

BRIDGEHEAD NITROGEN HETEROCYCLES. PART V[#]. SYNTHESIS OF
 SOME 1,3,4-OXA/THIADIAZOLO(3,2-a)PYRIMIDIN-5-ONES, 1,3,4-
 OXA/THIADIAZOLO(3,2-a)(1,3,5)TRIAZIN-7-THIONES, 1,3,4-
 THIADIAZOLO(3,2-a)(1,3,5)TRIAZINE-5(6H,7H)- THIONES, 1,2,4-
 TRIAZOLO(3,4-b)(1,3,4)THIADIAZINE AND THIADIAZOLES
 DERIVATIVES

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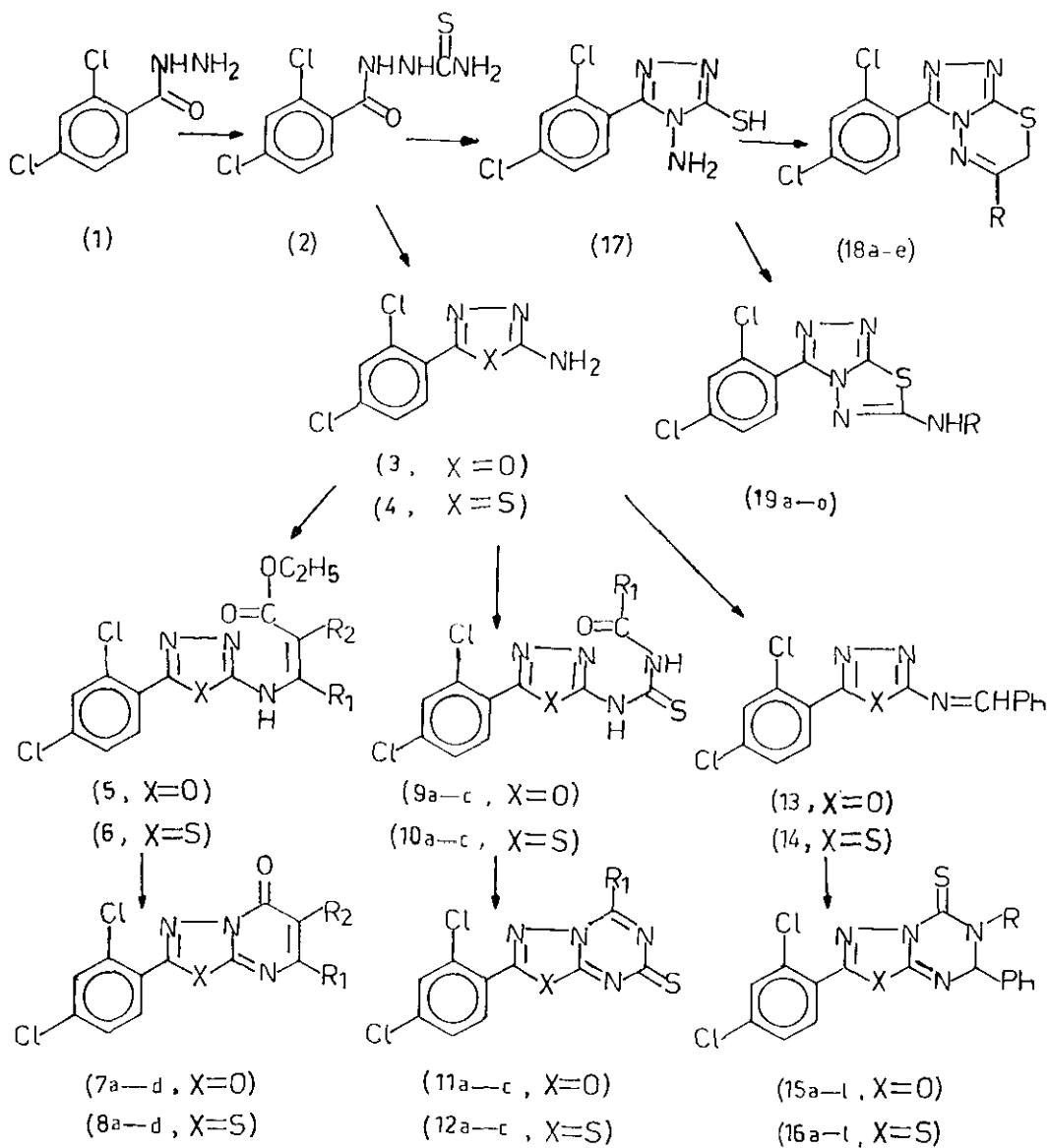
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Abstract - 1,3,4-Oxa/thiadiazolo(3,2-a)pyrimidin-5-ones
 (7a-d, 8a-d), 1,3,4-oxa/thiadiazolo(3,2-a)(1,3,5)triazin-
 7-thiones(11a-c, 12a-c), 1,3,4-oxa/thiadiazolo(3,2-a-
 (1,3,5)triazine-5(6H,7H)- thiones(15a-1, 16a-1), 1,2,4-
 triazolo(3,4-b)(1,3,4)thiadiazines (18a-e) and 1,2,4-
 triazolo(3,4-b)(1,3,4)thiadiazoles (19a-o) were
 synthesized. The physical and spectral data of the
 new compounds were described.

