SOME REACTIONS OF PYRAZOLO (1,5-C) PYRIMIDINETHIONES

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SUMMARY: Bromination and iodination of the 2,5-diaryl-6H-pyrazolo [1,5-c] pyrimidine-7-thiones gave mono-and/or dihalogenation products, whereas nitration yielded only monosubstitution derivatives. However, with benzenediazonium chloride in the presence of sodium hydroxide afforded the respective monophenylazo disulfides. Acetylation, benzoylation and benzylation of 5-p-chlorophenyl-2-phenyl-6H-pyrazolo [1,5-c] pyrimidine-7-thione furnished the N-substituted derivatives. The pyrazolopyrimidinones were obtained by reaction with alkaline hydrogen peroxide.

Key Word: Pyrazolo [1,5-c] pyrimidines.

INTRODUCTION

The interesting biological activities reported for pyrazolopyrimidines have stimulated chemists to develop the chemistry of this class of compounds. In the last 25 years, an enormous number of papers and patents dealing with the chemistry of biological activity of pyrazolopyrimidines have been reported (1). However this paper appears to be one of the first detailed study of the chemistry of the pyrazolo [1,5-c] pyrimidines.

The wide variety of applications (2, 3) of certain pyrazolo-[1,5-c] pyrimidines, particularly of 2,5-diphenyl-6*H*-pyrazolo-[1,5-c] pyrimidine-7-thione which shows antibacterial activity (4) prompted me to continue to study this area on the basis of the structural similarity with the expected active compounds and also because they can be used as organic ligands.

From all the synthetic methods which were not so many and carried out via a multistage inefficient synthesis and in most cases, from starting materials unavailable in the laboratory (5) described for the preparation of pyrazolo-[1,5-c] pyrimidines in bibliography what appears to give the best results is the one using the reaction of 1,5-diarylpent-1-yne-3,5-diones with thiosemicarbazide. In this simple and convenient reaction, either 2,5-diaryl-6*H*-or 3*H*, 6*H*-pyrazolo [1,5-c] pyrimidine-7-thiones are recently reported, by our group (6), to be formed depending on the medium as well as the nature of the substituents.

The present work deals with the exploitation of the reaction of 5-aryl-2-phenyl-6*H*-pyrazolo [1,5-c] pyrimidine-7-thiones with some electrophiles and alkaline hydrogen peroxide. Thus, 5-phenyl-(1a), 5-p-bromophenyl-(1b) and 5-p-chlorophenyl-(1c)-2phenyl-6H-pyrazolo [1,5-c] pyrimidine-7-thiones smoothly brominated or iodinated with a molar amount of bromine or iodine monochloride in chloroform at room temperature giving the corresponding 3-bromo 2a-c or 3-iodo 3a-c thiones respectively, whereas the 3,4-dibromo 4a-c or the same monoiodo 3a-c thiones were obtained on treatment with double molar amount of the above reagents. However, similar reactions of 5-p,methylphenyl-(1d) and 5-p-methoxy-phenyl-(1e)-2-phenyl-6*H*-pyrazolo [1,5-c] pyrimidine-7-thiones led to

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the formation of the corresponding 3-bromo *5*d, e or *3*-iodo *6*d, e and 3,4-dibromo *7*d, e ketones, respectively, (Scheme 1). The above products were also obtained by halogenating *1* using acetic acid as the solvent.

Furthermore, treatment of *1*b,c with a molar amount of bromine and iodine monochloride in refluxing acetic acid gave the corresponding 3-halo ketones *5*b,c and *6*b,c, while with double molar amounts afforded the corresponding 3,4-dibromo *7*b,c and 3,4-diiodo *8*b,c ketones, respectively. However, a mixture of the respective 3-iodo 3b,c and 3,4-diiodo *9*b,c thiones was formed from the reaction of *1*b,c with iodine monochloride in refluxing dry chloroform.

On the other hand, the 2,5-diphenylthione 1a was converted into a mixture of the 3-halo *5*a or *6*a and 3,4-dihalo *7*a or *8*a ketones on reaction with double molar amounts of bromine-water or iodine monochloride in acetic acid at room temperature, respectively.

