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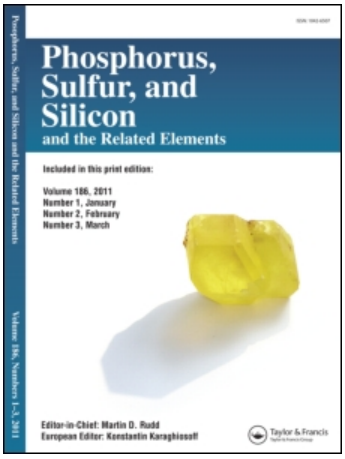

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SOME REACTIONS ON 2-(2-THIOXO-4-OXO-THIAZOLIDIN-3-YL)-6-(4-NITROPHENYLTHIO)BENZTHIAZOLE

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SOME REACTIONS ON 2-(2-THIOXO-4-OXO-THIAZOLIDIN-3-YL)-6-(4-NITROPHENYLTHIO)BENZTHIAZOLE

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2-(2-thioxo-4-oxo-thiazolidin-3-yl-)-6-(4-nitrophenylthio)-benzthiazole 1was prepared and condensed with two moles of aromatic amine to give the corresponding 2,4-diarylimino thiazolidines 2_{a-d}. The latter compounds undergo cycloaddition reaction with chloroacetylchloride and thioglycolic acid to give spiro compounds 5_{a-d} and 6_{a-d} The reaction of 1 with hydrazine hydrate afforded 2-hydrazono compound 3. Reaction of 3 with phenyl isothiocyanate gave the corresponding thiosemicarbazone 9. Cyclocondensation of chloroacetic acid with 9 afforded compound 10. Also, condensation of 3 with aromatic aldehydes gave the corresponding Schiff's bases 11_{a-c}. Reaction of compound 1 with malononitrile gave compound 4 which was reacted with sulfur in presence of diethylamine to give thienothiazole derivative 14. Compound 4 was reacted also with carbon disulfide in presence of triethylamine to afford thiopyranthione 15. Furthermore, the active methylene of 4 couples with benzene diazonium chloride followed by cyclization to give thiazolopyridazine derivative 17. Oxidation of compounds 5_{a-d}, 6_{a-d}, 10, 11_{a-c}, 14, 15 and 17 using H_2O_2/ACOH mixture afforded the corresponding diarylsulfones 7_{a-d}, 8_{a-d}, 12, 13_{a-c}, 18, 19 and 20.

Keywords: Thiazolodiaryl sulfides; diarylsulfones; arylthiobenzthiazole and thiazolidinone

INTRODUCTION

Diarylsulfides and diarylsulfones proved to be an interesting classes of compounds. Diarylsulfides display antimicrobial activity[1,2], whereas diaryl sulfones are known to be the drug of choice for the treatment of Leprosy[3] in addition to their antituberculstatic activity[4]. In view of the above facts, and in continuation of our previous work[5–7] directed towards the synthesis of some new thiazolodiaryl sulfides and diaryl sulfones containing variable heterocyclic moieties. The author wishes to report herein

* Correspondence author.

some new diaryl sulfides, sulfones incorporating other pharmacophores such as benzthiazole, azitidine, thiazolidinone, thiophene, thiopyran or pyridazine nucleus.

RESULTS AND DISCUSSION

The starting compound, 2-(2-thioxo-4-oxo-thiazolidin-3-yl)-6-(4-nitrophenylthio)benzthiazole 1 was prepared according to our previous method[6] by reaction of 2-amino-6-(4-nitrophenylthio)benzthiazole with carbon disulfide in concentrated sodium hydroxide and N,N-dimethylformamide followed by cyclization the produced dithiocarbimidate salt without isolation using sodium chloroacetate in the presence of hot concentrated hydrochloric acid.

Compound 1 was easily condensed with two equivalents of aromatic amines to give the corresponding 2 – (2,4-diaryliminothiazolidin-3 -yl) – 6 – (4-nitrophenylthio) benzthiazoles[6] 2_{a-d}. Also, the reaction of 1 with hydrazine hydrate at room temperature gave the hydrazono derivative 3. In contrast, compound 1 was reacted with malononitrile by refluxing in acetic anhydride to afford thiazolidinthione 4.

Compounds 2, 3 and 4 in turn were subjected to some sequence reactions to afford the target heterocycles. These reactions were summarized below.

