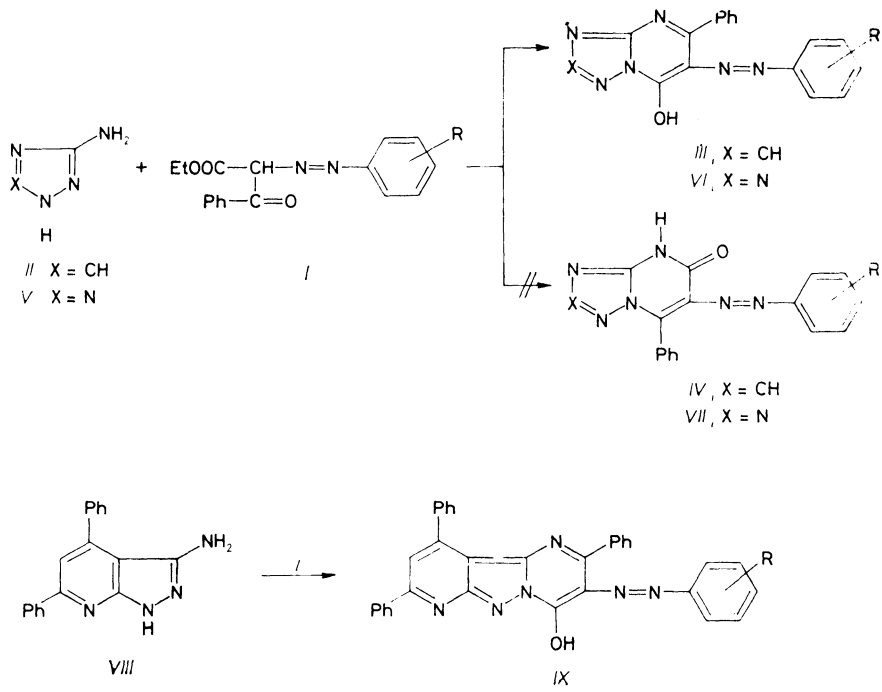
REACTIONS OF ETHYL (ARYLAZO)BENZOYL ACETATE WITH AMINO SUBSTITUTED AZOLES

Ali DEEB*

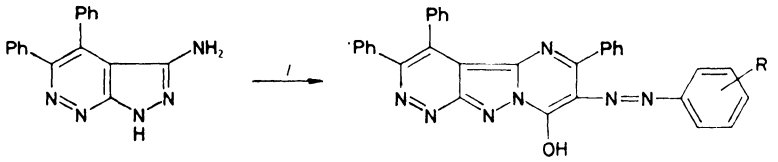
Department of Chemistry, Faculty of Science, Zagazig University, Zagazig, Egypt

Received November 2, 1990
Accepted November 13, 1990

In view of the close association of pyrimidines with important biodynamic agents[1,2], numerous compounds containing such a ring system have been extensively investigated. The fusion of pyrimidine nucleus with various nitrogen heterocyclic systems has been recently reviewed[3]. As a continuation of our studies in the field of fused heterocyclic compounds[4-7], we report here a relatively simple general method for the synthesis of azolopyrimidines by the reaction of ethyl (arylazo)benzoyl acetate with amino substituted azoles (see Scheme 1).



* Present address: Institut für Organische Chemie, Karl-Franzens-Universität, A-8010 Graz, Austria.



XI

In formulae *I*, *III*, *VI*, *IX*, *XI*: *a*, R = 2-CH_3 *b*, R = 4-NO_2 *c*, R = 2-OCH_3 *d*, R = 4-Br

SCHEME 1

EXPERIMENTAL

Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Hitachi Perkin–Elmer Va 60 spectrometer in $(CD_3)_2SO$ with TMS as an internal standard and chemical shifts are expressed in δ (ppm). IR spectra were obtained with a Perkin–Elmer 257 spectrometer (KBr). Analytical data were obtained from the Micro analytical centre, Cairo University.

Reaction of Ethyl (Arylazo)benzoyl Acetate *Ia*—*Id* with 5-Amino--1,2,4-triazole *II* and with 5-Amino-1,2,3,4-tetrazole *V*. General Procedure

To a solution of compound *II* or *V* (0·01 mol) in absolute ethanol (30 ml), the proper ethyl (arylazo)-benzoyl acetate *I* (0·01 mol) was added. The reaction mixture was heated under reflux for proper time (the progress of the reaction was followed by TLC). The reaction mixture was concentrated to give *IIIa*—*IIId* (from *I*) and *VIa*—*VId* (from *V*), respectively (see Table I).

4-Hydroxy-3-arylazo-2,8,10-triphenylpyrido[3′,2′:4,5]pyrazolo-[2,3-*a*]pyrimidines *IXa*—*IXd* and 4-Hydroxy-3-arylazo-2,8,10-tri-phenylpyrimido[1′,2′:2,3]pyrazolo[4,5-*c*]pyridazines *XIa*—*XId*. General Procedure

To a solution of 3-amino-4,6-diphenylpyrazolo[3,4-*b*]pyridine *VIII* or 3-amino-4,5-diphenyl-pyrazolo[3,4-*c*]pyridazine *X* (0·01 mol) in absolute ethanol (30 ml), ethyl (arylazo)benzoyl acetate *Ia*—*Id* (0·01 mol) was added. The reaction mixture was heated under reflux for proper time (the progress of the reaction was followed by TLC). The solvent was evaporated under reduced pressure. The solid product residue was triturated with ether to give compounds *IXa* to *IXd* and *XIa*—*XId*, respectively.

