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SYNTHESIS AND SOME REACTIONS OF 4'- NITROPHENYL-BENZTHIAZOL-6-YL SULFIDES AND 4'-NITROPHENYL-BENZTHIAZOL-6-YL-SULFIDES CONTAINING THIAZOLIDINONES

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SYNTHESIS AND SOME REACTIONS OF 4'-NITROPHENYL-BENZTHIAZOL-6-YL SULFIDES AND 4'-NITROPHENYL-BENZTHIAZOL-6-YL-SULFONES CONTAINING THIAZOLIDINONES

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2-(2'-Thioxo-4'-oxo-thiazolidin-3'-yl)-6-(*p*-nitrophenylthio)benzthiazole **1** has been prepared and was condensed with aromatic aldehydes to give the corresponding 5-arylidene-thiazolidinones **2**. Bromination of compound **2** gave 5-(α,β -dibromoarylidene)thiazolidinones **3**. Reaction of the dibromo compound **3** with *o*-aminophenol gave spiro(benzomorpholine-2'',5'-thiazolidine) derivatives **4**. Reaction of **2** with hydrazine hydrate or phenylhydrazine gave the azine compounds **5**. The reactivity of **1** with nitrous acid, nitroso compounds, acid chlorides and diazonium salts was examined. Oxidation of compounds **4**, **5**, **7** and **8** using H₂O₂/AcOH mixture gave the corresponding diarylsulfones **10**, **11**, **12** and **13**.

Key words: Thiazolodiarlylsulfides, diarylsulfones, arylthiobenzthiazole, thiazolidinones, NMR.

INTRODUCTION

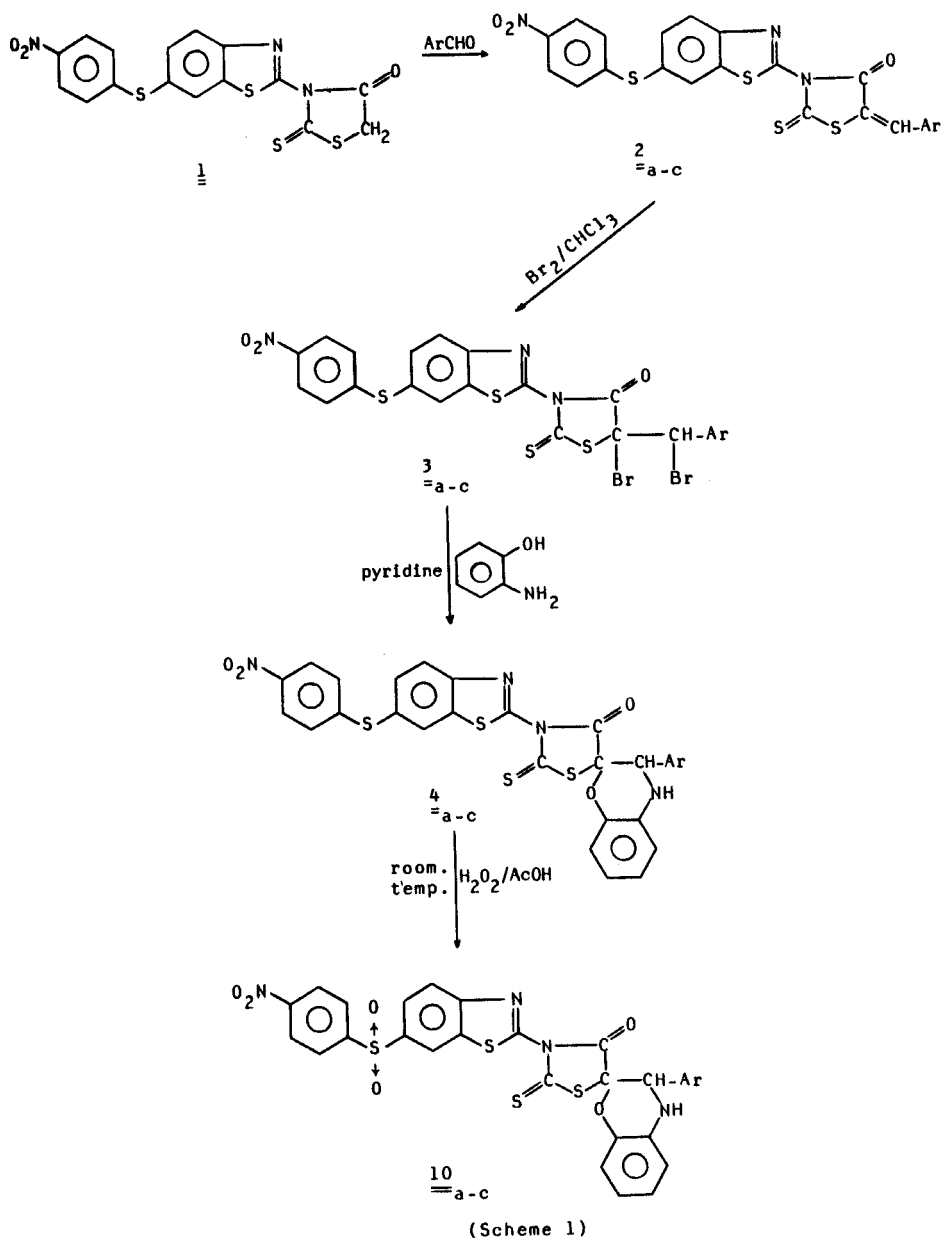
Diaryl sulfides and sulfones find wide clinical applications in the therapy of infectious diseases. These compounds exhibit antileprotic, bactericidal, insecticidal and antitubercular activities.^{1–3} Thiazoles and thiazolidinones were found to have a fungicidal activity⁴ due to the presence of the N-C-S linkage in these moieties.