The work described here forms a part of our general program¹ on the studies of the chemistry of heterocycles and in particular on bridgehead nitrogen heterocycles.^{2a-c} In recent years chemistry of nitrogen bridgehead heterocycles has made an impact in organic chemistry.^{3a-c} It was reported that active methylene compounds condensed with 2-amino-1,3,4-oxa/thiadiazoles yielded oxa/thiadiazolo-pyrimidine-5-ones.⁴ 2-Amino-1,3,4-oxa/thiadiazoles

[#]Part IV. P. C. Gogoi and J. C. S. Katakay, Heterocycles, 1991, 32, 237.

on treatment with acyl chlorides and ammonium thiocyanate gave the fused 2,5-disubstituted 1,3,4-oxa/thiadiazolo(3,2-a)(1,3,5)triazin-7-thiones.⁵ Cycloaddition reactions of aryl isothiocyanates to 2-benzylideneamino derivatives of 5-substituted 1,3,4-oxa/thiadiazoles constitute an ideal approach to the synthesis of bridgehead nitrogen heterocycles.^{3e,f} Cyclocondensation of 4-amino-3-aryl-1,2,4-triazole-5-thiol with α -chloroacetonitrile, α -halocarbonyl compounds and isothiocyanates is another approach for the synthesis of 7H-1,2,4-triazolo(3,4-b)(1,3,4)thiadiazine,⁶ and 1,2,4-triazolo(3,4-b)(1,3,4)thiadiazole.^{7,8} In a continuation of our interest in the chemistry of bridgehead nitrogen heterocycles^{1h,2a-c} we wish to describe here the synthesis of the fused 1,3,4-oxa/thiadiazoles and 1,2,4-triazoles. Exploration of these studies is principally directed towards the synthesis of new nitrogen bridged heterocycles. The results obtained during this attempt are reported in this paper. The required 2-amino-5-(2,4-dichlorophenyl)-1,3,4-oxa/thiadiazoles (3,4) were prepared by the reaction of 2,4-dichlorobenzohydrazide (1) with potassium thiocyanate and concentrated hydrochloric acid and subsequent cyclization of 2 in presence of iodine in potassium iodide or phosphoric acid respectively.⁹ The reaction of 2-amino-5-(2,4-dichlorophenyl)-1,3,4-oxa/thiadiazoles (3,4) with ethyl acetoacetate or diethyl malonate gave 7-substituted 2-(2,4-dichlorophenyl)-1,3,4-oxa/thiadiazolo(3,2-a)pyrimidin-5-ones (7a-b, 8a-b). When the reaction with diethyl malonate was carried out in the presence of phosphoryl chloride and polyphosphoric acid (PPA) the cyclized products 7-chloro-2-(2,4-dichlorophenyl)-5H-1,3,4-oxa/thiadiazolo(3,2-a)pyrimidin-5-ones (7c, 8c) were obtained. The same reaction of compound 3/4 when carried out with diethyl ethoxymethylenemalonate (DEMM) gave the cyclised product 6-ethoxycarbonyl-2-(2,4-dichlorophenyl)-1,3,4-oxa/thiadiazolo(3,2-a)pyrimidin-5-ones (7d, 8d). The reaction took place also with the formation of the uncyclized products (5,6) which were isolated and characterized. These uncyclized products were formed when the reactions were carried out at room temperature and the products isolated were subsequently cyclized to the desired compounds. In a



Scheme 1

similar manner 5-alkyl/aryl-2-(2,4-dichlorophenyl)-1,3,4-oxa/thiadiazolo (3,2-a)(1,3,5)triazin-7-thiones (11a-c, 12a-c) were obtained by the reaction of the amino compounds (3,4) with acyl halides and ammonium thiocyanates in acetone which gave the uncyclized thiourea derivatives (9a-c, 10a-c) then cyclized in the presence of phosphoryl chloride and phosphorus pentachloride to give the compounds (11a-c, 12a-c)(Scheme 1). 5-(2,4-Dichlorophenyl)-1,3,4-oxa/thiadiazol-2-iminobenzylidene (13,14) were prepared by the reaction of 3/4 with benzaldehyde using the reported method.^{1f}