Compound 2_{a-d} underwent cycloaddition reaction with chloroacetyl chloride in dioxane and with thioglycolic acid in dry benzene to give the corresponding spiro compounds: 2-[spiro(azetidin-4′,4-thiazolidin)-1′-aryl-3′-chloro-2′-oxo-2-arylimino-3-yl]-6-(4-nitrophenylthio)benzthiazole 5_{a-d} and 2-[spiro(thiazolidin-2′,4-thiazolidin) –3′-aryl-4′-oxo-2-arylimino-3-yl]-6-(4-nitrophenylthio)benzthiazole 6_{a-d} respectively[8] (Scheme 2).

The hydrazono compound 3 was reacted with phenyl isothiocyanate to give the corresponding 2-(2-phenyl thiosemicarbazono-4-oxo-thiazolidin-3-yl)-6-(4-nitrophenylthio)benzthiazole 9. The latter compound 9 underwent cyclocondensation reaction with chloroacetic acid to yield 2-[2-(3′-phenyl-4′-oxo-thiazolidin-2′-imino) hydrazono-4-oxo-thiazolidin-3-yl]-6-(4-nitrophenylthio)benzthiazole 10. When 3 was allowed to condense with aromatic aldehydes, the products were found to be 2-[2-ary-

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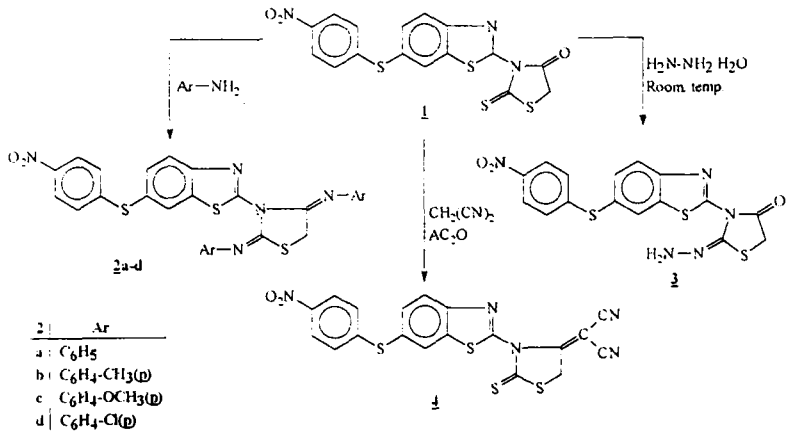

SCHEME 1

lidineamino) hydrazono-4-oxo-3-yl]-6-(4-nitrophenylthio)benzthiazole $\underline{11}_{a\text{-}c}$ (Scheme 3).

In a similar reaction to that reported by Gewald *et al*[9,10] compound $\underline{4}$ was reacted with sulfur in ethanol in the presence of diethylamine to give the corresponding o-aminocyanothiophene $\underline{14}$. Compound $\underline{4}$ was allowed to react with carbon disulfide in DMF and triethylamine, the product was identified as thiopyranthione $\underline{15}$.

Benzene diazonium chloride was coupled with $\underline{4}$ to form the phenyl hydrazone derivative $\underline{16}$. This latter compound was readily cyclized in alcoholic sodium hydroxide solution to give the thiazolopyridazine derivative[11] $\underline{17}$ (Scheme 4).

Oxidation of $\underline{5}_{a\text{-}d}$, $\underline{6}_{a\text{-}d}$, $\underline{10}$, $\underline{11}_{a\text{-}c}$, $\underline{14}$, $\underline{15}$ and $\underline{17}$, with 30% hydrogen peroxide in glacial acetic acid for 2–7 days at room temperature, led to the formation of the corresponding diarylsulfones $\underline{7}_{a\text{-}d}$, $\underline{8}_{a\text{-}d}$, $\underline{12}$, $\underline{13}_{a\text{-}c}$, $\underline{18}$, $\underline{19}$ and $\underline{20}$ respectively, in relatively lower yield. The sulfones obtained were highly crystalline compounds with well defined melting points that were higher than those of the corresponding sulfides, in most cases (Schemes 2,3,4).

The structural formula of all newly synthesized compounds were confirmed by elemental analyses (Table I) and spectroscopic data (Table II).