5-substituted rhodanine derivatives were reported to have antibacterial activities.⁵ In view of the above and in continuation of our work,^{6,7} it seemed of interest to incorporate the rhodanine moiety into diarylsulfides and/or sulfones containing the thiazole fragment hoping to get improved biological activities.

RESULTS AND DISCUSSION

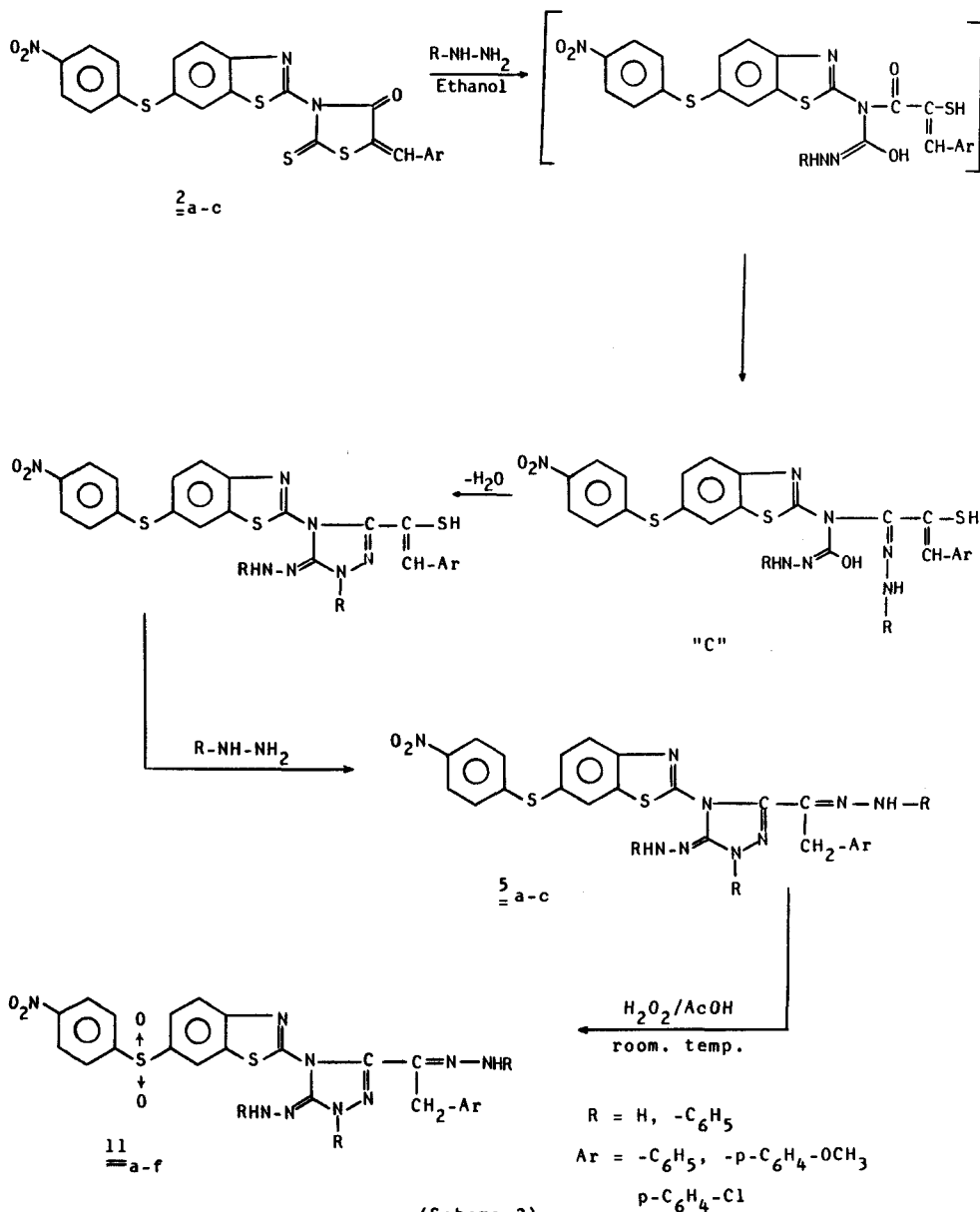
2-(2'-Thioxo-4'-oxo-thiazolidin-3'-yl)-6-(*p*-nitrophenylthio)benzthiazoles **1** was prepared and easily condensed with aromatic aldehydes at the active methylene group to give the corresponding 2-(5'-arylidene-2'-thioxo-4'-thiazolidinon-3'-yl)-6-(*p*-nitrophenylthio)benzthiazoles **2**_{a-c} according to the methods described in our previous work.⁷ Bromination of compounds **2**_{a-c} using Br₂/CHCl₃ gave 2-[5'(α,β -dibromo)arylidene - 2'-thioxo-4'-thiazolidinon-3'-yl]-6-(*p*-nitrophenylthio)benzthiazole **3**_{a-c}. It was stated that⁸ when a dibromochalcone of a heterocyclic compound reacts with *o*-aminophenol it produces a spiroheterocyclic compound. Applying this type of reaction to the dibromochalcone **3**_{a-c}, refluxing with *o*-aminophenol in pyridine gave the corresponding 2-[spiro-(benzomorpholine-2'',5'-thiazolidin-4'-one)-3'-aryl-2'-thioxo-3'-yl]-6-(*p*-nitrophenylthio)benzthiazole **4**_{a-c}. (Scheme 1).