Benzylidene derivatives (13,14) react with aryl isothiocyanates in refluxing toluene to give 1,4-cycloadducts (15a-1, 16a-1). 4-Amino-3-(2,4-dichlorophenyl)-1,2,4-triazol-5-thiol (17) was prepared by the reaction of 2,4-dichlorobenzoylhydrazine (1) and carbon disulphide in presence of potassium hydroxide and subsequent cyclisation in presence of hydrazine hydrate (98%) using the reported method.^{1a} Triazole (17) reacts with phenacyl halides in ethanol followed by neutralization with potassium carbonate afforded 7H-6-aryl-3-(2,4-dichlorophenyl)-1,2,4-triazolo(3,4-b)(1,3,4)thiadiazine (18a-d). Triazole (17) reacts with chloroacetonitrile to give cyanomethylthio derivative which on cyclization gave 7H-6-amino-3-(2,4-dichlorophenyl)-1,2,4-triazolo(3,4-b)(1,3,4)thiadiazine (18e, R=NH₂). Triazole (17) reacts with aryl isothiocyanates in dry dimethylformamide at room temperature to afford the uncyclized substituted thiourea derivatives which upon refluxing had cyclized into 6-arylamino-3-(2,4-dichlorophenyl)-1,2,4-triazolo(3,4-b)(1,3,4)thiadiazoles (19a-m).^{8b} In our attempt the reaction was carried in presence of dicyclohexylcarbodiimide (DCC) and fused triazoles were formed. Cyanogen bromide is finding increasing use in heterocyclic synthesis⁷ and when used in place of aryl isothiocyanates it gave 6-amino-3-(2,4-dichlorophenyl)-1,2,4-triazolo(3,4-b)(1,3,4)thiadiazole (19n, R=H). Triazole (17) on reaction with benzoyl isothiocyanate¹⁰ in acetone yielded 6-benzoylamino-3-(2,4-dichlorophenyl)-1,2,4-triazolo(3,4-b)(1,3,4)thiadiazole (19o, R=COC₆H₅)(Scheme 1).

EXPERIMENTAL

Melting points were determined with a Buchi oil heated apparatus in open capillaries and are uncorrected. Ir spectra were recorded with a Perkin-Elmer 580B spectrophotometer using potassium bromide discs unless otherwise stated (ν_{\max} in cm^{-1}). ^1H Nmr spectra were recorded in solutions stated with TMS as the internal reference in 60 MHz and 90 MHz on a Varian T-60 and Zeol Fx-90 spectrometers (chemical shifts in δ ppm). 2,4-Dichlorobenzhydrazide (1) was prepared from ethyl 2,4-dichlorobenzoate following the reported method.^{1b} 2-Amino-5-(2,4-dichlorophenyl)-1,3,4-oxa/thiadiazoles (3,4) were prepared using the known method.⁹ 4-Amino-3-(2,4-dichlorophenyl)-1,2,4-triazol-5-thiol (17) was prepared using the method of Goswami *et al.*^{1a}

2-(2,4-Dichlorophenyl)-7-methyl-5H-1,3,4-oxa/thiadiazolo(3,2-a)pyrimidin-5-ones (7a, 8a)

A mixture of compound (3)(1.61 g, 0.007 mol), ethyl acetoacetate (2 g, 0.015 mol) and *p*-toluenesulphonic acid (0.1 g) in toluene (100 ml) was refluxed for 24 h using a Dean Stark apparatus to remove water. The reaction mixture was cooled to room temperature and diluted with 100 ml of cyclohexane to give a grey solid. The solid was filtered and crystallized from $\text{C}_2\text{H}_5\text{OH}$ to give compound 7a. The filtrate was evaporated and triturated with cyclohexane to give a pasty mass which was dissolved in $\text{C}_2\text{H}_5\text{OH}$ and filtered hot. The solution on cooling gave colourless solid of ethyl 3-(5-(2,4-dichlorophenyl)-1,3,4-oxadiazol-2-ylamino)-2-butenate (5)(0.7 g). Compound (5)(0.5 g, 0.0015 mol) and *p*-toluenesulphonic acid (0.1 g) in toluene (30 ml) was refluxed for 36 h. The solvent was evaporated to half and the residue was cooled to room temperature to give a solid which was filtered and crystallized from $\text{C}_2\text{H}_5\text{OH}$ to afford compound 7a. Similarly the compound (8a) was also prepared. The physical and spectral data of these compounds are given in Table 1 and Table 2.

