(Table 1 contd.)

(iii) Ar=4-Chlorophenyl				
5k	Phenyl	166	75	$C_{25}H_{23}O_6N_3BrClS$
5l	2'-Chlorophenyl	145	78	$C_{25}H_{22}O_6N_3BrCl_2S$
5m	4'-Methylphenyl	105	82	$C_{26}H_{25}O_6N_3BrClS$
5n	3',5'-Methylenedioxy-phenyl	180	80	$C_{26}H_{22}O_8N_3BrClS$
5o	4'-Methoxyphenyl	190	87	$C_{26}H_{25}O_7N_3BrClS$
(iv) Ar=4-Acetamidophenyl				
5p	Phenyl	205	86	$C_{27}H_{27}O_7N_4BrS$
5q	2'-Chlorophenyl	127	72	$C_{27}H_{26}O_7N_4BrClS$
5r	4'-Methylphenyl	140	74	$C_{28}H_{29}O_7N_4BrNS$
5s	3',4'-Methylenedioxyphenyl	180	80	$C_{28}H_{27}O_8N_4BrS$
5t	4'-Methoxyphenyl	119	85	$C_{28}H_{29}O_8N_4BrS$

*N (and S) analysis found satisfactory.

1-Benzoyl-3-(2"-hydroxy-3"-bromo-4"-n-butoxy-5"-nitrophen-1"-yl)-5-phenyl-2-pyrazoline (**3a**) : A mixture of **2a** (0.001 mol) and benzoyl chloride (0.0011 mol) was dissolved in dry pyridine (10 ml) and stirred at room temperature for 1 h, after which the reaction mixture was treated with cold dilute HCl (2*N*). The resulting solid was filtered and washed successively with water, cold NaOH (2%) and water, and recrystallised from glacial acetic acid (82%), m.p. 190° (Fouud : C, 58.04 ; H, 4.42 ; N, 7.75. $C_{26}H_{24}O_5N_3Br$ requires : C, 57.99 ; H, 4.46 ; N, 7.80%).

Similarly, other benzoyl derivatives were prepared (Table 1).

1-Acetyl-3-(2"-hydroxy-3"-bromo-4"-n-butoxy-5"-nitrophen-1"-yl)-5-phenylpyrazoline (**4a**). *Indirect method :* A mixture of **2a** (0.001 mol) and acetic acid (10 ml) was refluxed for 2 h. The solution was then concentrated. On cooling, the resulting solid was filtered, washed with water and recrystallised from ethanol (90%), m.p. 165° (Found : C, 52.90 ; H, 4.65 ; N. 8.86. $C_{21}H_{22}O_5N_3Br$ requires : C, 52.94 ; H, 4.62 ; N, 8.82%). Similarly, other acetyl derivatives were prepared (Table 1).

Direct method : A mixture of the chalcone (**1** ; 0.0015 mol) and 99% hydrazine hydrate (0.002 mol) in acetic acid (15 ml) was refluxed for 2 h. The solvent was then removed under reduced pressure and the residual matter diluted with water. The resulting solid was washed with water and recrystallised from ethanol (80%), m.p. 165°. Analytical and spectroscopic data were identical with the sample prepared by indirect method.

1-p-Tolyl sulphonyl-3-(2"-hydroxy-3"-bromo-4"-n-butoxy-5"-nitrophen-1"-yl)-5-phenylpyrazoline (**5a**) : A solution of **2a** (0.001 mol) in dry pyridine (10 ml) was cooled in an ice-bath and to it *p*-tolyl sulphonyl chloride (0.0011 mol) was added. The mixture was stirred for 1 h at room temperature and was then treated with cold dilute HCl (2*N*). The resulting solid was filtered, washed with water and recrystallised from ethanol (75%), m.p. 125° (Found : C, 53.11 ; H, 4.38 ; N, 7.17 : $C_{28}H_{26}O_6N_3BrS$ requires : C, 53.06 ; H, 4.42 ; N, 7.14%).

Similarly, other sulphonamide derivatives were prepared (Table 1).

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Synthesis of some New Arylazopyrazoles and Arylazopyrimidines

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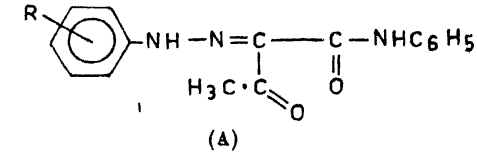
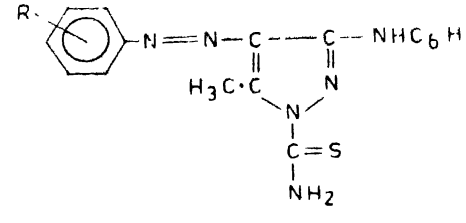
IN view of the important biological activities displayed by pyrazoles[1,2], pyrimidines[3] and azo group[4], it was considered worthwhile to synthesise some arylazo derivatives of pyrazoles and pyrimidines.