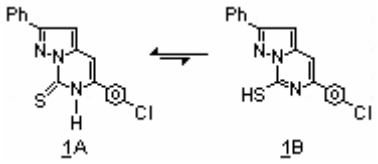
Nitration of the thione 1b with mixed nitric and sulfuric acids or fuming nitric acid at room temperature or in refluxing acetic acid afforded the 3-nitro ketone *10*b, whereas under the same conditions as above the thiones *1*a,c gave the respective 3-nitro thiones *11*a,c. TLC of the crude products *10* and *11* did not give any evidence for the presence of isomers.

The infrared spectra (cf. Experimental) of the halo as well as 3-nitro thiones *2, 3, 4, 9* and *11* showed the thiocarbonyl absorption at 1025-1192 cm^{-1}, while the halo and 3-nitro ketones *5, 6, 7, 8* and *10* gave the carbonyl stretching band at 1702-1756 cm^{-1}. The position of substitution was confirmed by ^1H nmr (Table 1) and mass spectra of which indicated that substitution had taken place in the 3- or 3,4-positions (7a).

It follows from the above data that attack of halogen under discussion in pyrazolopyrimidinethiones is directed to the C-3 and C-4 atoms; attack takes place first at the more nucleophilic C-3 center, after which the C-4 atom undergoes attack. Also, it is noted that in no case did C-4 substitution occurs. Moreover, it is worth noting that some pyrazolopyrimidinethiones undergo substitution as well as oxidation, whereas others only substitution occurs under the same conditions. Exactly why this occurs in not known.

Conflicting conclusions have been reported in the literature concerning the structure of pyrazolopyrimidinethiones. Some workers suggested that they exist in the thione form, whereas others favored their existence in thiol form (7b). However, the spectroscopic and chemical data of pyrazolopyrimidinethione *1*c indicated that the presence of this compound as an equilibrium mixture of thione-thiol tautomers *1*A and *1*B, respectively. Thus, its ^1H nmr spectrum (DMSO-d_6) showed two singlets at δ 12.65 and 4.33 for the NH and SH protons in ratio 5:1, respectively. Also, infrared spectrum (KBr) of *1*c gave bands characteristic of a thiocarbonyl and NH absorptions at 3173 and 1113 cm^{-1}, and the lack of USH band. These spectral results may suggest that the thione form *1*A predominates.

Acetylation, benzoylation or benzylation of *1*c gave an acetyl *12*c, a benzoyl *13*c or a benzyl *14*c derivative. These results pointed out that these compounds are either the N-substituted or the S-substituted *15* derivatives. However, from the presence of a sharp band in their infrared spectra at 1090-1110 cm^{-1} for the thioxo group and the lack of NH absorption, it



1A 1B

was concluded that they have structure *12*c, *13*c or *14*c rather than *15* (Scheme 1). This conclusion was substantiated by their ^1H nmr spectra (Table 1).

On the other hand, the pyrazolopyrimidine 1c was converted into the disulfide *16*c and 3-phenylazo disulfide *17*c on reactions with sodium nitrite and benzenediazonium chloride, respectively. These reactions are characteristic of thiols (8).

The reaction of the thiones *1*b,c with alkaline hydrogen peroxide led to the formation of the corresponding 6H-pyrazolo [1,5-c] pyrimidin-7-ones *18*b,c (Scheme 1). However, with the same reagent, 3-cyano-5,7-dimethylpyrazolo [1,5-a] pyrimidine gave *1*H-pyra-zolo [3,4-d] pyrimidine derivative (9). The structure of the ketones *18* is consistent with their spectral data and elemental analysis.

EXPERIMENTAL

Melting points were determined on a Kofler-Block and are uncorrected. Infrared spectra were measured with a Unicam SP 1025 spectrophotometer. The ^{1}H nmr spectra were recorded on a Varian EM-390 90 MHz spectrometer with TMS as internal standard. Chemical shifts were expressed in δ values. Mass spectra were recorded on an AEI MS 30 spectrometer. Microanalyses were performed by the Microanalysis Unit, Cairo University, Cairo. Thin layer chromatography (tlc) was run on silica gel Merck Kieselgel 60-F 254 precoated plastic plates, using ethly acetate-chloroform (2:1) as eluent.