Treatment of 5-arylidene rhodanines **2**_{a-c} with hydrazine hydrate or phenyl hy-



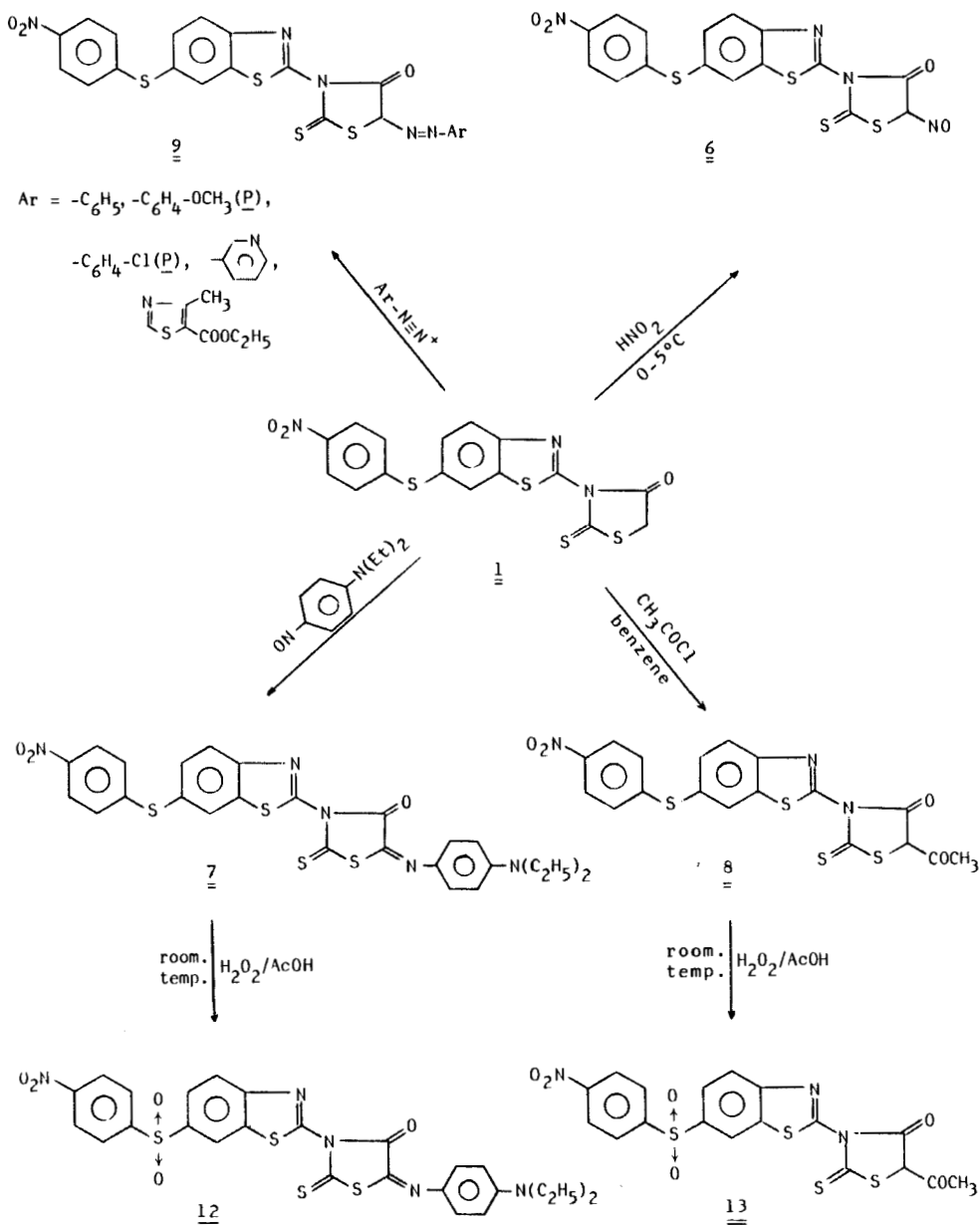
drazine in ethanol undergo ring cleavage leading to the formation of the azine compounds **5**_{a-c}.^{9,10} The reaction was thought to go through the formation of the intermediate (C) which was separated by carrying the reaction with hydrazines in benzene as a solvent, and the intermediate "C" was easily cyclized to compounds **5**_{a-c} by refluxing in ethanol. (Scheme 2).

