The Reaction of Phenylmalononitrile with Hydrazine. Synthesis and Properties of 3,5-Diamino-4-phenylpyrazole, 2-Amino-3-phenylpyrazolo[1,5-*a*]pyrimidine, and Related Compounds

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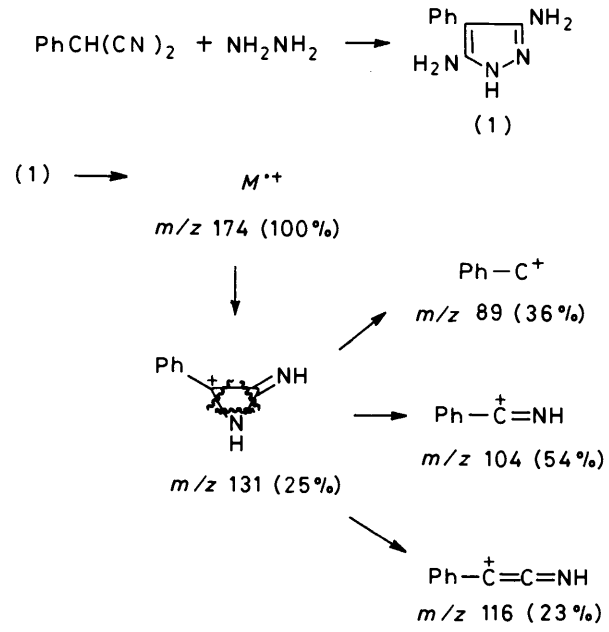
3,5-Diamino-4-phenylpyrazole was prepared by the reaction of phenylmalononitrile with hydrazine hydrate. This hitherto unknown polyfunctional heterocycle reacted with acetylacetone, ethyl acetoacetate, 5-oxobutyraldehyde, malonaldehyde, diethyl (ethoxymethylene)malonate, and mesityl oxide to give derivatives of 2-aminopyrazolo[1,5-*a*]pyrimidine. The free amino-group in the bicyclic system tends to react, in the presence of hydrochloric acid, with 1,3-dicarbonyl compounds to yield either 3-oxobut-1-enylamino side chains or a trimethine chain linkage between two aminopyrazolo[1,5-*a*]pyrimidine nuclei. The symmetric delocalized structure of the latter compounds was confirmed by a spectral study. In the case of diethyl (ethoxymethylene)malonate the amino-group gave a Michael addition product. Reaction with anisaldehyde followed by the reaction with (chlorocarbonyl)phenylketen led to a paraionic diazapentalene derivative.

3,5-Diaminopyrazole derivatives are polyfunctional starting materials for preparing derivatives of pyrazolo[1,5-*a*]pyrimidine, many of which have been found to exhibit biological and therapeutical properties.[1-3] Several derivatives have been found to be inhibitors of xanthine oxidase [1] and *c*AMP phosphodiesterase [3] and are under clinical evaluation as antianxiety drugs and in the treatment of hyperuricaemia.[3] The parent 3,5-diaminopyrazole has already been described; [4a] it reacted with ethyl acetoacetate and ethyl acrylate to yield the oxo-derivatives of dihydro- and tetrahydropyrazolo[1,5-*a*]-pyrimidine (17a) and (17b) respectively.[4b]

Attempts to prepare 3,5-diaminopyrazole by the reaction of malonitrile with hydrazine failed.[5,6] Taylor and Hartke have shown [5] that dimerization of malononitrile occurs prior to the reaction with hydrazine. The products which were isolated were the result of condensation of hydrazine with the dimer of malonitrile. At the same time Sato,[6] who reported the same results, observed the formation of 3-amino-5-hydrazinopyrazole which is the product of the reaction of malononitrile with two molecules of hydrazine followed by loss of ammonia and ring closure. This product was utilized by Gray, Stevens, and Stevens for the preparation of pyrazolo[5,1-*c*][1,2,4]triazine derivatives,[7] using 1,2-dicarbonyl compounds.