5-Aryl-3-halo-2-phenyl-6H-pyrazolo[1,5-c] pyrimidines (Table 1).

a) To a suspension of the pyrazolopyrimidinethione (6) *1*a-e (14 mmole) in chloroform (10 ml), bromine (14 mmole) or iodine monochloride (14 mmole) in chloroform (10 ml) was added drop wise at room temperature with stirring for about one hour. The precipitated 3-bromo *2*a-c or 3-iodo *3*a-c thione and 3-bromo *5*d, e or 3-iodo *6*d,e ketone were filtered, washed with methanol, dried and crystallized from benzene or chloroform-methanol as pale yellow or colorless needles; ir (KBr): $_{max}$(cm^{-1}) 3314-3500 (NH), 1702-1733 (C=0), 1513-1652 (C=N), 1482-1530 (pyrimidine C=C), 1025-1100 (C=S). MS for 5d: 379 (M^+), 300 (M-Br), 299 (M-HBr), 197 (M-Br-PhCN), 154 (M-Br-PhCN-HCNO), 141 ($C_9H_5N_2$), 116 (HC≡C-C_6H_4-Me-p), 115 (C_8H_5N), 77 (base peak).

b) A mixture of *1*b,c (14 mmole) in acetic acid (10 ml) was heated on a steam bath in a two-neck flask fitted with reflux condenser, and dropping funnel. To the mixture at reflux was added drop wise 14 mmole of bromine or iodine monochloride in acetic acid (10 ml) over a period of half hour; reflux was continued for an additional two hours. The mixture was evaporated and the residue was washed with water (50 ml) at room temperature. The insoluble 3-bromo *5*b,c or 3-iodo *6*b,c ketone was collected, dried and crystallized from benzene as pale yellow needles; ir (CH_3Cl): $_{max}$ (cm^{-1}) 3400-3425 (NH), 1720-1733 (C=O), 1545-1612 (C=N), 1486-1510 (pyrimidine C=C).

5-Aryl-3, 4-dihalo-2-phenyl-6H-pyrazolo [1,5-c] pyrimidines (Table 1).

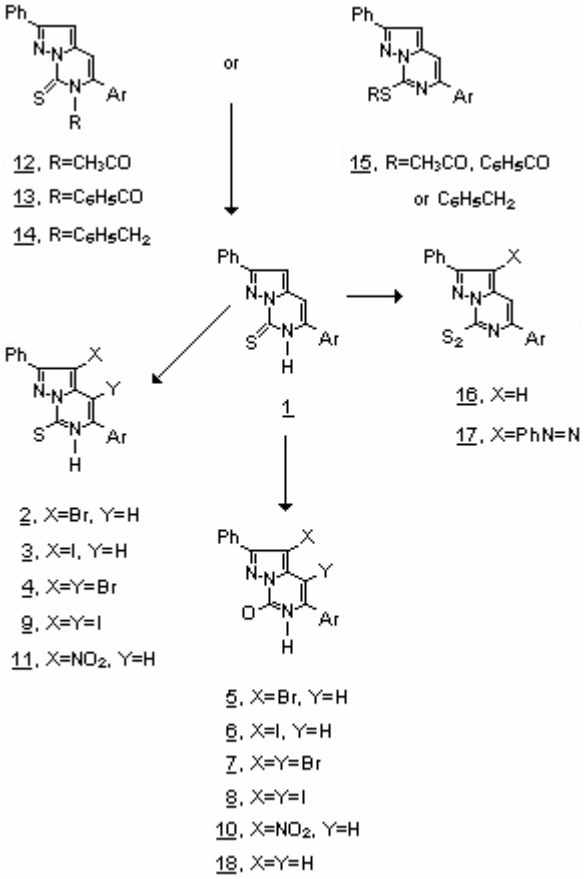
3,4-Dibromo derivative *4*a-c or *7*d,e and 3,4-dihalo ketone *7*b,c or *8*b,c were prepared as in procedure (a) and (b), respectively, except that only double molar amounts of bromine or iodine monochloride was used. The dihalo derivatives were crystallized from benzene or chloroform-methanol as pale yellow or colorless needles; ir (CH_2Cl_2): $_{max}$(cm^{-1}) 3400-3450 (NH), 3363-3383 (br, OH), 1734-1750 (C=O), 1500-1625 (C=N), 1482-1490 (pyrimidine C=C), 1070-1100 (C=S). MS for 7d: 457 (M^+), 378 (M-Br), 299 (M-Br_2), 196 (M-Br_2-PhCN), 153 (M-Br_2-PhCN, HCNO), 141 ($C_9H_5N_2$), 115 (C≡C-C_6H_4-Me-p).

