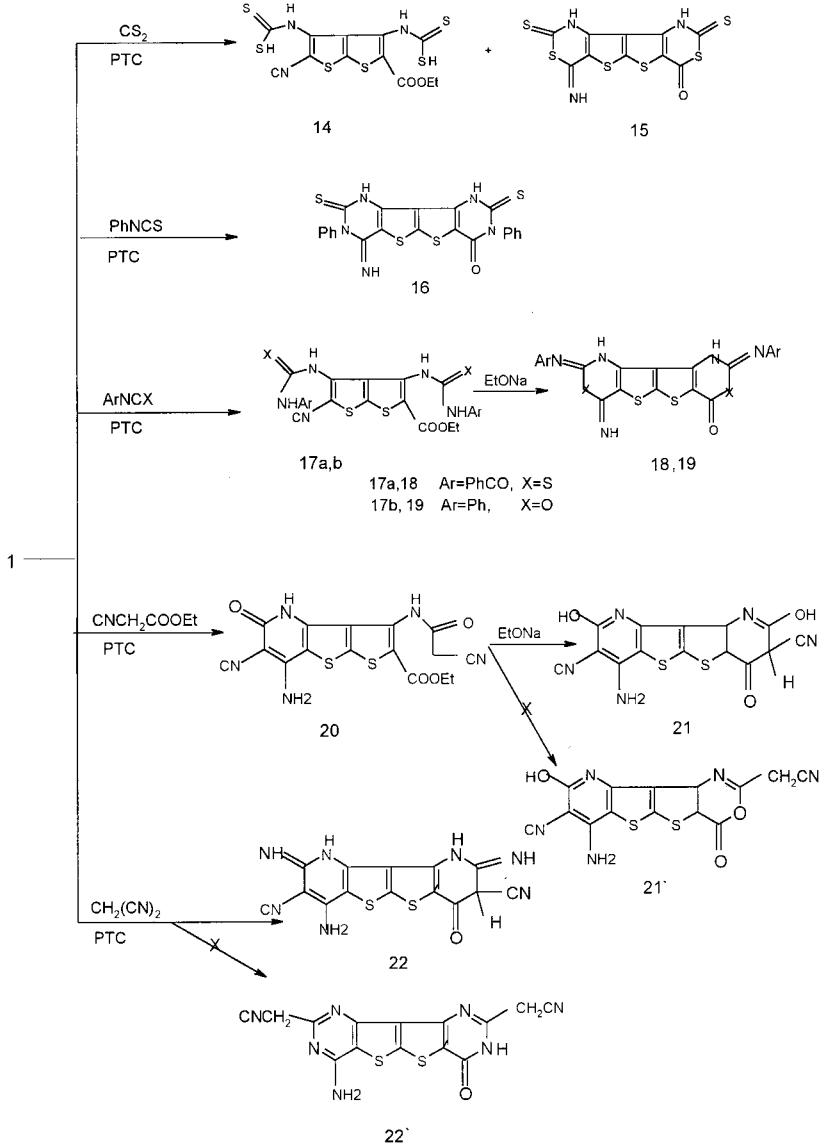
FIGURE 2

with elimination of EtOH molecule as well as at the olefinic cyano group forming NH_2 (Figure 2). The proposed structures of these compounds were established on the basis of their elemental and spectral analyses (Scheme 2, Table I).

Treatment of compound **1** with CS_2, NaOH in 1:1:2 molar ratio, and double molarty of CH_3I at room temperature afforded the corresponding dimethyl dithiacarbamate derivative **10** in 70% yield and the corresponding acid derivatives **11** in 20% yield (Scheme 2, Table I).

On treating compound **10** with selected o-substituted aromatic amines such as o-aminothiophenol or o-phenylenediamine afforded the corresponding spiro compounds **12a**,**b** with the elimination of CH_3SH molecules, whereas the treatment of compound **10** with hydrazine hydrate or phenyl hydraziene yielded the corresponding methylthiothienopyrimidine derivatives **13a**,**b** in a good yield.

Compound **1** was treated with CS_2, phenyl (benzoyl) isothiocyanate, or phenyl isocyanate in 1:2 molar ratio under solid-liquid phase-transfer catalysis (PTC) conditions [DMF/K_2CO_3/tetrabutyl ammonium bromide (TBAB)] to give compounds **14–17a**,**b**. Compounds **17a**,**b** underwent intramolecular cyclization on treating with EtONa in boiling DMF affording the corresponding thieno[3,2-d]1,3-thiazine or thieno[3,2-d]1,3-oxazine derivatives **18** and **19** respectively. The reaction pathway was postulated to proceed through a nucleophilic attack of NH groups at each of the ethoxy carbonyl group with the elimination of EtOH molecules, and at the olefinic CN group forming =NH (Scheme 3, Table I). Also, compound **1** was treated with ethyl cyanoacetate in 1:2 molar ratio under the same PTC experimental conditions to give compound **20**, which in turn underwent interamolecular cyclization in refluxing DMF and catalytic amount of EtONa yielding the polyfused



SCHEME 3

product **21** (Scheme 3, Table I). Although the isomeric cyclization products **21** or **21** were predicted, only the single product **21** was observed. The suggested mechanism for this compound formation is the intramolecular nucleophilic attack of the active CH_2CN at the carbonyl

ester group with the elimination of EtOH molecule to give thieno(2,3-b)pyridine derivative **21** (Scheme 3, Table I).