REFERENCES

1. Tam S. Y. K., Klein R. S., Wempen I., Fox J. J.: J. Org. Chem. *44*, 3437 (1979).
2. Sharm S. C., Lynch B. M.: Can. J. Chem. *57*, 3034 (1979).
3. Albert A.: Adv. Heterocycl. Chem. *32*, 1 (1982).
4. Deeb A., Essawy A., El-Gendy A. M., Shaban A.: Monatsh. Chem. *121*, 281 (1990).
5. Deeb A., Said A. S.: Collect. Czech. Chem. Commun. *55*, 2795 (1990).
6. Deeb A., El-Bahaie S., Assy M. G.: Pharmazie, submitted.
7. Deeb A., Essawy A., Yasine F., Fikry R. M.: Z. Naturforsch., submitted.

TABLE I
Physico-chemical data of synthesized compounds

Compound	React. time, h (Yield, %)	M.p. °C	IR spectrum cm^{-1}	^1H NMR spectrum	Formula (M.w.)	Calculated/Found		
						% C	% H	% N
IIIa	4 (60)	130[a]	3 570, 1 600, 1 580	2·7 s, 3 H (CH_3), 6·35 s, 1 H (COCH), 7·1—7·4 m, 9 H (Arom-H)	$C_{18}H_{14}N_6O$ (330·3)	65·44 65·60	4·27 4·10	25·44 25·30
IIIb	5 (64)	198[b]	1 680, 1 580, 1 500	5·7 s, 1 H (COCH), 7·3—7·5 m, 9 H (Arom-H)	$C_{17}H_{11}N_7O_3$ (361·3)	56·51 56·20	3·06 3·10	27·13 27·10
IIIc	7 (58)	166[c]	3 430, 1 610, 1 590	3·4 s, 3 H (CH_3), 6·1 s, 1 H (COCH), 7·2—7·5 m, 9 H (Arom-H)	$C_{18}H_{14}N_6O_2$ (346·3)	62·41 62·60	4·07 4·10	24·26 24·30
IIId	3 (60)	140[c]	3 310, 1 600, 1 580		$C_{17}H_{11}N_6OBr$ (395·2)	51·65 51·75	2·80 2·95	21·26 21·40
VIa	10 (50)	145[a]	3 560, 1 620, 1 570	2·6 s, 3 H (CH_3), 6·1 s, 1 H (COCH), 7·3—7·5 m, 9 H (Arom-H)	$C_{17}H_{13}N_7O$ (331·3)	61·62 61·80	3·95 4·10	29·59 29·70
VIb	12 (60)	270[b]	3 320, 1 660, 1 580		$C_{16}H_{10}N_8O_3$ (362·3)	53·03 53·30	2·78 2·50	30·93 30·60
VIc	9 (45)	170[c]	3 520, 1 620, 1 530		$C_{17}H_{13}N_7O_2$ (347·3)	58·78 58·60	3·77 3·50	28·23 28·10
VId	5 (60)	210[a]	3 410, 1 620, 1 540	5·7 s, 1 H (COCH), 7·4—7·7 m, 9 H (Arom-H)	$C_{16}H_{10}N_7OBr$ (396·2)	48·50 48·30	2·54 2·30	24·74 24·50

IXa	7 (40)	145[b]	3 560, 3 000, 1 600	2·3 s, 3 H (CH_3), 6·1 s, 1 H (COCH), 7·4—7·8 m, 19 H (Arom-H)	$C_{34}H_{24}N_6O$ (532·6)	76·67 76·60	4·54 4·60	15·78 15·80
IXb	10 (45)	160[d]	3 220, 1 650, 1 600		$C_{33}H_{21}N_7O_3$ (563·6)	70·32 70·00	3·75 3·50	17·39 17·40
IXc	12 (50)	210[c]	3 400, 3 000, 1 630		$C_{34}H_{24}N_6O_2$ (548·6)	74·43 74·20	4·30 4·30	15·14 15·40
IXd	10 (45)	170[d]	3 340, 2 970, 1 640	6·2 s, 1 H (COCH), 7·5—7·9 m, 20 H (Arom-H)	$C_{33}H_{21}N_6OBr$ (597·5)	66·33 66·20	3·54 3·20	14·06 14·20
XIa	14 (40)	300[b]	3 560,1 610, 1 580		$C_{33}H_{23}N_7O$ (533·6)	74·28 74·10	4·34 4·40	18·37 18·50
XIb	16 (55)	175[d]	3 300, 1 640, 1 600		$C_{32}H_{20}N_8O_3$ (564·5)	68·07 68·20	3·57 3·60	19·84 19·70
XIc	12 (60)	135[d]	3 400, 1 610, 1 580	3·5 s, 3 H (CH_3), 6·0 s, 1 H (COCH), 7·6—7·9 m, 19 H (Arom-H)	$C_{33}H_{23}N_7O_2$ (549·6)	72·11 72·30	4·21 4·30	17·84 17·60
XId	18 (50)	310[b]	3 300, 1 640, 1 570		$C_{32}H_{20}N_7OBr$ (598·4)	64·22 64·00	3·36 3·50	16·38 16·50

Crystallized from [a] methanol, [b] ethanol/benzene, [c] ethanol, [d] benzene.