By heating phenylmalononitrile for 15 min in neat hydrazine hydrate, the desired 3,5-diamino-4-phenylpyrazole (1) was obtained in 63% yield. Its ^{1}H n.m.r. spectrum indicated the absence of a methine proton and the presence of five exchangeable protons which gave one broad signal, as was previously observed in the 3,5-dihydroxy-derivatives of isoxazole and pyrazole.[8] † The electron-impact mass spectrum of 3,5-diamino-4-phenylpyrazole (1) showed an unusual fragmentation pattern (see Scheme 1). The *m/z* 104 fragment is the most intense peak apart from the molecular ion, and almost the only way this can be formed is *via* the aziridine fragment of *m/z* 131 (see Scheme 1).

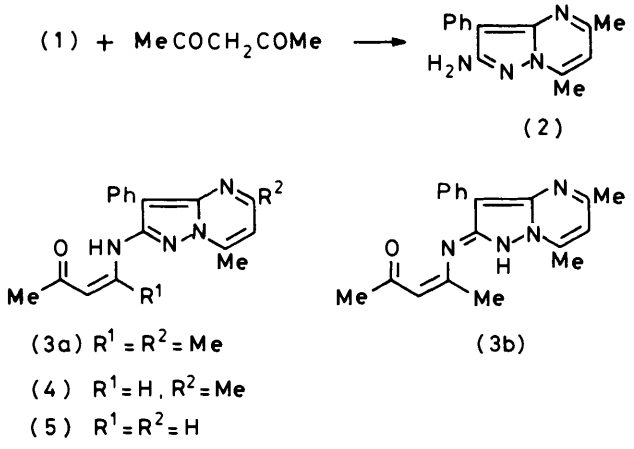
The reaction of (1) with acetylacetone in the absence of acid gave 2-amino-5,7-dimethyl-3-phenylpyrazolo[1,5-*a*]pyrimidine (2). Condensation of one molecule of the diketone with both the amino-group and the ring nitrogen atom yielded a pyrimidine ring, leaving the second amino-group free; a similar reaction of 3,5-diamino-4-(phenylazo)pyrazole was reported to yield the same 2-aminopyrazolo[1,5-*a*]pyrimidine



Scheme 1

system.[9] The ^{1}H n.m.r. spectrum of (2) indicated typical signals for the NH_2 group and the pyrimidine CH respectively (see Table). In the presence of hydrochloric acid, with acetylacetone the diaminopyrazole (1) yielded compound (2), together with a product which was the result of condensation of two molecules of acetylacetone with one molecule of (1) (Scheme 2). The same product was also obtained from the reaction of the pyrazolopyrimidine (2) with acetylacetone under the same conditions. We propose structure (3a) for this product, containing an unsaturated ketonic side chain. Similar structures have previously been observed [10] for monoimine derivatives of dicarbonyl compounds. The, exchangeable proton resonated at δ 13.20 in its n.m.r. spectrum, which seems an exceptionally low-field position for such a structure and would be more appropriate for a 1*H*-pyrazole system as in structure (3b). However, structure (3b) was excluded by ^{1}H n.m.r. comparison with the two similar compounds (4) and (5) which were prepared by the condensation

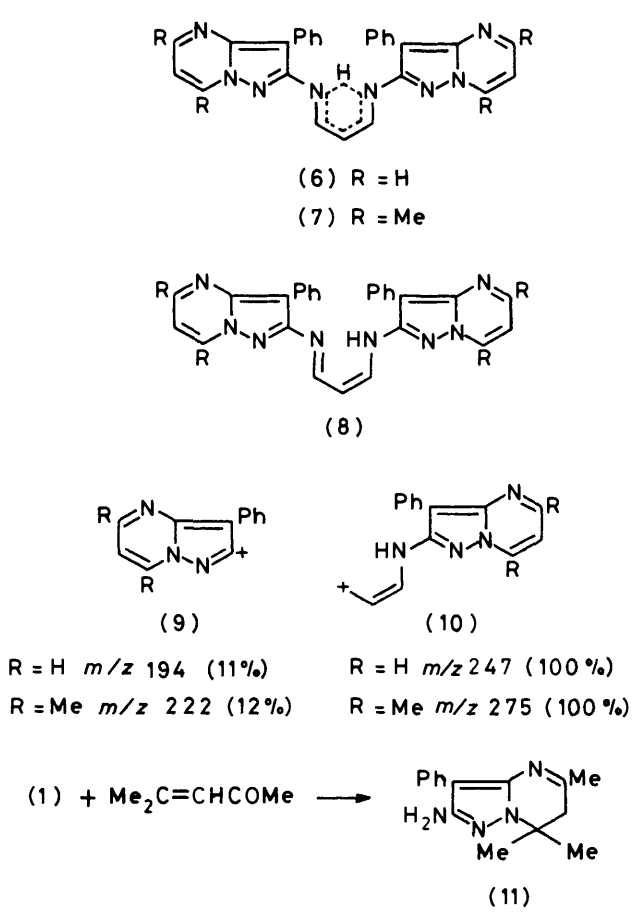
† ^{1}H N.m.r. spectrum of 3,5-dihydroxy-4-phenylpyrazole: δ(CD_3SOCD_3) 8.03—7.02 (Ph) and 5.86 (2 × OH, NH).