The dihalo derivatives *4*a-c or *7*d,e and *7*b,c or *8*b,c could also be obtained in 60-85% yield by reaction of the respective 3-bromo derivative *2*a-c or *5*d,e and mono halo ketone *5*b,c or *6*b,c with a molar amount of bromine or iodine monochloride as in procedure (a) and (b), respectively.

Formation of a mixture of *3*b,c and *9*b,c.

The 3-Iodo *3*b,c and 3,4-diiodo *9*b,c thiones were prepared from the respective thiones *1*b,c and double molar amounts of iodine monochloride in refluxing dry chloroform as described in procedure (b). After removal of most of the solvent under reduced pressure, two products were detected by tlc, the separated solid was subjected to fractional crystallization from chloroform-methanol. The diiodo thiones *9*b,c separated first, and from the mother liquors, the 3-iodo thiones *3*b,c (18-25% yield) were obtained. These monoiodo thiones were found to be identical (m.p. mixed m.p. tlc, ir and ^{1}H nmr spectra) with authentic samples *3*b,c. IR (CH_3Cl) for *9*b,c: $_{max}$(cm^{-1}) 3445-3450 (NH), 1489-1623 (C=N), 1447-1452 (pyrimidine C=C), 1182-1192 (C=S).

The diiodo thione *9*b,c could also be obtained (58-65%) by refluxing a solution of the respective 3-iodo thione *3*b,c in dry chloroform with a molar amount of iodine monochloride for about four hours as described in procedure (b).



Formation of a mixture of *5*a and *7*a or *6*a and *8*a (Table 1).

To a suspension of *1*a (7 mmole) in acetic acid (15 ml), bromine (14 mmole) or iodine monochloride (14 mmole) in water (10 ml) was added dropwise at room temperature with stirring for two hours. After this time, two products were detected by tlc. The pale yellow precipitate formed was removed by filtration, washed with water, dried, crystallized from chloroform-methanol as colorless fine needles and identified as 3-bromo-(5a) or 3-iodo-(6a)-2,5-diphenyl-6*H*-pyrazolo [1,5-c] pyrimidin-7-one; ir (CH_2Cl_2): max (cm^{-1}) 3214-3220 (NH), 1713-1715 (C=O), 1505-1620 (C=N), 1420-1430 (pyrimidine C=C).

From the mother liquors, 3,4-dibromo-(7a) or 3,4-diiodo-(8a)-2,5-diphenyl-6*H*-pyrazolo [1,5-c] pyrimidin-7-one was obtained by removal of most of the solvent and dilution with water. They were crystallized from benzene as pale yellow plates; ir ($CHCl_3$): max(cm^{-1}) 3373-3380 (NH), 1760-1769 (C=O), 1510-1635 (C=N), 1460-1465 (pyrimidine C=C).

5-p- Bromophenyl- 3-nitro-2-phenyl-6H-pyrazolo [1,5-c] pyrimidin-7-one (10b) (Table 1).

A nitrating mixture of nitric (d 1.41; 1 ml) and sulfuric (d 1.84; 1 ml) acids in acetic acid (10 ml) was gradually added to a solution of *1*b (14 mmole) in acetic acid (10 ml) with stirring for three hours at room temperature. The reaction mixture was then poured into ice-cold water. The solid which separated out filtered, washed with water, dried and crystallized from acetic acid as pale yellow needles; ir (CH_2Cl_2): max$^{(cm-1)}$ 3378 (NH), 1756 (C=O), 1510, 1613 (C=N), 1478 (pyrimidine C=C), 1570 and 1360 (NO_2).

The 3-nitro ketone *10*b was also obtained in 48 or

Table 1: Analytical and ^1H nmr data of pyrazolopyrimidine derivatives.