The structure of compound "C" [R=H, Ar=C₆H₄—OCH₃(*p*)] was confirmed by the IR spectra which revealed the disappearance of the bands due to the C=O



and $\text{C}=\text{S}$ groups, of the parent compound 2-a-c and gave bands at (3300 cm^{-1} , 3150 cm^{-1}) related to NH and NH_2 groups.

The reactivity of the methylene group in rhodanine **1** was tested by its reaction with different reagents. Thus when compound **1** was reacted with nitrous acid at $0-5^\circ$ it yielded 5-nitrosorhodanine **6**. Also, condensation of compound **1** with *p*-nitroso-*N*-diethylaniline gave 5-(*p*-diethylaminophenylimino)rhodanine **7**. Acylation of compound **1** with acetyl chloride in benzene afforded 5-acetyl-rhodanine **8**. The active methylene center in compound **1** was easily coupled with a variety of



Scheme (3)

diazonium salts to give the corresponding 5-aryl azo rhodanines **9_{a-e}** (Scheme 3). Oxidation of compounds **4**, **5**, **7** and **8** using H_2O_2 /glacial acetic acid mixtures for 2–3 days at room temperature gave the corresponding sulfones **10**, **11**, **12** and **13**.

EXPERIMENTAL

Completion of the reaction and purity of the compounds were checked by TLC. Melting points were uncorrected. Elemental analyses were performed on a Perkin-Elmer 240 C elemental analyzer. IR

TABLE I
Yields and physical data of compounds (3-9)

Compound	M.P	% Yield*	Molecular formula	Elemental analysis						
					%C	%H	%N	%S	%Cl	%Br
3 _a	199-201°C	78	C ₂₃ H ₁₃ N ₃ O ₃ S ₄ Br ₂	Calc.	41.37	1.94	6.29	19.19	-	14.99
				found	41.55	2.11	6.74	19.37	-	15.37
3 _b	208-210°C	84	C ₂₃ H ₁₅ N ₃ O ₄ S ₄ Br ₂	calc.	41.31	2.15	6.02	18.36	-	22.95
				found	41.62	2.23	5.77	18.82	-	23.25
3 _c	143-145°C	73	C ₂₃ H ₁₂ N ₃ O ₃ S ₄ ClBr ₂	calc.	39.34	1.71	5.98	18.24	5.06	22.80
				found	39.12	1.45	5.69	18.31	4.82	22.46
4 _a	128-130°C	82	C ₂₉ H ₁₈ N ₄ O ₄ S ₄	calc.	56.67	2.93	9.12	20.64	-	--
				found	56.23	3.25	9.34	20.46	-	-
4 _b	171-172°C	95	C ₃₀ H ₂₀ N ₄ O ₅ S ₄	calc.	55.90	3.10	8.69	19.87	-	-
				found	55.64	2.87	8.82	20.17	-	-
4 _c	179-180°C	75	C ₂₉ H ₁₇ N ₄ O ₄ S ₄ Cl	calc.	53.66	2.62	8.63	19.73	5.47	-
				found	53.29	2.44	8.94	19.45	5.28	-
5 _a	173-175°C	65	C ₂₃ H ₁₉ N ₉ O ₂ S ₂	calc.	53.38	3.67	24.37	12.37	-	-
				found	53.77	3.29	24.72	12.46	-	-
5 _b	170-172°C	68	C ₂₄ H ₂₁ N ₉ O ₃ S ₂	calc.	52.65	3.83	23.03	11.70	-	-
				found	52.54	4.12	22.71	11.95	-	-
5 _c	131-133°C	62	C ₂₃ H ₁₈ N ₉ O ₂ S ₂ Cl	calc.	50.04	3.26	22.84	11.60	6.43	-
				found	50.43	3.57	23.28	11.85	6.17	-
5 _d	158-160°C	48	C ₄₁ H ₃₁ N ₉ O ₂ S ₂	calc.	66.04	4.16	16.91	8.29	-	-
				found	65.87	4.22	17.35	8.66	-	-
5 _e	139-140°C	55	C ₄₂ H ₃₃ N ₉ O ₃ S ₂	calc.	65.03	4.25	16.25	8.25	-	-
				found	65.36	3.87	16.51	8.59	-	-
5 _f	140-142°C	42	C ₄₁ H ₃₀ N ₉ O ₂ S ₂ Cl	calc.	63.11	3.84	16.16	8.21	4.55	-
				found	62.68	3.47	16.55	8.52	4.28	-
6 _v	169-170°C	76	C ₁₆ H ₈ N ₄ O ₄ S ₄	calc.	42.85	1.78	12.50	28.57	-	-
				found	42.65	2.15	12.92	28.84	-	-
7 _v	153-155°C	88	C ₂₆ H ₂₁ N ₅ O ₃ S ₄	calc.	53.88	3.62	12.08	22.10	-	-
				found	53.76	3.52	11.87	22.41	-	-
8 _v	195-196°C	78	C ₁₈ H ₁₁ N ₃ O ₄ S ₄	calc.	46.85	2.38	9.11	27.76	-	-
				found	46.93	2.49	9.24	27.35	-	-
9 _{wa}	180-182°C	74	C ₂₂ H ₁₃ N ₅ O ₃ S ₄	calc.	50.47	2.48	13.38	24.47	-	-
				found	50.65	2.17	13.54	24.35	-	-