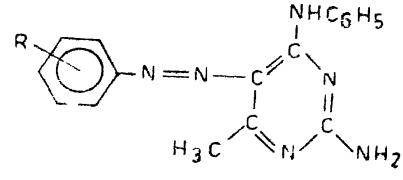
The arylazopyrazoles (**1**) and arylazopyrimidines (**2**) have been synthesised[5] by reacting 2-arylhydrazono-1-phenylaminobutan-1,3-diones (A) with thiosemicarbazide and guanidine nitrate respectively.



(A)



1



2

Experimental

Ir spectra were scanned on a Perkin-Elmer 577 spectrophotometer, electronic spectra on a Carl-Zeiss spectrophotometer, and pmr spectra (DMSO-d_6) on a Varian 270 MHz using tetramethylsilane as an internal standard. All the melting points are uncorrected. Compounds were routinely checked for their purity on silica gel-G plates.

N-Thiocarbamoyl-3-aminophenyl-5-methyl-4-arylazopyrazoles (**1**) · 2-Phenylhydrazono-1-phenylaminobutane-1,3-dione[5] (0.004 mol) dissolved in ethanol (25 ml), was added to a solution of thiosemicarbazide (0 004 mol) in ethanol (25 ml). Glacial acetic acid (15 ml) was also added to facilitate the dissolution. The reaction mixture was refluxed for 6 h. On cooling, the resulting shining crystals (**1**, R=H) were recrystallised from DMF-water mixture, yield (70%), m.p. 100° (Found : C, 60.42 ; H, 4.45 ; N, 24.60. $C_{17}H_{16}N_6S$ calcd for : C, 60.70 ; H, 4.70 ; N, 25 70%) ; λ_{max}(CH_3OH) 270 and 360 nm ; ν_{max} (KBr) 3 180 (NH), 1 635 (C=C or C=N), 1 495 (N=N) and 750 cm^{-1} (phenyl) ; δ (DMSO-d_6) 2.65 (3H, CH_3), 3.4 (2H, NH_2), 7.0–8.0 (10H, ArH) and 11.1 (1H, NHC_6H_5).

Similarly, other arylazopyrimidines were prepared by reacting suitable substituted 2-arylhydrazono-1-phenylaminobutan-1,3-diones with thiosemicarbazide (Table 1).

2-Amino-5-arylazo-4-phenylamino-6-methylpyrimidine (**2**) : An alcoholic solution of 2-arylhydrazono-1-phenylaminobutane-1,3-dione[5] (25 ml, 0.004 mol) was added to a solution of guanidine nitrate (0.004 mol) in methanolic (15 ml) 1.0 *N* NaOH solution. The contents were refluxed for 6 h and the reaction mixture was allowed to cool overnight. The resulting shining crystals were recrystallised from ethanol (60%), m.p. 147° (Found : C, 66.82 ; H, 5.0 ; N, 27.32. $C_{12}H_{18}N_5$ calcd. for : C, 67.1 ; H, 5.2 ; N, 27.6%) ; λ_{max} (CH_3OH) 240 and 350 nm ; ν_{max} (KBr) 3 150 (NH), 1 600 (N=N), 1 630 (C=C or C=N) and 760 cm^{-1} (phenyl) ; δ (DMSO-d_6) 2.70 (3H, 6-CH_3), 3.5 (2H, NH_2), 7.0–8.0 (10H, ArH) and 9.8 (H, NHC_6H_5).

Similarly, other derivatives of 2-amino-5-arylazo-4-phenylamino-6-methylpyrimidine were prepared by taking appropriate 2-arylhydrazono-1-phenylaminobutan-1,3-dione (Table 2).