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TABLE I Melting points, yields and analytical data of the prepared compounds

Comp.	M.P. (Yield; %)	Molecular formula	Elemental Analysis Calc./Found				
			%C	%H	%N	%S	%Cl
3	171–172° 87	$C_{16}H_{11}N_5O_3S_3$	46.04 45.73	2.63 2.27	16.78 16.34	23.02 23.48	
4	128°C 60	$C_{19}H_9N_5O_2S_4$	48.82 49.13	1.92 1.55	14.98 15.36	27.40 27.67	
5a	167°C 65	$C_{30}H_{20}N_5O_3S_3Cl$	57.18 56.83	3.17 3.45	11.11 10.94	15.25 15.55	5.63 5.24
5b	135°C 67	$C_{32}H_{24}N_5O_3S_3Cl$	58.40 58.14	3.65 3.71	10.64 10.43	14.60 14.25	5.39 5.52
5c	145°C 72	$C_{32}H_{24}N_5O_3S_3Cl$	55.69 55.42	3.48 3.27	10.15 9.87	13.92 14.27	5.14 4.76
5d	110°C 68	$C_{30}H_{18}N_5O_3S_3Cl_3$	51.53 51.97	2.57 2.64	10.02 9.65	13.74 13.37	15.24 14.78
6a	122°C 64	$C_{30}H_{21}N_5O_3S_4$	57.41 57.63	3.34 3.29	11.16 10.87	20.41 20.35	– –
6b	126°C 65	$C_{32}H_{25}N_5O_3S_4$	58.62 58.37	3.81 4.04	10.68 10.47	19.54 19.28	– –
6c	125°C 62	$C_{32}H_{25}N_5O_5S_4$	55.89 55.47	3.63 4.02	18.18 18.52	18.63 18.32	– –
6d	139°C 71	$C_{30}H_{19}N_5O_3S_4Cl_2$	51.79 51.47	2.73 2.87	10.07 10.29	18.41 18.69	10.07 9.84
9	195–197° 76	$C_{23}H_{16}N_6O_3S_4$	50.00 50.33	2.89 3.14	15.21 15.64	23.18 23.51	
10	111°C 63	$C_{25}H_{16}N_6O_4S_4$	50.67 51.15	2.70 2.67	14.18 13.75	21.62 21.24	
11a	197°C 66	$C_{23}H_{15}N_5O_3S_3$	54.65 54.43	2.97 3.14	13.86 14.25	19.00 19.22	
11b	174°C 78	$C_{24}H_{17}N_5O_4S_3$	53.83 54.24	3.17 2.87	13.08 13.36	17.94 18.23	
11c	145°C 75	$C_{23}H_{14}N_5O_3S_3Cl$	51.15 51.36	2.59 2.27	12.97 13.25	17.79 17.52	6.58 6.73
14	142°C 73	$C_{19}H_9N_5O_2S_5$	45.69 45.35	1.80 2.13	14.02 14.37	32.06 31.87	
15	158°C 80	$C_{20}H_9N_5O_2S_6$	44.19 43.87	1.65 1.72	12.89 13.06	35.35 35.25	