TABLE I (Continued)

Compound	M.P	% Yield *	Molecular formula	Elemental analysis					
					%C	%H	%N	%S	%Cl %Br
9_{b}	134-135°C	65	$\text{C}_{23}\text{H}_{15}\text{N}_5\text{O}_4\text{S}_4$	calc.	49.90	2.71	12.65	23.14	- -
				found	50.19	2.53	12.78	23.56	- -
9_{c}	190-192°C	82	$\text{C}_{22}\text{H}_{12}\text{N}_5\text{O}_3\text{S}_4\text{Cl}$	calc.	47.35	2.15	12.55	22.95	6.36 -
				found	47.72	1.98	12.43	23.36	6.27 -
9_{d}	182-184°C	76	$\text{C}_{21}\text{H}_{12}\text{N}_6\text{O}_3\text{S}_4$	calc.	48.09	2.29	16.03	24.42	- -
				found	47.63	2.47	16.34	24.16	- -
9_{e}	177-179°C	72	$\text{C}_{23}\text{H}_{16}\text{N}_6\text{O}_5\text{S}_5$	calc.	45.54	2.64	13.86	26.40	- -
				found	45.86	2.54	13.59	26.13	- -

*The percentage yield of crude product (before recrystallization).

TABLE II
Yields and physical data of compounds (10-13)

Compound	M.P	% Yield *	Molecular formula	Elemental analysis				
					%C	%H	%N	%S %Cl
10_{a}	213-215°C	64	$\text{C}_{29}\text{H}_{18}\text{N}_4\text{O}_6\text{S}_4$	calc.	53.86	2.78	8.66	19.81 -
				found	53.47	3.12	8.54	20.18 -
10_{b}	195-197°C	68	$\text{C}_{30}\text{H}_{20}\text{N}_4\text{O}_7\text{S}_4$	calc.	53.25	2.95	8.28	18.93 -
				found	53.63	2.76	8.19	18.81 -
10_{c}	234-235°C	61	$\text{C}_{29}\text{H}_{17}\text{N}_4\text{O}_5\text{S}_4\text{Cl}$	calc.	51.13	2.49	8.22	18.80 5.21
				found	51.49	2.64	8.58	19.21 5.64
11_{a}	218-220°C	58	$\text{C}_{23}\text{H}_{19}\text{N}_9\text{O}_4\text{S}_2$	calc.	45.02	3.09	20.55	20.88 -
				found	44.87	3.41	20.67	20.64 -
11_{b}	204-205°C	65	$\text{C}_{24}\text{H}_{21}\text{N}_9\text{O}_5\text{S}_2$	calc.	50.61	3.69	22.14	11.24 -
				found	50.23	3.76	21.79	11.47 -
11_{c}	196-197	60	$\text{C}_{23}\text{H}_{18}\text{N}_9\text{O}_4\text{S}_2\text{Cl}$	calc.	47.30	3.08	21.59	10.96 6.08
				found	47.26	2.85	21.74	10.58 6.43
11_{d}	182-183°C	57	$\text{C}_{41}\text{H}_{31}\text{N}_9\text{O}_4\text{S}_2$	calc.	63.32	3.98	16.21	8.23 -
				found	63.54	4.23	16.61	8.57 -
11_{e}	163-165°C	56	$\text{C}_{42}\text{H}_{33}\text{N}_9\text{O}_5\text{S}_2$	calc.	62.45	4.08	15.61	7.93 -
				found	62.13	3.73	15.42	8.26 -