2-(2,4-Dichlorophenyl)-7-hydroxy-5H-1,3,4-oxa/thiadiazolo(3,2-a)pyrimidin-5-ones (7b, 8b)

A mixture of compound (3)(2.3 g, 0.01 mol), diethyl malonate (DEM)

(3.2 g, 0.02 mol), *p*-toluenesulphonic acid (0.1 g) and 1,2,4-trichlorobenzene (25 ml) was heated at 240°C for 2 h. The oily mass was dissolved in ethyl acetate and filtered through a silica gel column. The filtrate was evaporated and the solid mass thus obtained was refluxed in toluene (12 ml) and *p*-toluenesulphonic acid (0.001 g) for 40 h. Then the solvent was removed and the solid obtained was crystallized from C₂H₅OH to give compound 7b. Similarly compound (8b) was also prepared.

7-Chloro-2-(2,4-dichlorophenyl)-5H-1,3,4-oxa/thiadiazolo(3,2-a)pyrimidin-5-ones (7c, 8c)

A mixture of compound (3)(2.3 g, 0.01 mol), diethyl malonate (3.2 g, 0.02 mol) and phosphoryl chloride (4.6 g, 0.03 mol) was heated in presence of PPA (1 g) at 120°C for 3 h. Dry C₂H₅-OH was then carefully added and the resulting solid was filtered and washed with ether. It was then neutralized with 10% aqueous sodium hydrogen carbonate solution and recrystallized from acetone:hexane mixture (3:1) to afford compound 7c. Similarly compound (8c) was also prepared.

6-Ethoxycarbonyl-2-(2,4-dichlorophenyl)-1,3,4-oxa/thiadiazolo(3,2-a)pyrimidin-5-ones (7d, 8d)

A mixture of compound (3)(2.3 g, 0.01 mol) and DEMM (3.2 g, 0.015 mol) was heated at 170-180°C for 6 h. The reaction mixture was then cooled, filtered and washed with petroleum spirit and then with ethyl acetate. The solid thus separated was recrystallized from acetone to afford compound 7d. Following the same procedure compound (8d) was prepared. The physical and spectral data are given in Table 1 and Table 2.

N-Acyl-N'-(5-(2,4-dichlorophenyl)-1,3,4-oxa/thiadiazol-2-yl)thiourea (9a-c, 10a-c)

A mixture of ammonium thiocyanate (0.076 g, 0.01 mol) and acid chloride

(0.01 mol) in acetone (25 ml) was refluxed for 30 min. Compound (3)(2.3 g, 0.01 mol) was then added to it and the mixture was refluxed further 3 h. The mixture was then poured into excess water (500 ml). The resulting solid was dried and crystallized from C_2H_5OH : acetone (50 : 50 v/v) to give compound (9a). Following the same procedure compounds (9b-c, 10b-c) were prepared.

5-Alkyl/aryl-2-(2,4-dichlorophenyl)-1,3,4-oxa/thiadiazolo(3,2-a)(1,3,5)-triazin-7-thiones (11a-c, 12a-c)

A mixture of compounds (9a-c)(0.015 mol), phosphoryl chloride (15 ml, 0.16 mol) and phosphorus pentachloride (3.12 g, 0.015 mol) was refluxed for 4 h. The excess phosphoryl chloride was then removed by distillation and the residue was poured into crushed ice. The resulting solid was filtered, washed with water and crystallized from C_2H_5OH to give compounds (11a-c). The same procedure was followed to convert (10a-c) to (12a-c). The physical and spectral data are given in Table 1 and Table 2.

5-(2,4-Dichlorophenyl)-2-iminobenzylideneamino-1,3,4-oxa/thiadiazoles (13,14)

A mixture of 3,4 (0.01 mol) and benzaldehyde (1.06 g, 0.01 mol) was refluxed in C_2H_5OH (50 ml) in the presence of 2 drops of piperidine. After refluxing for 2 h, solvent was removed under reduced pressure to give solid on cooling. The solid was filtered and recrystallized from C_2H_5OH to get compounds (13,14)(80% yield).