Compd. No.	m.p. (°C)	Yield (%)	Molecular formula	Analysis Calcd./Found (%)					Solvent	Chemical H-3 and H-4 (s, 2H)	Shift NH* (s, 1H)	(δ/ppm) Ar-H (m)	Others (s)
				C	H	N	S	X					
2a	234-236	80	$C_{18}H_{12}BrN_3S$	56.5	3.1	10.9	8.4	20.9	C_5D_5N	7.07		7.77	
				(56.2	2.8	10.6	8.7	21.2)					
2b	225-229	68	$C_{18}H_{11}Br_2N_3S$	46.9	2.4	9.1	6.9	34.7	C_5D_5N	7.03	12.3	7.62	
				(50.2	2.5	9.4	6.6	34.2)					
2c	212-214	78	$C_{18}H_{11}BrClN_3S$	51.9	2.6	10.1	7.7	19.2,8.5	C_5D_5N	6.94		7.67	
				(52.2	2.4	10.4	7.4	19.5,8.0)					
3a	262-264	90	$C_{18}H_{12}IN_3S$	50.3	2.8	9.8	7.5	29.6	C_5D_5N	7.00		7.68	
				(50.7	2.4	9.6	7.2	30.0					
3b	250-253	70	$C_{18}H_{11}BrIN_3S$	42.5	2.2	8.3	6.3	15.7,25.0	C_5D_5N	7.17		7.72	
				42.8	2.1	8.7	6.1	15.4,25.5)					
3c	228-230	65	$C_{18}H_{11}ClIN_3S$	46.6	2.4	9.1	6.9	7.7.27.4	C_5D_5N	7.10		7.78	
				(46.9	2.2	9.4	6.6	8.0,27.0)					
4a	273-275	53	$C_{18}H_{11}Br_2N_3S$	46.9	2.4	9.1	6.9	34.7	DMSO-d_6			7.80	
				(46.6	2.6	9.4	7.2	35.1)					
4b	210-212	78	$C_{18}H_{10}Br_3N_3S$	40.0	1.9	7.8	5.9	44.4	DMSO-d_6			7.66	
				(40.3	2.1	8.1	6.0	44.9)					
4c	221-222	73	$C_{18}H_{10}Br_2ClN_3S$	43.6	2.0	8.5	6.5	32.3,7.2	DMSO-d_6			7.15	
				(43.3	2.1	8.3	6.7	32.0,7.6)					
5a	233-235	62	$C_{18}H_{12}BrN_3O$	59.0	3.3	11.5		21.9	DMSO-d_6	6.63		7.55	
				59.3	3.6	11.3		22.3)					
5b	205-207	65	$C_{18}H_{11}Br_2N_3O$	48.5	2.5	9.4		36.0	DMSO-d_6	6.58		7.72	
				(48.2	2.4	9.7		36.4)					
5c	178-180	63	$C_{18}H_{11}BrClN_3O$	53.9	2.8	10.5		20.0,8.9	DMSO-d_6	6.71	12.3	7.60	
				(53.6	3.0	10.3		20.5,8.5)					
5d	208-210	57	$C_{19}H_{14}BrN_3O$	60.0	3.7	11.1		21.1	DMSO-d_6	6.63	11.73	7.32	2.33(3H,CH_3)
				(60.3	3.5	11.4		(20.7					
5e	250-253	54	$C_{19}H_{14}BrN_3O_2$	57.6	3.5	10.6		20.2	DMSO-d_6	6.60		7.50	3.80(3H,OCH_3)
				(57.3	3.3	10.9		20.7)					
6a	210-212	78	$C_{18}H_{12}IN_3O$	52.3	2.9	10.2		30.8	C_5D_5N	6.72		7.50	
				(52.6	3.0	10.5		30.4)					
6b	232-235	90	$C_{18}H_{11}BrIN_3O$	43.9	2.2	8.5		16.3,25.8	C_5D_5N	6.63		7.65	
				43.7	2.0	8.8		16.7,25.3					
6c	224-226	88	$C_{18}H_{11}ClIN_3O$	48.3	2.5	9.4		7.9,28.4	C_5D_5N	6.75		7.59	
				(48.0	2.7	9.2		8.3,28.0)					
6d	196-198	85	$C_{19}H_{14}IN_3O$	53.4	3.3	9.8		29.7	C_5D_5N	6.83		7.58	2.00(3H,CH_3)
				53.1	3.0	9.5		30.1)					
6e	225-227	86	$C_{19}H_{14}IN_3O_2$	51.5	3.2	9.5		28.7	C_5D_5N	6.60		7.60	3.43(3H,OCH_3)
				(51.7	3.0	9.8		28.4)					
7a	210-215	72	$C_{18}H_{11}Br_2N_3O$	48.5	2.5	9.4		36.0	C_5D_5N			7.59	
				48.2	2.8	9.7		36.4)					
7b	202-204	65	$C_{18}H_{10}Br_3N_3O$	41.0	1.9	8.0		45.8	C_5D_5N			7.39	
				(41.4	3.0	8.3		45.4)					
7c	195-197	73	$C_{18}H_{10}Br_2ClN_3O$	45.0	2.1	8.8		33.4,7.4	C_5D_5N			7.62	
				(45.3	2.0	8.5		33.0,7.9)					
7d	230-232	63	$C_{19}H_{10}Br_3N_3O$	49.7	2.8	9.2		34.9	DMSO-d_6		13.00	7.11	2.11(3H,CH_3)
				(49.4	2.7	9.5		35.3)					
7e	270-273	68	$C_{19}H_{13}Br_2N_3O_2$	48.0	2.7	8.8		33.7	DMSO-d_6			7.81	3.50(3H,OCH_3)
				(48.4	2.3	8.5		33.2)					
8a	215-217	75	$C_{18}H_{11}I_2N_3O$	40.1	2.0	7.8		47.1	C_5D_5N			7.47	
				(39.8	2.2	7.5		47.6)					
8b	192-193	86	$C_{18}H_{10}BrI_2N_3O$	35.0	1.6	6.8		12.9,41.1	C_5D_5N			7.63	
				(35.3	1.9	6.6		12.5,41.6)					
8c	170-172	83	$C_{18}H_{10}Cl_{12}N_3O$	37.7	1.7	7.3		6.2,4.3	C_5D_5N			7.70	
				(37.4	1.9	7.6		6.6,44.0)					
9b	320-323	65	$C_{18}H_{10}BrI_2N_3S$	34.1	1.6	6.6	5.0	12.6,40.1	C_5D_5N			7.78	
				(34.4	1.4	6.3	4.8	12.1,40.5)					
9c	211-214	72	$C_{18}H_{10}ClI_2N_3S$	36.6	1.7	7.1	5.4	6.0,43.1	C_5D_5N			7.56	
				(36.9	1.9	7.4	5.7	6.3,43.5)					
10b	198-200	75	$C_{18}H_{11}BrN_4O_3$	52.6	2.7	13.6		19.5	DMSO-d_6	7.23		7.66	
				(52.3	2.9	13.9		20.0					
11a	273-275	87	$C_{18}H_{12}N_4O_2S$	62.1	3.5	16.1	9.2		DMSO-d_6	7.14		7.53	
				(61.8	3.1	16.4	9.5						Cont.