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Comp.	M.P. (Yield; %)	Molecular formula	Elemental Analysis Calc./Found				
			%C	%H	%N	%S	%Cl
16	185°C 64	$C_{25}H_{13}N_7O_2S_4$	52.53 52.94	2.27 2.86	17.16 16.73	22.41 22.14	
17	145°C 58	$C_{25}H_{12}N_6O_3S_4$	52.44 52.16	2.09 1.78	14.68 15.15	22.37 22.76	
7_a	185°C 62	$C_{30}H_{20}N_5O_5S_3Cl$	54.42 54.23	3.02 2.75	10.58 10.36	14.51 14.43	5.36 5.57
7_b	180°C 73	$C_{32}H_{24}N_5O_5S_3Cl$	55.69 55.78	3.48 3.79	10.15 9.87	13.92 13.66	5.14 4.83
7_c	175°C 68	$C_{32}H_{24}N_5O_7S_3Cl$	53.22 53.17	3.32 3.16	9.70 9.46	13.30 13.65	4.92 5.27
7_d	182°C 64	$C_{30}H_{18}N_5O_5S_3Cl_3$	49.28 49.55	2.46 2.73	9.58 9.37	13.14 12.75	14.57 14.12
8_a	195°C 59	$C_{30}H_{21}N_5O_5S_4$	54.62 54.33	3.18 2.77	10.62 10.37	19.42 19.25	
8_b	202°C 67	$C_{32}H_{25}N_5O_5S_4$	55.89 56.27	3.63 3.86	10.18 9.86	18.63 18.57	
8_c	205°C 74	$C_{32}H_{25}N_5O_7S_4$	53.40 53.61	3.47 3.25	9.73 10.12	17.80 17.49	
8_d	215°C 72	$C_{30}H_{19}N_5O_5S_4Cl_2$	49.51 49.87	2.61 2.35	9.62 9.40	17.62 17.72	9.62 9.85
12	182°C 69	$C_{25}H_{16}N_6O_6S_4$	48.07 47.83	2.56 2.79	13.46 13.26	20.51 20.62	
13_a	220°C 77	$C_{23}H_{15}N_5O_5S_3$	51.39 51.13	2.79 2.61	13.03 12.87	17.87 17.53	
13_b	205°C 68	$C_{24}H_{17}N_5O_6S_3$	50.79 50.32	2.99 3.25	12.34 12.65	16.93 17.22	
13_c	195°C 71	$C_{23}H_{14}N_5O_5S_3Cl$	48.29 48.52	2.44 2.37	12.24 12.69	16.79 16.89	6.21 6.58
18	239°C 65	$C_{19}H_9N_5O_4S_5$	42.93 43.25	1.69 2.15	13.18 13.49	30.13 30.56	
19	189°C 63	$C_{20}H_9N_5O_4S_6$	41.73 41.35	1.56 1.87	12.17 11.96	33.39 33.14	
20	245°C 40	$C_{19}H_9N_6O_5S_4$	49.66 49.83	1.98 2.15	13.90 14.22	21.19 21.65	

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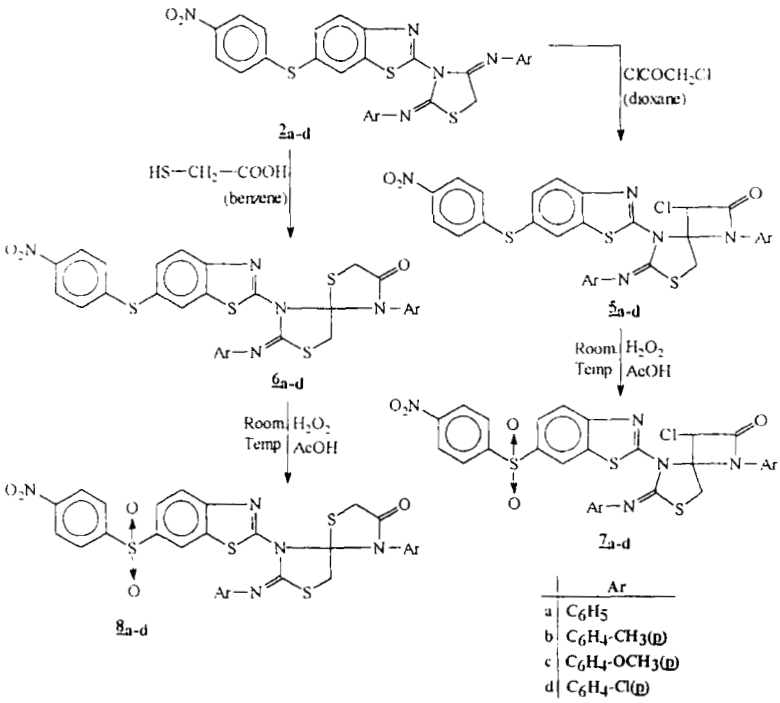

SCHEME 2

EXPERIMENTAL

The time allowed for the completion of the reaction and the purity of the prepared compounds were controlled by means of T.L.C. Melting points were determined on Fisher-Johns melting point apparatus and were uncorrected. Elemental analyses were performed on a Perkin-Elmer 240 C elemental analyser. IR spectra were recorded on a Pye-Unicam infrared spectrophotometer, using the KBr wafer technique. ^{1}H-NMR spectra were recorded on a 90 MHz Varian NMR spectrophotometer, in a suitable deutrated solvent, using TMS as an internal standard. Melting points, yields and analytical data of all newly synthesized compounds are given in Table I.