6-Aryl-2-(2,4-dichlorophenyl)-7-phenyl-1,3,4-oxa/thiadiazolo(3,2-a)(1,3,5)-triazin-5(6H,7H) thiones (15a-l, 16a-l)

General Method :

A mixture of compounds (13,14)(0.01 mol) and aryl isothiocyanates (0.01 mol) in toluene (100 ml) was refluxed for 6 h. The solvent was removed by distillation and the residue was washed with small amount of C_2H_5OH (15 ml) followed by water (25 ml). The solid was recrystallised from C_2H_5OH to give

Table 1 : Physical data of compounds (7-19)

Compd No	R/R ₁	R ₂	Yield (%)	mp (°C)	Analysis (%)					
					Found			Calcd		
					C	H	N	C	H	N
1	2	3	4	5	6	7	8	9	10	11
7a	CH ₃	H	84	219	48.60	2.30	14.12	48.64	2.36	14.18
7b	OH	H	70	198	44.21	1.61	14.03	44.29	1.68	14.09
7c	Cl	H	70	215	41.70	1.20	13.25	41.77	1.27	13.29
7d	H	COOC ₂ H ₅	70	220	47.42	2.49	11.82	47.45	2.54	11.86
8a	CH ₃	H	73	215	46.10	2.18	13.40	46.15	2.24	13.46
8b	OH	H	86	205	42.10	1.50	13.30	42.03	1.53	13.37
8c	Cl	H	74	221	39.70	1.16	12.59	39.75	1.20	12.65
8d	H	COOC ₂ H ₅	71	212	45.49	2.40	11.29	45.40	2.43	11.35
9a	CH ₃	-	70	208	39.81	2.38	16.89	39.87	2.42	16.91
9b	C ₆ H ₅	-	72	200	48.80	2.50	14.28	48.85	2.54	14.24
9c	2,4-Cl ₂ -C ₆ H ₃	-	81	187	41.50	1.70	12.18	41.55	1.73	12.12
10a	CH ₃	-	83	290	38.09	2.28	16.19	38.04	2.31	16.13
10b	C ₆ H ₅	-	79	224	46.98	2.40	13.60	46.94	2.44	13.69
10c	2,4-Cl ₂ -C ₆ H ₃	-	82	192	40.12	1.60	11.78	40.16	1.67	11.71
11a	CH ₃	-	71	198	42.11	1.58	17.82	42.17	1.61	17.89
11b	C ₆ H ₅	-	68	178	51.28	2.09	14.98	51.20	2.13	14.93
11c	2,4-Cl ₂ -C ₆ H ₃	-	72	172	43.28	1.30	12.67	43.24	1.35	12.61
12a	CH ₃	-	75	261	40.18	1.78	17.08	40.12	1.82	17.02
12b	C ₆ H ₅	-	69	201	49.16	2.01	14.38	49.10	2.05	14.32
12c	2,4-Cl ₂ -C ₆ H ₃	-	72	180	41.76	1.27	12.13	41.73	1.30	12.17
13	-	-	80	205	56.65	2.80	13.10	56.60	2.83	13.20
14	-	-	80	222	53.82	2.61	12.53	53.89	2.69	12.57
15a	C ₆ H ₅	-	65	210	58.35	3.05	12.38	58.28	3.09	12.36
15b	4-Br-C ₆ H ₄	-	72	230	49.68	2.41	10.55	49.62	2.44	10.53
15c	4-Cl-C ₆ H ₄	-	70	190	54.27	2.61	11.58	54.21	2.67	11.50
15d	2-Cl-C ₆ H ₄	-	75	180	54.26	2.63	11.56	54.21	2.67	11.50