11c	212-215	85	$C_{18}H_{12}ClN_4O_2S$	56.5 56.8	2.9 3.0	14.6 14.9	8.4 8.6	9.3 4.0)	DMSO-d_6	7.12		7.47	
12c	169-171	75	$C_{20}H_{14}ClN_3OS$	63.2 (63.5	3.7 3.9	11.1 11.4	8.4 8.7	9.4 9.9)	$CDCl_3$	6.67,6.92		7.61	2.25(3H,CH_3)
13c	132-135	78	$C_{25}H_{16}ClN_3OS$	68.0 (68.3	3.6 3.9	9.5 9.8	7.3 7.0	8.0 8.5)	$CDCl_3$	6.20,6.68		7.55	
14c	118-120	67	$C_{25}H_{18}ClN_3S$	70.2 (70.4	4.2 4.0	9.8 9.9	7.9 7.6	8.3 8.8)	$CDCl_3$	6.78,6.96		7.99	4.13(2H,CH_2)
16c	240-242	45	$C_{36}H_{22}Cl_2N_6S_2$	64.3 (64.0	3.3 3.4	12.5 12.8	9.5 9.9	10.4 10.0)	CF_3COOD	(a)		7.78	
17c	132-134	49	$C_{48}H_{30}Cl_2N_{10}S_2$	65.5 (65.8	3.4 3.7	15.9 15.6	7.3 7.0	8.0 8.4)	$CDCl_3$	(a)		7.55	
18b	340-342	96	$C_{18}H_{12}BrN_3O$	59.0 (59.2	3.3 3.2	11.5 11.8		21.9 21.5)	DMSO-d_6	6.70,6.82	12.20	7.75	
18c	320-322	92	$C_{18}H_{12}ClN_3O$	67.2 (67.0	3.7 3.9	13.1 12.9		11.0 10.6)	DMSO-d_6	6.71,6.80		7.80	

s : Singlet, m : Multiplet, * : Exchangeable with D_2O.