TABLE II (Continued)

Compound	M.P	% Yield*	Molecular formula	Elemental analysis					
					%C	%H	%N	%S	%Cl
11 <i>u</i>	178-179°C	53	C ₄₁ H ₃₀ N ₉ O ₄ S ₂ Cl	calc.	60.62	3.69	15.52	7.88	4.37
				found	60.93	3.47	15.88	7.64	4.76
12 <i>u</i>	213-215°C	74	C ₂₆ H ₂₁ N ₅ O ₅ S ₄	calc.	51.06	3.43	11.45	20.94	-
				found	51.42	3.56	11.69	20.73	-
13 <i>u</i>	269-270°C	78	C ₁₈ H ₁₁ N ₃ O ₆ S ₄	calc.	43.81	2.23	8.51	25.96	-
				found	43.65	2.47	8.29	26.27	-

*The percentage yield of crude product (before recrystallization).

TABLE III
IR and 1H NMR spectra of compounds (3-9)

Compound	IR Spectra (cm^{-1})	1H NMR spectra (δ in ppm)	Ref.
3a ✓	1710 ($C=O$), 1580 ($C=N$), 1500 ($N-C=S$), 1540, 1340 (NO_2) and 550 ($C-Br$).	-	14
3b ✓	1700 ($C=O$), 1585 ($C=N$), 1500 cm^{-1} ($N-C=S$), 1540, 1335(NO_2) and 550 ($C-Br$).	in DMSO, d_6 : δ 3.73(s, 3H, CH_3O), δ 5.80(s, 1H, Br-CH-Ar) and δ 7.15-8.20(m, 11H, Ar-H).	14
3c ✓	1700 ($C=O$), 1580 ($C=N$), 1500 ($N-C=S$), 1540, 1340 (NO_2), 550 ($C-Br$) and 750 ($C-Cl$).	-	14
4a ✓	3200 (NH), 1720 ($C=O$), 1500 ($N-C=S$) and 1540, 1340 (NO_2).	in DMSO, d_6 : δ 4.00 (s, 1H, NH) and δ 7.00-8.00 (m, 16H, Ar-H).	8
4b ✓	3200 (NH), 1720 ($C=O$), 1500 ($N-C=S$) and 1540, 1340 (NO_2).	in DMSO, d_6 : δ 3.33 (s, 2H, NH, CH), δ 3.80 (s, 3H, CH_3O) and δ 7.25-8.10 (m, 15H, Ar-H).	8
4c ✓	3150 (NH), 1690 ($C=O$), 1500 ($N-C=S$), 1545, 1440 (NO_2) and 750 ($C-Cl$).	-	8
5a ✓	3300, 3200 (NH, NH_2), 1600 ($C=N$) and 1540, 1340 (NO_2).	-	9,10

TABLE III (Continued)

Compound	IR Spectra (cm ⁻¹)	¹ H NMR spectra (in ppm)	Ref.
5 _{wb}	3300, 3150 (NH, NH ₂), 1600 (C=N) and 1540, 1340 (NO ₂).	in DMSO, d ₆ : δ3.75 (s, 5H, 9,10 NH, two NH ₂), δ3.83 (s, 3H, CH ₃ O), δ5.18 (s, 1H, C=CH) and δ6.80-8.10 (m, 11H, Ar-H).	
5 _{wc}	3300, 3160 (NH, NH ₂), 1600 (C=N) and 1540, 1340 (NO ₂).	in DMSO, d ₆ : δ3.40 (m, 7H, 9,10 NH, two NH ₂ , CH ₂) and δ7.15-8.38 (m, 11H, Ar-H).	
5 _{wd}	3200 (NH), 1580 (C=N) and 1540, 1340 (NO ₂).	-	
5 _{we}	3240 (NH), 1585 (C=N) and 1545, 1340 (NO ₂).	in DMSO, d ₆ : δ3.70 (s, 2H, two 9,10 NH), δ3.80 (s, 3H, CH ₃ O), δ3.20 (s, 2H, CH ₂), and δ6.80-8.00 (m, 26H, Ar-H).	
5 _{wf}	3200 (NH), 1580 (C=N) and 1545, 1340 (NO ₂).	-	9,10
6 _w	1720 (C=O), 1700 (NO), 1580 (C=N), 1500 (N-C=S) and 1525, 1340 (NO ₂).	-	
7 _w	1710 (C=O), 1580 (C=N), 1500 (N-C=S), and 1525, 1340 (NO ₂).	in DMSO, d ₆ : δ1.32 [t, 6H, 2CH ₃ (CH ₃ CH ₂)], δ3.85 [q, 4H, 2CH ₂ (CH ₃ CH ₂)] and δ7.20-8.40 (m, 11H, Ar-H).	
8 _w	1730, 1700 (C=O), 1585 (C=N), 1505 (N-C=S) and 1540, 1325 (NO ₂)	in DMSO, d ₆ : δ2.28 (s, 3H, CH ₃ C=O) and δ7.26-8.20 (m, 7H, Ar-H).	
9 _{wa}	1720 (C=O), 1580 (N=N), 1500 (N-C=S) and 1545, 1340 (NO ₂).	-	
9 _{wb}	1710 (C=O), 1585 (N=N), 1500 (N-C=S) and 1540, 1325 (NO ₂).	in DMSO, d ₆ : δ3.80 (s, 3H, CH ₃ O), δ4.1 (s, 1H, NH), δ4.40 (s, 1H, CH-N=N) and δ7.21-8.50 [m, 11H (7H, Ar-H, 4H of pyridine)].	15
9 _{wc}	1720 (C=O), 1580 (N=N), 1500 (N-C=S) and 1540, 1340 (NO ₂).	-	15