Scheme 2

of 3-oxobutyraldehyde (in the presence of hydrochloric acid) with compounds (2) and (1) respectively. The spectra of compounds (4) and (5) showed coupling between the NH protons and the CH of the side chain (*J ca.* 11—12 Hz), with doublets for the NH groups and double doublets for the CH groups respectively (see Table). The existence of this mutual coupling was demonstrated by irradiation of (5) at the frequency of the absorption of the NH proton, which resulted in the collapse of the double doublet into a doublet. A careful study of the ^{1}H n.m.r. spectra of the three homologues (3), (4), and (5) enabled the signals of the various methyl and CH groups to be assigned (see Table). It also enabled the location of the methyl group in the pyrimidine ring of (5) to be determined as well as the structure of the side chain. The latter was verified by mass spectroscopy.

With malonaldehyde bis(dimethyl acetal) in the presence of hydrochloric acid compound (1) yielded a product which contained three residues originating from the malonaldehyde and two from the pyrazole (1) and to which structure (6) was assigned. A similar product (7) was obtained from the reaction of the pyrazolopyrimidine (2) with malonaldehyde under the same conditions. The presence of the bicyclic systems linked by a three-carbon, two-nitrogen bridge was established by the routes for the synthesis as well as by spectral results. The nature of the bridging chain is illustrated by the appearance of the fragment ions (9) and (10) in the electron-impact mass spectrum (Scheme 3), and the ^{1}H n.m.r. and u.v. spectra are in agreement with the proposed structures. The completely symmetrical structure of the molecules of (6) and (7) is well demonstrated by their ^{1}H n.m.r. spectra in deuteriochloroform, which showed only one signal for each kind of proton on both sides of the molecule. This symmetry can arise either from fast tautomerism of the open-chain structure (8) or from the existence of a six-membered ring that contains a three-centre two-electron bond (*e.g.* a hydrogen bond stabilized by electron delocalization), as was observed for similar di-imino-derivatives of malonaldehyde.[11] The presence of a ring of this type is supported by the observation of the coupling between the NH proton and the protons of both CH groups adjacent to nitrogen, resulting in a triplet for the NH proton (*J ca.* 6 Hz) and a double doublet for the protons of the two CH groups. The coupling constant is in agreement with that previously observed for such a system.[11] The reduction in the J_{trans} coupling constant is caused by s-orbital electron density at the NH proton.[11] This was also confirmed by a decoupling experiment. When the product is dissolved in [$^2H_6$]dimethyl sulphoxide this ring is probably partly cleaved and isomerisation around the double bonds occurs; the ^{1}H



Scheme 3

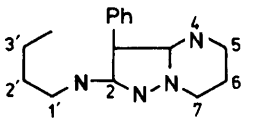
n.m.r. spectrum in this solvent is more complex than in deuteriochloroform, as observed in similar systems by Webb and Richards.[12]

The reaction of (1) with mesityl oxide afforded the dihydropyrazolopyrimidine (11). This structure is a result of both the condensation of the carbonyl group with the amino-group and a Michael addition of the ring nitrogen to the α,β-unsaturated system. A product resulting from Michael addition to the amino-group should contain a vinylic proton at the 6-position, and is excluded by the ^{1}H n.m.r. results (see Table).

Diethyl (ethoxymethylene)malonate gives with (1) the ethyl pyrazolopyrimidinecarboxylate (12). Besides the cyclization to form the oxo-pyrimidine ring, the amino-group forms a Michael addition product with the α,β-double bond. Out of the four possible isomers and tautomers (12)—(15), structure (12) is the only one in which a heterocyclic NH proton is coupled with a CH proton, and this coupling (*J* 14 Hz) was observed in the ^{1}H n.m.r. spectrum of the product. The doublet due to the =CH proton becomes a singlet after exchange with D_2O. The ^{1}H n.m.r. resonances due to the side chain (R) at the 2-position are in agreement with structure (12).