	1	2	3	4	5	6	7	8	9	10	11
15e	3-Cl-C ₆ H ₄	-	72	210	54.27	2.62	11.58	54.21	2.67	11.50	
15f	2-NO ₂ -C ₆ H ₄	-	68	220	53.11	2.55	14.10	53.01	2.61	14.06	
15g	4-NO ₂ -C ₆ H ₄	-	68	235	53.09	2.58	14.03	53.01	2.61	14.06	
15h	3-NO ₂ -C ₆ H ₄	-	70	260	53.08	2.57	14.12	53.01	2.61	14.06	
15l	2-CH ₃ -C ₆ H ₄	-	72	205	59.15	3.41	11.95	59.10	3.43	11.99	
15j	4-CH ₃ -C ₆ H ₄	-	65	209	59.18	3.40	12.00	59.10	3.43	11.99	
15k	2-OCH ₃ -C ₆ H ₄	-	72	195	57.10	3.27	11.53	57.14	3.31	11.59	
15l	4-OCH ₃ -C ₆ H ₄	-	70	229	57.19	3.27	11.53	57.14	3.31	11.59	
16a	C ₆ H ₅	-	65	202	56.32	2.91	11.98	56.29	2.98	11.94	
16b	4-Br-C ₆ H ₄	-	62	195	48.12	2.30	10.25	48.18	2.37	10.22	
16c	4-Cl-C ₆ H ₄	-	70	190	52.52	2.50	11.18	52.49	2.58	11.13	
16d	2-Cl-C ₆ H ₄	-	80	220	52.55	2.52	11.15	52.49	2.58	11.13	
16e	3-Cl-C ₆ H ₄	-	65	218	52.46	2.53	11.19	52.49	2.58	11.13	
16f	2-NO ₂ -C ₆ H ₄	-	72	206	51.38	2.50	13.65	51.36	2.53	13.62	
16g	4-NO ₂ -C ₆ H ₄	-	59	190	51.42	2.49	13.65	51.36	2.53	13.62	
16h	3-NO ₂ -C ₆ H ₄	-	62	228	51.40	2.49	13.64	51.36	2.53	13.62	
16l	2-CH ₃ -C ₆ H ₄	-	72	230	52.18	3.32	11.52	57.14	3.31	11.59	
16j	4-CH ₃ -C ₆ H ₄	-	70	252	52.19	3.28	11.55	57.14	3.31	11.59	
16k	2-OCH ₃ -C ₆ H ₄	-	65	205	55.38	3.18	11.28	55.31	3.21	11.22	
16l	4-OCH ₃ -C ₆ H ₄	-	68	209	55.36	3.25	11.27	55.31	3.21	11.22	
18a	CH ₃	-	45	180	44.27	2.74	18.65	44.15	2.66	18.73	
18b	C ₆ H ₅	-	50	220	53.25	2.68	15.40	53.18	2.77	15.51	
18c	2,4-Cl ₂ -C ₆ H ₃	-	60	210	44.42	1.73	13.05	44.65	1.86	13.02	
18d	4-Br-C ₆ H ₄	-	65	180	43.82	2.11	12.84	43.63	2.04	12.72	
18e	NH ₂	-	62	250	40.10	2.38	23.40	40.00	2.33	23.33	
19a	C ₆ H ₅	-	55	215	49.82	2.54	19.38	49.72	2.48	19.34	
19b	4-Br-C ₆ H ₄	-	60	280	40.92	1.87	15.80	40.82	1.81	15.87	
19c	4-Cl-C ₆ H ₄	-	65	250	45.39	2.10	17.69	45.34	2.01	17.63	
19d	2-Cl-C ₆ H ₄	-	68	189	45.30	2.08	17.70	45.34	2.01	17.63	

	1	2	3	4	5	6	7	8	9	10	11
19e	3-Cl-C ₆ H ₄	-	65	230	45.38	2.09	17.69	45.34	2.01	17.63	
19f	2-NO ₂ -C ₆ H ₄	-	75	190	44.28	1.91	20.71	44.23	1.96	20.64	
19g	N-NO ₂ -C ₆ H ₄	-	65	280	44.27	1.92	20.72	44.23	1.96	20.64	
19h	3-NO ₂ -C ₆ H ₄	-	70	275	44.28	1.91	20.70	44.23	1.96	20.64	
19i	2-CH ₃ -C ₆ H ₄	-	50	210	51.12	2.98	18.61	51.06	2.92	18.62	
19j	4-CH ₃ -C ₆ H ₄	-	55	230	51.15	2.95	18.68	51.06	2.92	18.62	
19k	2-OCH ₃ -C ₆ H ₄	-	60	260	48.90	2.85	17.91	48.98	2.81	17.86	
19l	4-OCH ₃ -C ₆ H ₄	-	65	280	48.95	2.86	17.95	48.98	2.81	17.86	
19m	C ₆ H ₄ CH ₂	-	50	198	51.28	2.60	18.72	51.20	2.66	18.66	
19n	H	-	50	240	37.81	1.80	24.53	37.76	1.74	24.47	
19o	CO-C ₆ H ₅	-	49	160	49.28	2.38	17.90	49.23	2.31	17.95	

Table 2 : Spectral data of compounds (7-19)