TABLE III (Continued)

Compound	IR Spectra (cm ⁻¹)	¹ H NMR spectra (δ in ppm)	Ref.
ν_d^g	1710 (C=O), 1575 (N=N), 1500 (N-C=S) and 1545, 1340 (NO ₂).	-	
ν_e^g	1720 (C=O), 1585 (N=N), 1500 (N-C=S) and 1545, 1340 (NO ₂).	-	

TABLE IV
IR and NMR spectra of compounds (10-13)

Compound	IR spectra (cm ⁻¹)	¹ H NMR spectra (ppm)	Ref.
10 _{wa}	3200(NH), 1700(C=O), 1500(N-C=S), 1530, 1340(NO ₂) and 1350, 1160(SO ₂).	-	
10 _{wb}	3220(NH), 1710(C=O), 1540, 1325(NO ₂) and 1350, 1160(SO ₂).	-	
10 _{wc}	3240(NH), 1700(C=O), 1500(N-C=S), 1535, 1340(NO ₂) and 1350, 1160(SO ₂).	-	
11 _{wa}	3300, 3200(NH, NH ₂), 1600(C=N), 1540, 1325(NO ₂) and 1350, 1160(SO ₂).	-	
11 _{wb}	3300, 3150(NH, NH ₂), 1600(C=N), 1540, 1340(NO ₂) and 1350, 1160(SO ₂).	-	
11 _{wc}	3300, 3150(NH, NH ₂), 1600(C=N), 1540, 1335(NO ₂), 1350, 1160(SO ₂) and 750(C-Cl).	-	
11 _{wd}	3200(NH), 1600(C=N), 1540, 1325(NO ₂) and 1350, 1160(SO ₂).	in DMSO-d ₆ : δ 3.30[s, 4H(2H, NH; 2H, CH ₂)] and δ 6.80-8.20(m, 27H, Ar-H).	
11 _{we}	3250(NH), 1600(C=N), 1545, 1340(NO ₂) and 1350, 1160(SO ₂).	in DMSO-d ₆ : δ 3.40[4H(s, 2H, NH; 2H, CH ₂)] and δ 7.20-8.30(m, 27H, Ar-H).	
11 _{wf}	3200(NH), 1600(C=N), 1540, 1325(NO ₂) and 1350, 1160(SO ₂).	-	
12 _w	1720(C=O), 1580(C=N), 1505(N-C=S), 1540, 1340(NO ₂) and 1350, 1160(SO ₂).		
13 _w	1720(C=O), 1580(C=N), 1500(N-C=S), 1540, 1325(NO ₂) and 1340, 1165(SO ₂).	-	

spectra were taken on a Pye-Unicam infrared spectrophotometer using the KBr wafer technique. ^1H NMR spectra were recorded by a 90 MHz varian NMR spectrometer in a suitable deuterated solvent using TMS as the internal standard.

2-(2'-Thioxo-4'-oxo-thiazolidin-3'-yl)-6-(*p*-nitrophenylthio)benzthiazole **1** has been prepared according to the method described in our previous work⁷ by reaction of 2-amino-6-(*p*-nitrophenylthio)benzthiazole with carbon disulfide in the presence of aqueous sodium hydroxide in *N,N*-dimethyl formamide as solvent, to form the sodium salt of the dithiocarbonimidic acid, which was alkylated with mono chloroacetic acid and treated with HCl to give compound **1**.

2-(5'-Arylidene-4'-oxo-2'-thioxo-thiazolidin-4'-yl)-6-(*p*-nitrophenylthio)benzthiazole **2_{a-c}** was prepared by a method described previously⁷ through interaction of **1** with the appropriate aromatic aldehydes.