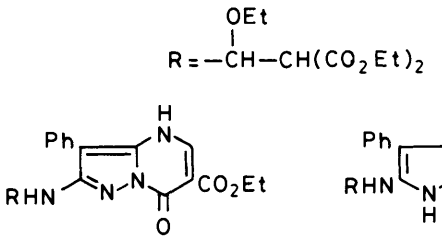
The most probable structure of the product of the reaction of (1) with ethyl acetoacetate is (16a). Its i.r. spectrum shows three bands in the double bond region (1 670, 1 630, and 1 600 cm^{-1}), consistent with structure (16a). Williams has shown [13] that compounds similar to the 7-oxo-derivative (16a) show three bands in this region whereas compounds similar to the 5-oxo-derivative (16b) exhibit two bands. The vinyl signal for

[1]H N.m.r. and u.v. spectra of derivatives of 3-phenylpyrazolo[1,5-*a*]pyrimidines

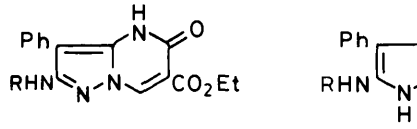


Compd. \ Position	2	4	5	6	7	1′	2′	3′	$\lambda_{max.}$/nm (ε) (in MeCN)
(2) [a]	4.40br (s, NH_2)		2.50 (s, Me)	6.40 (s)	2.80 (s, Me)				249 (15 600), 278 (14 800)
(3a)	13.20 (s, NH)		2.50 (s, Me)	6.50 (s)	2.70 (s, Me)	2.30 (s, Me)	5.23 (s)	2.06 (s, Me)	278 (21 980), 330 (22 990)
(4)	12.20 (d, NH, $J_{N1'}$ 11)		2.48 (s, Me)	6.46 (s)	2.60 (s, Me)	7.85 (dd, $J_{1'N}$ 11, $J_{1'2'}$ 8)	5.40 (d, $J_{2'1'}$ 8)	2.17 (s, Me)	
(5) [b]	12.06 (d, NH, $J_{N1'}$ 11.7)		8.33 (d, J_{56} 4.7)	6.63 (d, J_{65} 4.7)	2.72 (s, Me)	7.85 (dd,[c] $J_{1'N}$ 11.7, $J_{1'2'}$ 8.2)	5.43 (d, $J_{2'1'}$ 8.2)	2.18 (s, Me)	277 (22 070), 333 (21 870)
(6) [b]	12.25 (t, NH, $J_{N1'3'}$ 5.9)		2.71 (s, 2 Me)	6.53 (s)	2.56 (s, Me)	8.21 (dd,[d] $J_{1'N}$ 5.9, $J_{1'2'}$ 6.0)	5.33 (t, $J_{2'1'3'}$ 6.0)		275 (37 830), 377 (29 970)
(7) [b]	12.26 (t, NH, $J_{N1'3'}$ 6.0)		8.46 (dd, J_{56} 4.0, J_{57} 1.7)	6.78 (dd, J_{65} 4.0, J_{67} 6.8)	8.55 (dd, J_{76} 6.8, J_{75} 1.7)	8.19 (dd,[d] $J_{1'N}$ 6.0, $J_{1'2'}$ 6.1)	5.39 (t, $J_{2'1'3'}$ 6.1)		276 (41 080), 370 (32 370)
(11)	4.20 (s, NH_2)		2.23 (s, Me)	2.53 (s, CH_2)	1.40 (s 2 Me)				270 (13 140)
(12)	4.2 (s, NH)	11.22 (d, J_{N5} 14)	9.14 (d, J_{5N} 14)	4.31 (q), 1.30 (t) (CO_2Et)		6.85 (d, $J_{1'2'}$ 10), 3.60 (q), 1.30 (t, OEt)	4.4 (d, $J_{1'2'}$ 10) 4.31(q), 1.30 (t, 2 CO_2Et)		262 (11 070), 318 (21 760)
(16a) [a]	5.10br (s, NH_2)	11.53 (s, NH)	2.16 (s, Me)	5.36 (s)					244 (20 890), 265 (19 890)