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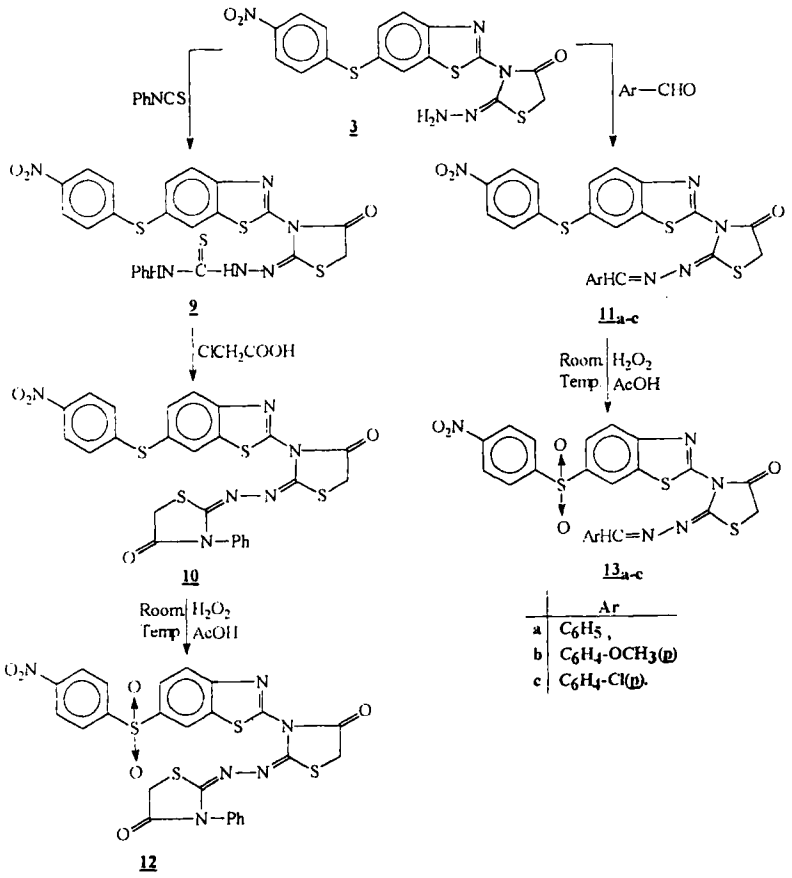

SCHEME 3

2-(2-Thioxo-4-oxo-thiazolidin-3-yl)-6-(4-nitrophenyl thio)benzthiazole 1

This compound was prepared according to the method described in our previous work[6].

2-(2,4-Diarylimino-thiazolidin-3-yl)-6-(4-nitrophenylthio) benzthiazole 2_{a-d}

They were prepared by a method described previously[6] through condensation of 1 with two equivalents of aromatic amines.

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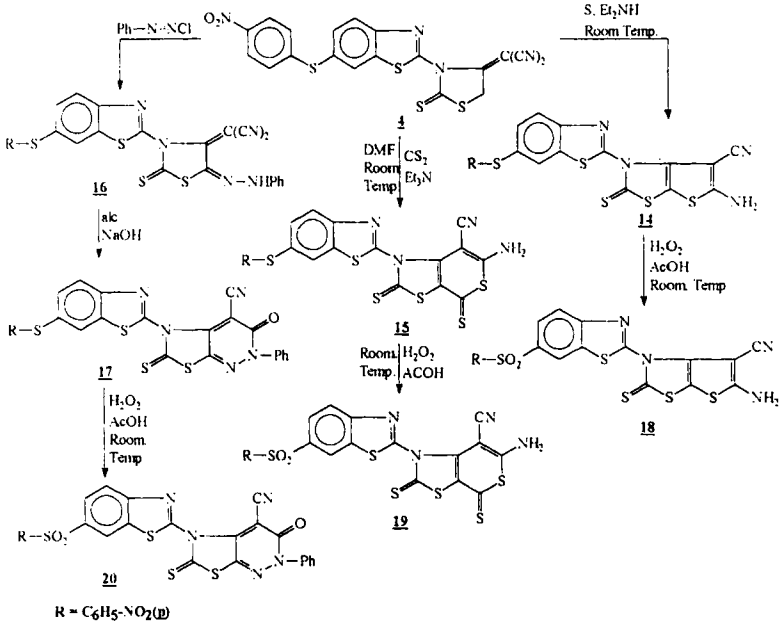

SCHEME 4

2-(2-Hydrazono-4-oxo-thiazolidin-3-yl)-6-(4-nitrophenylthio) benzthiazole 3

To a stirred solution of 1 (0.01 mole) in dioxane (15 ml) and ethanol (10 ml) there was added hydrazine hydrate (0.01 mole). The reaction mixture was stirred for further 10 hours at room temperature, left overnight and poured into ice. The formed precipitate was filtered and recrystallized from ethanol.