2-(5'- α,β -Dibromo-4'-oxo-2'-thioxo-thiazolidin-3'-yl)-6-(*p*-nitrophenylthio)benzthiazole **3_{a-c}**: To 2-(5'-arylidene-4'-oxo-2'-thioxo-thiazolidin-3'-yl)-6-(*p*-nitrophenylthio)benzthiazole **2_{a-c}** (0.02 mole) dissolved in chloroform (20 ml), bromine (0.02 mole) dissolved in chloroform (20 ml) was added dropwise with vigorous shaking. The reaction mixture stood overnight. The precipitate was filtered and recrystallized from ethanol to give compounds **3_{a-c}**. Yields and physical constants of compounds **3_{a-c}** are listed in Table I.

2-[Spiro-(benzomorpholine - 2',5'-thiazolidin-4'-one)-3"-aryl - 2'-thioxo - 3'-yl]-6-(*p*-nitrophenylthio)benzthiazole **4_{a-c}**: To a solution of the dibromo compound **3_{a-c}** (0.01 mole) in pyridine (20 ml), *o*-aminophenol (0.01 mole) was added and the resulting mixture heated on a water bath for one hour. The reaction mixture was diluted with water (20 ml), the precipitated product filtered and recrystallized from ethanol to give compounds **4_{a-c}**. Yields and physical constants of compounds **4_{a-c}** are listed in Table I.

Reactions of 2-(5'-arylidene-4'-oxo-2'-thioxo-thiazolidin-3'-yl)-6-(*p*-nitrophenylthio)benzthiazole **2_{a-c} with hydrazines:** To a solution of **2_{a-c}** (0.01 mole) in ethanol (50 ml) there was added excess phenylhydrazine or hydrazine hydrate (0.038 mole). The reaction mixture was refluxed on a water bath for about 4 hours, cooled and the resulting precipitate filtered and recrystallized from chloroform-pet-ether (40–60) mixture to give compounds **5_{a-f}**.

The yields and physical constants of compounds **5_{a-f}** are listed in Table I.

2-(5'-Nitroso-4'-oxo-2'-thioxo-thiazolidin-3'-yl)-6-(*p*-nitrophenylthio)benzthiazole **6**: To an ice-cooled solution of 2-(2'-thioxo-4'-oxo-thiazolidin-3'-yl)-6-(*p*-nitrophenylthio)benzthiazole **1** (0.01 mole) in ethanol (20 ml) and hydrochloric acid (5 ml), sodium nitrite solution (0.12 mole) was added dropwise over a period of 30 minutes while stirring (temperature did not exceed 5°C). The reaction mixture was allowed to remain at 0–5°C overnight. The precipitate was separated, washed with water and recrystallized from ethanol to give orange crystals of **6**, mp. 169–170°C.

2-[5'-(*p*-Diethylamino-phenylimino)-4'-oxo-2'-thioxo-4'-thiazolidin-3'-yl]-6-(*p*-nitrophenylthio)benzthiazole **7**: An equimolar amount of **1** (0.01 mole) and *p*-nitroso-*N*-diethylaniline (0.01 mole) were heated on a water bath for about 3–4 minutes, ethanol (20 ml) was added and the mixture refluxed for about 2 hours, and then cooled. The product was filtered off and recrystallized from ethanol to give compound **7** (in 88% yield), mp. 153–155°C.

2-(5'-Acetyl-4'-oxo-2'-thioxo-4'-thiazolidin-3'-yl)-6-(*p*-nitrophenylthio)benzthiazole **8**: To a solution of compound **1** (0.01 mole) in benzene there was added acetyl chloride (0.012 mole) and the reaction mixture then heated on a water bath for 4 hours. The solvent was evaporated, the residue washed well with petroleum ether (40–60) and then recrystallized from acetic acid, mp. 195–196°C.

2-(5'-Arylazo-4'-oxo-2'-thioxo-4'-thiazolidin-3'-yl)-6-(*p*-nitrophenylthio)benzthiazole **9_{a-c}**: A solution of diazotized aromatic amine (0.01 mole) (prepared following the procedure described by Vogel)¹¹ and heterocyclic amine (prepared according to the procedure described in literature)^{12,13} was added dropwise in an ice-cooled mixture of **1** (0.01 mole), acetone (10 ml) and acetic acid (10 ml). After one hour the mixture was diluted with water and kept overnight. The solid product was filtered, washed well with water and recrystallized from chloroform pet-ether (40–60) mixture. Yields and physical constants of compounds **9_{a-c}** are listed in Table I.

Oxidation of diarylsulfides **4, **5**, **7** and **8** to their corresponding diarylsulfones **10**, **11**, **12** and **13**:** *General Procedure:* To diarylsulfides **4–8** (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 2–3 days and the deposited diarylsulfone collected and recrystallized from glacial acetic acid to give compounds **10**, **11**, **12**, and **13**.

Yields and physical constants of compounds **10–13** are listed in Table II.

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