(a) The H-3 and H-4 signals are overlapped by the aromatic protons multiplet.

40% yield by refluxing a solution of the thione *1*b in acetic acid with a mixture of nitric and sulfuric (1:1) acids or fuming nitric acid (d 1.5; 2 ml) for two hours.

5-Aryl-3-nitro-2-phenyl-6*H*-pyrazolo[1,5-c] pyrimidine-7-thione *11*a,c (Table 1).

They were prepared from the respective thiones 1a,c as above and crystallized from chloroform-methanol as yellow needles; ir (CH_2Cl_2): max$^{(cm-1)}$ 3410-3430 (NH), 1510-1609 (C=N), 1475-1486 (pyrimidine C=C), 1525-1540 and 1352-1370 (NO_2), 1028-1100 (C=S).

6-Acetyl- 5-p,chlorophenyl-2-phenylpyrazolo [1,5-c] pyrimidine-7- thione 12c (Table 1).

A solution of *1*c (12 mmole) in glacial acetic acid (6 ml) was refluxed with acetic anhydride (5 ml) for thirty hours. After removal of most of the solvent under reduced pressure and dilution with water, the separated 6-acetyl thione *12*c was crystallized from benzene as needles; ir (CH_2Cl_2): max$^{(cm-1)}$ 1730 (C=O), 1510, 1609 (C=N), 1482 (pyrimidine C=C), 1090 (C=S).

6-Benzoyl-(13c) and 6-Benzyl-(14c)- 5-p-chlorophenyl-2-phenyl-pyrazolo [1,5-c] pyrimidine-7-thiones (Table 1).

A mixture containing a solution of *1*c (12 mmole) in dry pyridine (5 ml) and benzoyl chloride (12 mmole) or benzyl chloride (12 mmole) was refluxed on a steam bath for fifteen hours. After removal of most of the solvent and dilution with water, the separated 6-benzoyl *13*c or 6-benzyl *14*c thione was crystallized from methanol as yellow needles; ir (CH_2Cl_2): max$^{(cm-1)}$ 1720 (C=O), 1513-1615 (C=N), 1482-1488 (pyrimidine C=C), 1095-1110 (C=S).

7,7'-Bis(5-p-chlorophenyl-2-phenylpyrazolo [1,5-c] pyrimidinyl) disulfide *16*c (Table 1).

A solution of *1*c (12 mmole) in glacial acetic acid (12 ml) was treated portion wise with a 25% aqueous solution of sodium nitrite (10 ml). The mixture was heated on a steam bath with stirring for half hour, where by a yellow solid started to separate. The reaction mixture was then diluted with water and the precipitated *16*c was filtered and crystallized from benzene as yellow needles; ir (CH_3Cl): max$^{(cm-1)}$ 1575, 1615 (C=N), 1503 (pyrimidine C=C).

7,7'-Bis(5-p,chlorophenyl- 3-phenylazo-2-phenyl-pyrazolo [1,5-c] pyrimidinyl) disulfide *17*c (Table 1).

An aqueous solution of sodium hydroxide (8 ml, 10%) was added to a suspension of *1*c (15 mmole) in ethanol (15 ml). The reaction mixture was gradually treated with a solution of benzenediazonium chloride (prepared from 1 ml of aniline) at 5°C with stirring for one hour. The disulfide *17*c, so formed, was collected by filtration and crystallized from ethanol as reddish brown needles; ir (CH_2Cl_2): max$^{(cm-1)}$ 1583, 1630 (C=N), 1550 (pyrimidine C=C).

5-Aryl-2-phenyl-6H-pyrazolo [1,5-c] pyrimidin-7-ones *18* (Table 1).

A mixture of *1*b,c (15 mmole), 30% hydrogen peroxide (4 ml) and 10% aqueous sodium hydroxide (15 ml) was heated on a steam bath for three hours. The pH of the resulting solution was adjusted to 6 by addition of concentrated hydrochloric acid. The precipitated ketone *18*b,c was washed several times with water, dried and crystallized from methanol as pale yellow needles; ir (KBr): $\nu_{max}^{(cm-1)}$ 3385-3412 (OH), 1695-1710 (C=O), 1586-1640 (C=N), 1510-1520 (pyrimidine C=C).

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