2-(4-Dicyanomethylidine-2-thioxo-thiazolidin-3-yl)-6-(4-nitrophenylthio)benzthiazole 4

A mixture of compound 1 (0.01 mole) and malononitrile (0.01 mole) in acetic anhydride (30 ml) was heated under reflux for one hour, then allowed to cool. The solid product was collected and recrystallized from dioxane-pet. ether (40–60°C).

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TABLE II IR and ^{1}H NMR spectra of the prepared compounds

IR Spectra (cm^{-1})	*^{1}H NMR spectra (δ in ppm)*
00, 3200 (NH_2), 1700 (C=O) and 1540, 1535 (NO_2).	in DMSO,d_6: δ 3.40(s, 2H, CH_2), δ 3.90(s, 2H, NH_2) and δ 7.20–8.18 (m, 7H, Ar-H).
00 (C≡N), 1600 (C=C), 1500 (C=S) and 1540, 1340 (NO_2)	–
35 (C=O), 1600 (C=N), 1535, 1335 (NO_2) and 750 (C-Cl).	–
00 (C=O), 1600 (C=N), 1540, 1340 (NO_2) and 740 (C-Cl).	in DMSO,d_6: δ 2.35(s, 6H, $2CH_3$), δ 4.25(s, 1H, CH-Cl), δ (s, 2H, CH_2) and δ 7.25–8.33(m, 15H, Ar-H).
25 (C=O), 1630 (C=N), 1540, 1340 (NO_2) and 740 (C-Cl).	–
00 (C=O), 1585 (C=N), 1540, 1340 (NO_2) and 740 (C-Cl).	–
10 (C=O), 1610 (C=N) and 1540, 1340 (NO_2).	–
10 (C=O), 1620 (C=N) and 1535, 1340 (NO_2).	in DMSO,d_6: δ 2.30(s, 6H, $2CH_3$), δ 3.50(s, 4H, $2CH_2$) and δ 7.15–8.00 (m, 15H, Ar-H).
00 (C=O), 1610 (C=N) and 1540, 1340 (NO_2).	–
00 (C=O), 1610 (C=N), 1535, 1340 (NO_2) and 750 (C-Cl).	–
00 (NH), 1700 (C=O), 1610 (C=N) and 1520 (C=S).	in DMSO,d_6: δ 3.30(s, 2H, CH_2), δ 3.45 (s, 1H, $-\overset{\overset{S}{\|}}{C}-NH-N$ δ 4.00(s, 1H, $Ph-NH-\overset{\overset{S}{\|}}{C}-$) and δ 6.90–8.20(m, 12H, Ar-H)
90 (C=O), 1600 (C=N) and 1540, 1535 (NO_2).	in DMSO,d_6: δ 3.35(s, 4H, $2CH_2$) and δ 7.20–8.30(m, 7H,