Another derivative of thieno(2,3-b)pyridine, derivative **22**, was obtained by the reaction of compound **1** with malononitrile in 1:2 molar ratio under the same solid-liquid (PTC) experimental condition at 70°. The H-NMR spectral data of compound **22** showed the presence of a signal corresponding to CH group (Scheme 3, Table I).

The elemental and spectral analyses were in agreement with the proposed structures.

EXPERIMENTAL

Synthesis of Compound 2

To a solution of compound **1** (0.02 mol, 5.34 g) in DMF (5 ml) was added CS_2 (25 ml) and ethylenediamine (0.04 mol, 4.4 g). The reaction mixture was stirred for 20 h at room temperature. The reaction mixture was poured into ice cold water (200 ml) in presence of few drops of HCl. The resulting solid was filtered washed with water, dried, and recrystallized from dioxane (Table I).

Synthesis of Compound 3

To a solution of compound **2** (0.01 mol, 3.06 g) and triethylamine (0.04 mmol, 4.05 g) in DMF (20 ml) chloroacetyl chloride (0.02 mol, 2.26 g) was added dropwise. The solution was stirred for 6 h. The reaction mixture was poured into cold water. The resulting solid mass was filtered off and crystallized from DMF/H_2O (Table I).

Synthesis of Compound 4

A solution of compound **2** (0.01 mol, 3.06 g) and p-chlorobenzaldehyde (0.02 mol, 2.81 g) in DMF (20 ml) was refluxed for 5 h. After cooling the mixture was poured into ice cold water (100 ml). The separated solid was filtered off and crystallized from DMF/H_2O (Table I).

Synthesis of Compound 5

To a solution of compound **2** (0.01 mol, 3.06 g) in acetic anhydride (10 ml) triethylorthoformate (0.03 mol, 4.44 g) was added. The reaction mixture was refluxed for 5 h and evaporated *in vacuo*. The residual solid was washed with water and crystallized from acetic acid (Table I).

Synthesis of Compound 6

A mixture of compound **2** (0.01 mol, 3.06 g) and LR (0.02 mol, 4.04 g) was refluxed in DMF (20 ml) till H_2S was ceased ($\simeq$ 20 h). The reaction mixture was concentrated and cooled to room temperature. The separated solid was filtered, washed with water, dried, and crystallized from DMF/H_2O (Table I).

Synthesis of Compounds 7 and 8a,b: General Procedure

A solution of compound **1** (0.005 mol, 1.34 g) and formaldehyde (10 ml) in dioxane (20 ml) was refluxed for 1 h. The proper amine (p-nitroaniline, morpholine, piperidine) (0.01 mol) was added to the reaction mixture and the reflux was continued for 4 h. The reaction mixture was concentrated and cooled. The precipitate was filtered off and crystallized from the suitable solvent (Table I).

Synthesis of Compounds 9a,b: General Procedure

To a solution of compound **8a** or **8b** (0.005 mol) in DMF (20 ml) malononitrile (0.01 mol, 0.66 g) was added. The reaction mixture was refluxed for 2 h and cooled. The precipitate was filtered off and crystallized from the proper solvent (Table I).

Synthesis of Compounds 10 and 11: General Procedure

A mixture of compound **1** (0.01 mol, 2.67 g), CS_2 (0.02 mol, 1.52 g), NaOH (0.04 mol, 1.60 g in 10 ml water), and DMF (30 ml) was stirred for 4 h and CH_3I (0.04 mol, 5.68 g) was added. The reaction mixture was stirred for an additional 5 h and poured into ice cold water (200 ml). The resulting solid mass was filtered and dried. The solid product was dissolved in $NaHCO_3$ solution and filtered off. The precipitate was crystallized from DMF where compound **10** was obtained. The filtrate was acidified with dil. HCl; where compound **11** was separated, filtered off, and crystallized from DMF/H_2O (Table I).

Synthesis of Compounds 12a,b and 13a,b: General Procedure

To a solution of compound **10** (0.002 mol, 0.95 g) in DMF (20 ml) o-aminothiophenol, o-phenylenediamen, hydrazine hydrate, or phenyl hydrazine, (0.004 mol) was added. The reaction mixture was refluxed till the evaluation of MeSH was ceased. The reaction mixture was poured

into ice-cold water (100 ml). The separated solid was collected by filteration and crystallized from the suitable solvent (Table I).

Synthesis of Compound 14–17a,b, 20 and 22: General Procedure

A mixture of 4 g anhydrous potassium carbonate, compound **1** (0.004 mol, 1.07 g), DMSO (20 ml), and catalytic amount of TBAB was treated with 0.008 mol of CS_2, phenylisothiocyanate, benzoyliso-thiocyanate, phenylisocyanate, ethylcyanoacetate, or malononitrile and stirred for 5 h at 70°C. The reaction mixture was filtered off and the filtrate was added to ice-cold water. The separated solid was filtered off and crystallized from the proper solvent to give compounds **14**, **16**, **17a**,**b**, and **20**. The residual solid potassium carbonate was dissolved in distilled water (50 ml). The separated solid was collected by filteration and crystallized from dioxane where compound **22** was obtained (Table I).

Synthesis of Compounds 18, 19, and 21: General Procedure

A solution of compound **17a**,**b** or **20** (0.002 mol) in DMF (20 ml) was treated with catalytic amount of EtONa. The reaction mixture was refluxed for 5 h and poured into ice-cold water (100 ml). The solid product was filtered off and crystallized from the proper solvent (Table I).

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