Compd No	ir (KBr) ν cm^{-1}	^1H nmr (δ ppm, DMSO- d_6)
1	2	3
7a	1695	3.4(s, 3H), 6.5(s, 1H), 7.2-7.6(m, Ar-H)
7b	1700, 3300	6.5(s, 1H), 7.1-7.5(m, Ar-H)
7c	1695	6.5(s, 1H), 7.3-7.6(m, Ar-H)
7d	1680, 1710	1.4(t, J=7Hz, 3H), 4.4(q, J=7Hz, 2H), 7.1(s, 1H), 7.2-7.7(m, Ar-H)
8a	1690	3.5(s, 3H), 6.8(s, 1H), 7.5-7.8(m, Ar-H)
8b	1700, 3300	6.5(s, 1H), 7.2-7.5(m, Ar-H)
8c	1680	6.7(s, 1H), 7.5-7.8(m, Ar-H)
8d	1690, 1720	1.3(t, J=7Hz, 3H), 4.4(q, J=7Hz, 2H), 7.1(s, 1H), 7.5-7.8(m, Ar-H)
9a	1035, 1100, 1600, 1660	2.3(s, 3H), 7.4-7.7(m, Ar-H)
9b	1035, 1100, 1660, 3320	7.3-7.8(m, Ar-H)
9c	1030, 1100, 1660, 3300	7.4-7.7(m, Ar-H)
10a	1060, 1610, 1670, 3320	2.2(s, 3H), 7.5-7.7(m, Ar-H)
10b	1060, 1610, 1670, 3330	7.4-8.0(m, Ar-H)
10c	1060, 1610, 1665, 3320	7.4-7.9(m, Ar-H)
11a	1030, 1090	2.2(s, 3H), 6.9-7.2(m, Ar-H)
11b	1030, 1100	6.8-7.8(m, Ar-H)
11c	1030, 1100	6.8-7.6(m, Ar-H)
12a	1070	6.6-7.0(m, Ar-H)
12b	1075	6.7-7.7(m, Ar-H)
12c	1070	6.6-7.4(m, Ar-H)

1	2	3
13	1610, 1030	6.7(s, 1H), 6.9-7.4(m, Ar-H)
14	1600, 680	6.8(s, 1H), 7.2-7.5(m, Ar-H)
15a	1090, 1030	5.2(s, 1H), 6.9-7.4(m, Ar-H)
15b	1100, 1030	5.2(s, 1H), 7.1-7.5(m, Ar-H)
15c	1100, 1030	5.3(s, 1H), 6.8-7.5(m, Ar-H)
15d	1100, 1035	5.2(s, 1H), 7.3-7.8(m, Ar-H)
15e	1095, 1030	5.2(s, 1H), 7.2-7.5(m, Ar-H)
15f	1090, 1030	5.1(s, 1H), 7.1-7.6(m, Ar-H)
15g	1100, 1030	5.2(s, 1H), 7.2-7.5(m, Ar-H)
15h	1105, 1030	5.3(s, 1H), 6.9-7.4(m, Ar-H)
15i	1100, 1030	1.9(s, 3H), 5.2(s, 1H), 7.2-7.6(m, Ar-H)
15j	1090, 1030	1.7(s, 3H), 5.3(s, 1H), 6.9-7.5(m, Ar-H)
15k	1090, 1030	3.5(s, 3H), 5.2(s, 1H), 6.9-7.5(m, Ar-H)
15l	1100, 1030	3.5(s, 3H), 5.2(s, 1H), 7.2-7.8(m, Ar-H)
16a	1080, 680	5.2(s, 1H), 6.8-7.5(m, Ar-H)
16b	1100, 685	5.2(s, 1H), 7.2-7.5(m, Ar-H)
16c	1100, 685	5.2(s, 1H), 7.0-7.6(m, Ar-H)
16d	1090, 680	5.1(s, 1H), 6.9-7.4(m, Ar-H)
16e	1080, 680	5.2(s, 1H), 7.2-7.5(m, Ar-H)
16f	1090, 680	5.3(s, 1H), 7.1-7.6(m, Ar-H)
16g	1100, 685	5.3(s, 1H), 7.2-7.5(m, Ar-H)
16h	1100, 680	5.2(s, 1H), 6.8-7.3(m, Ar-H)
16i	1090, 680	1.9(s, 3H), 5.1(s, 1H), 7.2-7.5(m, Ar-H)
16j	1100, 680	1.7(s, 3H), 5.1(s, 1H), 6.8-7.4(m, Ar-H)
16k	1100, 680	3.5(s, 3H), 5.2(s, 1H), 6.9-7.5(m, Ar-H)
16l	1080, 690	3.5(s, 3H), 5.2(s, 1H), 7.0-7.6(m, Ar-H)
18a	1600	1.3(s, 3H), 3.8(s, 2H), 7.3-8.1(m, Ar-H)
18b	1610	3.9(s, 2H), 7.5-8.2(m, Ar-H)
18c	1600	3.8(s, 2H), 7.1-8.0(m, Ar-H)