TABLE 1—PHYSICAL DATA OF COMPOUNDS 1*

Sl. no.	R	M.p. °C	Yield %	Colour	Mol. formula	λ_{max} nm
1.	H	100	70	Yellow	$C_{17}H_{16}N_6S$	270, 360
2.	2'-NO_2	180	60	Yellow	$C_{17}H_{15}N_7O_2S$	276, 388
3.	3'-NO_2	185	64	Light yellow	$C_{17}H_{15}N_7O_2S$	250, 365
4.	4'-NO_2	167	65	Yellowish orange	$C_{17}H_{15}N_7O_2S$	245, 390
5.	2'-Cl	140	58	Brownish yellow	$C_{17}H_{15}N_6ClS$	255, 380
6.	3'-Cl	115	60	Mud orange	$C_{17}H_{15}N_6ClS$	249, 370
7.	4'-Cl	130	60	Yellow	$C_{17}H_{15}N_6ClS$	249, 388
8.	2'-CH_3	152	65	Yellow	$C_{18}H_{18}N_6S$	245, 390
9.	3'-CH_3	109	69	Yellow	$C_{18}H_{18}N_6S$	248, 380
10.	4'-CH_3	120	67	Orange	$C_{18}H_{18}N_6S$	249, 388
11.	2',5'-$(Cl)_2$	170	61	Yellowish orange	$C_{17}H_{14}N_6Cl_2S$	254, 380
12.	2',3'-$(CH_3)_2$	100	60	Yellowish orange	$C_{19}H_{20}N_6S$	248, 390
13.	2',5'-$(CH_3)_2$	185	58	Brownish orange	$C_{19}H_{20}N_6S$	255, 388
14.	4'-OCH_3	120	67	Brownish orange	$C_{18}H_{18}N_6OS$	248, 405
15.	3'-OCH_3	88	71	Brownish orange	$C_{18}H_{18}N_6OS$	240, 370
16.	2'-OC_2H_5	122	69	Yellow	$C_{12}H_{20}N_6OS$	250, 400
17.	4'-COOH	220	72	Yellow	$C_{18}H_{17}N_6O_2S$	238, 380
18.	3'-NO_2, 4'-CH_3	150	65	Brownish orange	$C_{12}H_{16}N_7O_2S$	248, 390

*All compounds gave consistent C, H and N analyses.

TABLE 2—PHYSICAL DATA OF COMPOUNDS 2*

Sl. no.	R	M.p. °C	Yield %	Colour	Mol. formula	λ_{max} nm
1.	H	147	60	Light yellow	$C_{17}H_{16}N_6$	240, 350
2.	2′-NO_2	195	70	Yellow	$C_{17}H_{15}N_7O_2$	250, 390
3.	3′-NO_2	300d	75	Brown	$C_{17}H_{15}N_7O_2$	255, 370
4.	4′-NO_2	200d	65	Yellow	$C_{17}H_{15}N_7O_2$	240, 390
5.	2′-Cl	150	60	Yellow	$C_{17}H_{15}N_6Cl$	250, 380
6.	3′-Cl	130	63	Yellow	$C_{17}H_{15}N_6Cl$	250, 380
7.	4′-Cl	170	60	Yellow	$C_{17}H_{15}N_6Cl$	250, 360
8.	2′-CH_3	155	69	Yellow	$C_{18}H_{18}N_5$	245 255
9.	3′-CH_3	137	70	Orange	$C_{18}H_{18}N_6$	240, 350
10.	4′-CH_3	110	75	Brown	$C_{18}H_{18}N_6$	240, 390
11.	2′,5′-$(Cl)_2$	172	75	Light yellow	$C_{17}H_{14}N_6Cl_2$	250, 360
12.	2′,3′-$(CH_3)_2$	130	63	Orange	$C_{19}H_{20}N_6$	250, 360
13.	2′,5-$(CH_3)_2$	170	63	Yellow	$C_{19}H_{20}N_6$	240, 350
14.	4′-OCH_3	230	69	Yellow	$C_{18}H_{18}N_6O$	250, 380
15.	3′-OCH_3	180	61	Brown	$C_{18}H_{18}N_6O$	260, 350
16.	2′-OC_2H_5	125	67	Yellow	$C_{19}H_{20}N_6O$	250, 400
17.	4′-COOH	290	70	Yellow	$C_{18}H_{16}N_6O_2$	260, 385
18.	3′-NO_2,4′-CH_3	105	67	Blackish brown	$C_{19}H_{19}N_7O_2$	250, 360

*All compounds gave consistent C, H and N analyses.

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Nucleophilic Addition-Elimination Reactions of 2-Hydrazinobenzothiazoles with Indolin-2,3-diones

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IT has been observed that 2-aminobenzothiazoles do not undergo uncleophilic addition-elimination reactions with indolin-2,3-diones due to poor nucleophilicity of amino group. However, the moment 2-amino group is replaced with 2-hydrazino group, the reaction takes place with ease. In the present communication, we report nucleophilic reactions of 2-hydrazinobenzothiazoles[1] with