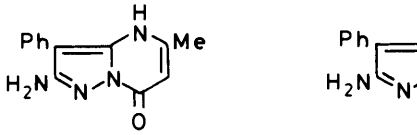
[a] Spectra of compound (2) and (16) were taken in $(CD_3)_2SO$. All other spectra in the Table were taken in $CDCl_3$. [b] Spectra of compounds (5), (6), and (7) were determined in a 300 MHz spectrometer and all others in a 60 MHz. [c] This double doublet turns into a doublet by irradiation at the frequency of the NH proton. [d] The shape of this double doublet is close to that of a triplet; irradiation in the frequencies of either the NH or 2′H gave doublets respectively.



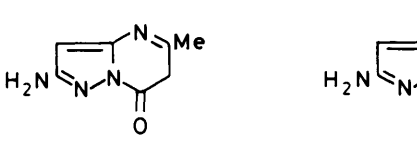
(12) (13)



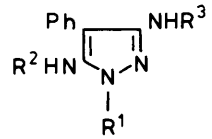
(14) (15)



(16a) (16b)



(17a) (17b)



(18) $R^1 = R^3 = MeCO$, $R^2 = H$

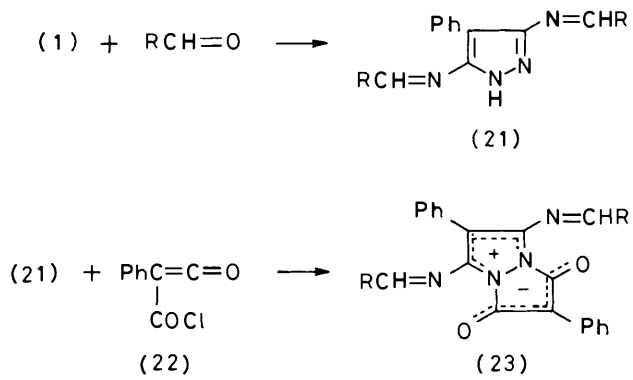
(19) $R^2 = R^3 = MeCO$, $R^1 = H$

(20) $R^1 = R^2 = MeCO$, $R^3 = H$

6-H and the NH signal at δ 11.53 (see Table) indicate a different structure from that reported [4b] for compound (17a).

The major product of the reaction of the pyrazole (1) with either acetic anhydride or acetyl chloride is assumed to be 3-acetamido-1-acetyl-5-amino-4-phenylpyrazole (18). The resonances for the protons of the two acetyl groups differ by more than 0.3 p.p.m. (δ 2.26 and 2.60 respectively), excluding the isomer (19) in which both acetyl groups are on the amino-groups. Isomer (20) is excluded by its failure to react with acetylacetone to yield a 2-imino-3-phenylpyrazolo[1,5-*a*]-pyrimidine derivative.

Compound (1) with anisaldehyde gave the bis-*p*-methoxybenzylidene derivative (21) which reacted with (chlorocarbonyl)phenylketen (22) to give the diazapentalene derivative (23). Its u.v.-visible spectra and other spectral features were comparable with those for similar betaines that have been described previously.[14]



(21) (22) (23)

$R = p\text{-}MeOC_6H_4$

Experimental

M.p.s were taken with a Thomas Hoover apparatus. I.r. spectra were determined with a Perkin-Elmer spectrophotometer model 157, u.v. and visible spectra with a Varian Techtrone spectrophotometer model 635, n.m.r. spectra either with a Varian T-60 or with a Bruker WH-300 spectrometer with tetramethylsilane as internal reference, and mass spectra with a Varian MAT-311 spectrometer. For column chromatography, the mixture was dissolved in dichloromethane and mixed with a small amount of silica gel (Merck 70—230 mesh). The solvent was evaporated off, the residue placed on top of a silica gel column, and elution then carried out with a suitable solvent. Unless stated otherwise, light petroleum had a boiling range of 40—60 °C.

Phenylmalonitrile.—This compound was prepared from α-phenylmalonamide [15] using phosphorus pentaoxide by a known procedure [16] and recrystallized from methanol–water, m.p. 65 °C (lit.,[14] 64 °C); ^1H n.m.r. ($CDCl_3$): δ 7.43 (s, Ph) and 5.03 (s, CH); ^{13}C n.m.r. ($CDCl_3$); δ 130.90, 130.28, 127.44, and 125.84 (Ph); 111.97 (CN); 77.40 p.p m. (CH).