1	2	3
18d	1600	4.2(s, 2H), 7.2-7.9(m, Ar-H)
18e	3200, 1600	3.9(s, 2H), 6.9(s, 2H), 7.2-8.0(m, Ar-H)
19a	3250, 1610	7.4-8.2(m, Ar-H), 10.6(s, 1H)
19b	3200, 1615	7.8-8.3(m, Ar-H), 10.8(s, 1H)
19c	3300, 1620	7.0-8.1(m, Ar-H), 10.7(s, 1H)
19d	3200, 1600	7.5-8.2(m, Ar-H), 10.8(s, 1H)
19e	3200, 1610	7.2-8.0(m, Ar-H), 10.5(s, 1H)
19f	3250, 1615	7.2-8.1(m, Ar-H), 10.7(s, 1H)
19g	3200, 1600	7.0-7.8(m, Ar-H), 10.8(s, 1H)
19h	3250, 1610	7.4-8.0(m, Ar-H), 10.7(s, 1H)
19i	3280, 1620	2.5(s, 3H), 7.1-7.8(m, Ar-H), 10.6(s, 1H)
19j	3200, 1600	2.4(s, 3H), 7.2-7.8(m, Ar-H), 10.8(s, 1H)
19k	3250, 1600	3.8(s, 3H), 7.0-7.8(m, Ar-H), 10.6(s, 1H)
19l	3200, 1610	3.6(s, 3H), 7.2-8.1(m, Ar-H), 10.8(s, 1H)
19m	3250, 1600	3.9(s, 3H), 7.0-7.9(m, Ar-H), 10.7(s, 1H)
19n	3200, 1610	7.7(s, 2H), 6.8-7.3(m, Ar-H)
19o	3020, 1610	6.8-7.2(m, Ar-H), 10.2(s, 1H)

pure products (15a-1, 16a-1). The physical data of the compounds are given in Table 1 and Table 2.

7H-6-Aryl-3-(2,4-dichlorophenyl)-1,2,4-triazolo(3,4-b)(1,3,4)thiadiazine
(18a-d)

General Method :

Aroylmethyl halid (0.01 mol) was added dropwise to a stirred solution of the triazole (17)(2.61 g, 0.01 mol) in absolute C_2H_5OH (50 ml). The mixture was then refluxed for 5 h, cooled to room temperature and neutralized with 10% aqueous sodium carbonate solution. The solid product was recrystallized from C_2H_5OH water mixture to give pure product (18a-d).

7H-6-Amino-3-(2,4-dichlorophenyl)-1,2,4-triazolo(3,4-b)(1,3,4)thiadiazine
(18e)

Triazole (17) (2.61 g, 0.01 mol) dissolved in 30 ml of absolute C_2H_5OH was mixed with 1.2 ml (0.02 mol) of chloroacetonitrile and heated for 4 h. The solvent was removed and the residue was dissolved in 25 ml of water. After neutralization with 10% aqueous sodium carbonate gave a precipitate which was filtered, washed with cold water (2 x 20 ml) and dissolved in 20 ml of concentrated sulphuric acid and left for 3 h at room temperature. It was then diluted with water and neutralized with 20% ammonium hydroxide. The precipitated product was filtered and crystallized from C_2H_5OH water mixture to give compound (18e).

6-Arylamino-3-(2,4-dichlorophenyl)-1,2,4-triazolo(3,4-b)(1,3,4)thiadiazoles
(19a-m)

General Method :

Aryl isothiocyanate (0.015 mol) was added to a solution of the triazole (17) (2.61 g, 0.01 mol) in absolute C_2H_5OH (150 ml) and the mixture was stirred for 4 h. To the stirred solution, dicyclohexylcarbodiimide (DCC) (3.1 g, 0.015 mol) was added and the whole mixture was refluxed for 6 h. On cooling to room temperature a white solid was separated. The solid was filtered and recrystallized from C_2H_5OH to give the products (19a-m).

6-Amino-3-(2,4-dichlorophenyl)-1,2,4-triazolo(3,4-b)(1,3,4)thiadiazole (19n)

Cyanogen bromide (2.1 g, 0.02 mol) and the triazole (17) (2.61 g, 0.01 mol) were refluxed in 75% aqueous C_2H_5OH (50 ml) for 4 h. The reaction mixture was evaporated to one fourth of its volume and then diluted with a saturated solution of sodium acetate in water. The precipitated solid was filtered and recrystallized from C_2H_5OH to afford compound (19n).

6-Benzoylamino-3-(2,4-dichlorophenyl)-1,2,4-triazolo(3,4-b)(1,3,4)-thiadiazole (19o)

To a stirred solution of ammonium thiocyanate (0.76 g, 0.01 mol) in acetone

(30 ml), benzoyl chloride (1.41 g, 0.01 mol) was added. The mixture was stirred for 15 min and a solution of the triazole (17) (2.61 g, 0.01 mol) in acetone (50 ml) was added into the mixture. The mixture was then heated under reflux for 3 h. The solvent was partly removed and cooled to room temperature. The mixture was then diluted with ice cooled water. The solid thus separated was filtered, washed with 5% aqueous sodium hydrogen carbonate solution and then with water (2 x 25 ml). The solid was recrystallized from acetone to give the pure compound (19o).

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