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IR Spectra (cm^{-1})	*^1H NMR spectra (δ in ppm)*
90 (C=O), 1600 (C=N) and 1540, 1340 (NO_2).	in DMSO,d_6: δ 3.35(s, 2H, CH_2) and δ 7.20–8.20[m, 13H (12H, Ar-H; 1H, HC=N)].
00 (C=O), 1600, 1580 (C=N, N=CH) and 1540, 1340 (NO_2).	in DMSO,d_6: δ 3.30(s,2H, CH_2), δ 3.70 (s, 3H, CH_3-O-Ar) and δ 7.20–8.15 [m, 12H (11H, Ar-H; 1H, HC=N)].
90 (C=O), 1595 (C=N), 1535, 1340 (NO_2) and 740 (C-Cl).	–
00, 3200 (NH_2), 2200 (CN), 1505 (C=S) and 1535, 1340 (NO_2).	in DMSO,d_6: δ 3.75(s, 2H, NH_2) and δ 7.20–8.20(m, 7H, A
00, 3200 (NH_2), 2200 (C≡N), 1505 (C=S) and 1540, 1340 (NO_2).	in DMSO,d_6: δ 3.80(s, 2H, NH_2) and δ 7.10–8.25(m, 7H, A
50 (NH), 2200 (C≡N), 1605 (C=N) and 1535, 1340 (NO_2).	in DMSO,d_6: δ 3.85(s, 1H, NH) and 7.20–8.18(m, 12H, Ar-
00 (C≡N), 1705 (C=O), 1500 (C=S) and 1535, 1350 (NO_2).	in DMSO,d_6: δ 7.20–8.18(m, 12H, Ar-H).
10 (C=O), 1600 (C=N), 1535, 1320 (NO_2), 1350, 1160(SO_2) and 740 -Cl).	–
90 (C=O), 1600 (C=N), 1535, 1340 (NO_2), 1350, 1170 (SO_2) and 750 Cl).	in DMSO,d_6: δ 2.30(s, 6H, $2CH_3$-Ar), δ 3.40(s, 2H, CH_2), δ 4.30(s, 1H, CH-Cl) and δ 7.15–8.45(m, 15H, Ar-H).
20 (C=O), 1630 (C=N), 1540, 1340 (NO_2), 1350, 1160 (SO_2) and 740 Cl).	–
00 (C=O), 1600 (C=N), 1350, 1160 (SO_2) and 750 (C-Cl).	–
95 (C=O), 1595 (C=N) and 1350, 1160 (SO_2).	–
00 (C=O), 1600 (C=N) and 1345, 1160 (SO_2).	in DMSO,d_6: δ 2.40(s, 6H, $2CH_3$-Ar), δ 3.40(s, 2H, S-CH_2- δ 3.60 (s, 2H,S-CH_2-C=O) and δ 7.15–8.30 (m, 15H, Ar-H)

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IR Spectra (cm^{-1})	*^1H NMR spectra (δ in ppm)*
00 (C=O), 1600 (C=N) and 1340, 1160 (SO_2).	in DMSO,d_6 δ 3.40(s, 4H, $2CH_2$), 3.70(s, 6H, $2CH_3$-O-Ar) and δ 7.00–8.35(m, 15H, Ar-H).
95 (C=O), 1600 (C=N) and 1350, 1160 (SO_2).	–
40 (C=O), 1600 (C=N) and 1350, 1160 (SO_2).	in DMSO,d_6 δ 3.75(s, 4H, $2CH_2$) and δ 7.20–8.30(m, 12H,
90 (C=O), 1590 (C=N) and 1350, 1160 (SO_2).	–
00 (C=O), 1580 (C=N) and 1350, 1160 (SO_2).	–
90 (C=O), 1590 (C=N) and 1340, 1150 (SO_2).	–
00, 3200 (NH_2), 2200 (C≡N), 1520 (C=S) and 1340, 1160 (SO_2).	in DMSO,d_6: δ 3.75(s, 2H, NH_2) and δ 7.20–8.40(m, 7H, A
50, 3200 (NH_2), 2200 (C≡N), 1520 (C=S) and 1350, 1160 (SO_2).	in DMSO,d_6: δ 3.80(s, 2H, NH_2) and δ 7.85–8.75(m, 7H, Ar-H).
00 (C≡N), 1690 (C=O), 1520 (C=S) and 1340, 1160 (SO_2).	–

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2-[Spiro(azetidin-4′,4-thiazolidin)-1′-aryl-3′-chloro-2′-oxo-2-arylimino-3-yl]-6-(4-nitrophenylthio)benzthiazole $\underline{5}_{a-d}$

To a mixture of $\underline{2}_{a-d}$ (0.01 mole), dioxane (20 ml) and triethylamine (0.02 mole), chloro acetylchloride (0.011 mole) was added while shaking. The reaction mixture was shaked for further 4 hours, then left to stand overnight. Triethylamine hydrochloride was filtered off and the filtrate was concentrated by evaporation under reduced pressure, then the residue washed well with petroleum ether and recrystallized from chloroform-pet. ether (40–60°) to give compounds $\underline{5}_{a-d}$.

2-[Spiro(thiazolidin-2′,4-thiazolidin)-3′-aryl-4′-oxo-2-arylimino-3-yl]-6-(4-nitrophenylthio)benzthiazole $\underline{6}_{a-d}$

A mixture of $\underline{2}_{a-d}$ (0.01 mole) and thioglycolic acid (0.01 mole) was refluxed in dry benzene for about 5 hours. The solution was evaporated and the residue was washed with petroleum ether several times, then washed with sodium carbonate solution (5%), the precipitate was separated out and recrystallized from ethanol to give compounds $\underline{6}_{a-d}$.