3,5-*Diamino-4-phenylpyrazole* (1).—Phenylmalononitrile (14.2 g) was dissolved in hydrazine hydrate (28 g); the reaction was moderately exothermic. The mixture was heated under reflux for 15 min, then cooled to room temperature. Ethanol (50 ml) was added and the precipitate collected, washed with tetrahydrofuran (THF), and recrystallized from acetonitrile to give the *pyrazole* (1) (11.0 g, 63% yield), m.p. 230—232 °C; $\nu_{max.}$ (Nujol): 3 460 and 3 140 cm^{-1} (HN); ^1H n.m.r. (CD_3SOCD_3), δ 7.25 (Ph) and 5.50 (s, NH_2, NH); *m/z*; 174 (100%), 143 (22), 131 (24), 117 (34), 116 (23), 104 (54), 89 (35), and 77 (24%); $\lambda_{max.}$ (MeCN): 270 nm (ε 9 700) (Found: C, 62.3; H, 5.7; N, 32.7. $C_9H_{10}N_4$ requires C, 62.05; H, 5.8; N, 32.2%).

2-*Amino*-5,7-*dimethyl*-3-*phenylpyrazolo*[1,5-a]*pyrimidine* (2).—3,5-Diamino-4-phenylpyrazole (1) (1.75 g) was heated in acetylacetone (2.8 ml) until the solution started to boil. An exothermic reaction took place and a precipitate started to form. After the temperature dropped to about 30 °C, the mixture was reboiled for 1 min. Ether was added (4 ml) and the precipitate was collected, washed with ether, and recrystallized from THF–ether to give the *pyrazolopyrimidine* (2) (2.1 g, 86%), m.p. 215—216 °C; $\nu_{max.}$: 3 120 cm^{-1} (NH); *m/z*: 238 (100%) and 108 (19); $\lambda_{max.}$ (MeCN): 249 (ε 15 600) and 278 nm (ε 14 800) (Found: C, 70.3; H, 6.0. $C_{14}H_{14}N_4$ requires C, 70.6; H, 5.9%).

5,7-Dimethyl-2-(1-methyl-3-oxobut-1-enylamino)-3-phenylpyrazolo[1,5-a]*pyrimidine* (3a).—3,5-Diamino-4-phenylpyrazole (1) (1.75 g) was suspended in THF (50 ml) and conc. hydrochloric acid (1.7 ml) was added. The solid dissolved and a slight turbidity appeared. Acetylacetone (24 ml) was added and the mixture stirred for 15 min. The mixture of hydrochlorides of (2) and (3) which precipitated was collected (3.5 g) and resuspended in 5% aqueous sodium hydrogen carbonate (40 ml). The mixture was stirred for 1 h, the solid was filtered off (2.24 g), and the two products were separated on a silica gel column, with ethyl acetate–light petroleum (2:3) as eluant. Compound (3a) was eluted first and was recrystallized from THF–light petroleum (1.66 g, 52%). Compound (2) was recrystallized as before (0.58 g, 24% yield). The *pyrazolopyrimidine* (3) had m.p. 133 °C, $\nu_{max.}$ (Nujol): 1 605 cm^{-1} (CO); ^{13}C n.m.r. ($CDCl_3$): δ 197.02 (C=O); 159.24, 159.04, 150.56, and 145.44 (C=N and =C–N); 144.78, 131.06, 129.42, and 128.90 (Ph); 108.50 (heterocyclic =CH); 100.95 and 100.53 (C=C); 29.53; 25.38; 23.78; and 17.35 p.p.m. (Me); *m/z*: 320 (100%), 277 (71), 263 (18), and 237 (8.7) (Found: C, 71.4; H, 6.2; N, 17.65. $C_{19}H_{20}N_4O$ requires C, 71.2; H, 6.3, N, 17.5%).