2-(2-Phenyl thiosemicarbazono-4-oxo-thiazolidin-3-yl)-6-(4-nitro-phenylthio)benzthiazole 9

To a solution of 3 (0.01 mole) in acetonitrile (10 ml), phenyl isothiocyanate (0.01 mole) was added. The reaction mixture was heated for one hour on a water bath and cooled. The formed crystals were separated and recrystallized from acetonitrile to give compound 9.

2-[2-(3′-Phenyl-4′-oxo-thiazolidin-2′-imino)hydrazono-4-oxo-thiazolidin-3-yl]-6-(4-nitrophenylthio)benzthiazole 10

A mixture of thiosemicarbazone 9 (0.01 mole), monochloroacetic acid (0.01 mole) and anhydrous sodium acetate (0.015 mole) in ethanol (25 ml) was heated under reflux for 5–6 hours on a water bath with occasional shaking. The solvent was evaporated and the reaction poured into ice-water mixture. The formed precipitate was filtered, washed with hot water and recrystallized from dilute acetic acid to give compound 10.

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2- [2-(Arylidineamino)hydrazono-4-oxo-thiazolidin-3-yl]-6-(4-nitrophenylthio)benzthiazole $\underline{11}_{a-c}$

To a mixture of 3 (0.01 mole) and the appropriate aromatic aldehyde (0.01 mole) in absolute ethanol (30 ml), there was added few drops of piperidine. The reaction mixture was heated under reflux for 3–5 hours and cooled. The formed precipitate was filtered, washed with water and recrystallized from chloroform-pet ether (40–60°C) to give compounds $\underline{11}_{a-c}$.

2-(5-Amino-4-cyano-2-thioxothieno[3,2-d]thiazol-3-yl)-6-(4-nitrophenylthio)benzthiazole 14

To a mixture of compound 4 (0.01 mole) and powdered sulfur (0.011 gm atom) in ethanol (20–30 ml). There was added with stirring diethylamine (about 1 cc) at 40–60°C during 1–3 hours, refrigerated several hours, and stirred into 2–3 volumes of water. The precipitate recrystallized from a little ethanol to give compound 14.

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2-(2-Amino-3-cyano-5,7-dithioxo thiopyrano[4,3-d]thiazol-4-yl)-6-(4-nitrophenylthio)benzthiazole 15

To a mixture of compound 4 (0.01 mole), carbon disulfide (2 ml, 0.01 mole), methanol (3 ml) and dimethyl formamide (0.5 ml) there was added triethylamine (0.6 ml) dropwise. The mixture was stirred at room temperature until the product starts to precipitate, the solid product was then filtered off, washed well with alcohol and recrystallized from chloroform-pet. ether (40–60°C).

2-(4-Dicyanomethylidine-5-phenylhydrazono-2-thioxo-thiazolidin-3-yl)-6-(4-nitrophenylthio)benzthiazole 16

To a solution of 4 (0.01 mole) in ethanol (50 ml) and sodium hydroxide solution (5 ml, 5%). There was added a solution of benzene diazonium chloride (prepared by adding sodium nitrite (0.01 mole) to the appropriate quantity of aniline in hydrochloric acid). The mixture was left at room temperature for 15 min. The solid obtained was collected and recrystallized from ethanol to give compound 16.

2-(4-Cyano-3-oxo-2-phenyl-6-thioxo thiazolo[5,4-c] pyridazin-5-yl)-6-(4-nitrophenylthio)benzthiazole 17

A solution of compound 16 (0.01 mole) in 50 ml of ethanol containing two pellets of sodium hydroxide was heated under reflux and evaporated in vacuo, the remaining product was triturated with water containing few drops of hydrochloric acid. The so formed solid product was collected by filtration.

Oxidation of diarylsulfides 5_{a-d}, 6_{a-d}, 10, 11_{a-c}, 14, 15 and 17 to their corresponding diarylsulfones 7_{a-d}, 8_{a-d}, 12, 13_{a-c}, 18, 19 and 20

GENERAL PROCEDURE

To diarylsulfide (0.02 mole) dissolved in glacial acetic acid (20 ml), there was added hydrogen peroxide (30%, 20 ml), the mixture was left at room temperature for 2–7 days and the deposited diarylsulfone collected and recrystallized from glacial acetic acid to give the corresponding diarylsulfone.

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