5,7-Dimethyl-2-(3-oxobut-1-enylamino)-3-phenylpyrazolo[1,5-a]*pyrimidine* (4).—To a solution of compound (2) (0.48 g) in THF (5 ml) were added 3-oxobutyraldehyde dimethyl acetal (0.72 ml) and conc. hydrochloric acid (0.5 ml), and the solution was stirred for 70 min. The precipitated hydrochloride of (4) was filtered off and suspended in 5% aqueous sodium hydrogen carbonate (20 ml); filtration and recrystallization from propan-2-ol–light petroleum gave the *pyrazolopyrimidine* (4) (0.35 g, 56%), m.p. 144 °C, $\nu_{max.}$ (Nujol): 1 620 cm^{-1} (C=O); *m/z*: 306 (2.5%), 204 (59), 190 (34), 161 (50), 189 (100), and 119 (25) (Found: C, 70.7; H, 5.9; N, 18.6. $C_{18}H_{16}N_4O$ requires C, 70.6; H, 5.9; N, 18.3%).

7-Methyl-2-(3-oxobut-1-enylamino)-3-phenylpyrazolo[1,5-a]*pyrimidine* (5).—3,5-Diamino-4-phenylpyrazole (1) (0.44 g) was suspended in THF (12 ml). Conc. hydrochloric acid (0.45 ml) and 3-oxobutyraldehyde dimethyl acetal (5.5 ml) were added and the mixture was stirred for 1 h. The precipitated hydrochloride was filtered off and suspended in 5% aqueous sodium hydrogen carbonate (15 ml), and the mixture stirred for 5 min and filtered. Recrystallization from propan-2-ol, gave the *pyrazolopyrimidine* (5) (0.32 g, 40%), m.p. 165 °C; $\nu_{max.}$ (Nujol): 1 635 cm^{-1} (C=O) (Found: C, 70.1; H, 5.7; N, 19.4. $C_{17}H_{16}N_4O$ requires C, 69.85; H, 5.5; N, 19.2%).

3-Phenyl-2-{*3-(3-phenylpyrazolo*[1,5-a]*pyrimidin-2-ylamino)prop-2-enylideneamino*}*pyrazolo*[1,5-a]*pyrimidine* (6).—3,5-Diamino-4-phenylpyrazole (1) (0.44 g) was suspended in THF (6 ml). Conc. hydrochloric acid (0.5 ml) and malonaldehyde bis(dimethyl acetal) (1.4 ml) were added and the solution was stirred for 1.5 h. The hydrochloride which precipitated was collected and resuspended in 5% aqueous sodium hydrogen carbonate (25 ml). The solid was collected, washed with water, and recrystallized from chloroform. On drying at 80 °C the crystals retained one molecule of chloroform (0.3 g, 46% yield), m.p. 221—223 °C (decomp.); $\nu_{max.}$ (Nujol): 3 500 cm^{-1} (NH); *m/z*: 456 (15%), 247 (100), 221 (5.6), 195 (11), 194 (7.7), and 169 (7.5). An analytically pure sample of (6) was obtained by drying at 125 °C for 36 h (Found: C, 71.2; H, 4.5; N, 24.6. $C_{27}H_{20}N_8$ requires C, 71.0; H, 4.4; N, 24.5%).

5,7-Dimethyl-3-phenyl-2-{*3-(5,7-dimethyl-3-phenylpyrazolo*[1,5-a]*pyrimidin-2-ylamino)prop-2-enylideneamino*}*pyrazolo*[1,5-a]*pyrimidine* (7).—The pyrazolopyrimidine (2) (0.6 g) was suspended in THF (10 ml). Malonaldehyde bis(dimethyl acetal) (2 ml) and conc. hydrochloric acid (0.8 ml) were added, the mixture was stirred for 1.5 h, and the hydrochloride which precipitated was collected and resuspended in a solution of 5% aqueous sodium hydrogen carbonate (15 ml). The solid was collected and recrystallized twice from dimethyl sulphoxide–propan-2-ol (1 : 1) to give the *tetramethyl compound* (7) (0.4 g, 64%), m.p. 223—225 °C (decomp.); $\nu_{max.}$ (Nujol) 3 300 cm^{-1} (NH); *m/z*: 512 (3.2%), 275 (100), 249 (12), 238 (52), 236 (4.1), and 222 (12) (Found: C, 72.4; H, 5.7; N, 21.7 $C_{31}H_{28}N_8$ requires C, 72.6; H, 5.5; N, 21.9%)

2-Amino-6,7-dihydro-5,7,7-trimethyl-3-phenylpyrazolo[1,5-a]*pyrimidine* (11).—3,5-Diamino-4-phenylpyrazole (1) (0.44 g) was heated under reflux in mesityl oxide (1.2 ml) for 3 min. The solution became red and on cooling a crystalline solid deposited. After two recrystallizations from THF–light petroleum, the *trimethyl compound* (11) was colourless (0.31 g, 47%), m.p. 123—125 °C; $\nu_{max.}$ (Nujol): 3 130 cm^{-1} (NH) (Found: C, 70.9; H, 7.4; N, 22.1. $C_{15}H_{18}N_4$ requires C, 70.8; H, 7.1; N, 22.0%).

Ethyl 2-(2,2-Bisethoxycarbonyl-1-ethoxyethylamino)-4,7-dihydro-7-oxo-3-phenylpyrazolo[1,5-a]*pyrimidine-6-carboxylate* (12).—3,5-Diamino-4-phenylpyrazole (1) (0.44 g) was heated under reflux with diethyl (ethoxymethylene)malonate (0.6 ml) for 2 min. The solution, which became yellow and viscous, was cooled and ether was added gradually. After the oil which separated had solidified, it was filtered off and chromatographed on a silica gel column. Elution with ethyl acetate–light petroleum (3 : 2) gave (12) as the first product. Evaporation and recrystallization from propan-2-ol–light petroleum gave the *ester* (12) (0.35 g, 27%), m.p. 163 °C; $\nu_{max.}$ (Nujol): 3 200 (NH); 1 745, 1 720, and 1 685 cm^{-1} (C=O); *m/z*; 514 (4.8%), 344 (31), 298 (81), 252 (75), 217 (20), 171 (95), 143 (61), and 115 (100) (Found: C, 58.4; H, 6.3; N, 10.5. $C_{25}H_{30}N_4O_8$ requires C, 58.4; H, 5.9; N, 10.9%).

2-Amino-5-methyl-3-phenylpyrazolo[1,5-a]*pyrimidin-7*(4H)*-one* (16a).—3,5-Diamino-4-phenylpyrazole (1) (0.44 g) was heated under reflux in ethyl acetoacetate (0.75 ml) for 5 min. On cooling a precipitate formed. Ether (2 ml) was added, and the solid was collected, recrystallized from dimethyl sulphoxide–water, and dried *in vacuo* at 100 °C for 24 h to give the *pyrazolopyrimidinone* (16a) (0.22 g, 35%), m.p. >300 °C; $\nu_{max.}$ (Nujol): 3 160 (NH), 1 670 (C=O); 1 630, and 1 600 cm^{-1} (C=N) (Found: C, 64.9; H, 5.35. $C_{13}H_{12}N_4O$ requires C, 65.0; H, 5.03%).

3-Acetamido-1-acetyl-5-amino-4-phenylpyrazole (18).—3,5-Diamino-4-phenylpyrazole (1) (0.44 g) was dissolved in acetic anhydride (0.75 ml). The reaction is exothermic. After all the solid had dissolved, ether (25 ml) was added and the mixture left at room temperature for complete precipitation. The crystalline *pyrazole derivative* (18) obtained (0.53 g, 81%) had m.p. 134 °C, $\nu_{max.}$ (Nujol): 3 240 (NH); 1 690 and 1 650 cm^{-1} (C=O); δ (^1H; $CDCl_3$) 7.33 (br s, Ph and NH), 5.73 (br s, NH_2), 2.60 (s, CH_3), and 2.26 (s, CH_3); *m/z*: 258 (41%), 216 (56), 174 (100), 169 (21), 154 (19), and 141 (18), $\lambda_{max.}$ (MeCN): 245 nm (ε 17 720) (Found: C, 60.1; H, 5.6; N, 21.8. $C_{13}H_{14}N_4O_2$ requires C, 60.5; H, 5.5; N, 21.7%).

3,5-Bis(*p-methoxybenzylideneamino*)*-4-phenylpyrazole* (21).—3,5-Diamino-4-phenylpyrazole (1) (0.35 g) was heated under reflux with anisaldehyde (0.6 ml) for 2 min. After 1 min a yellow precipitate deposited. The mixture was cooled to room temperature, ether (9.5 ml) added, and the solid filtered off, washed with ether, and recrystallized from ethyl acetate–light petroleum, to give the *di-imine* (21) (0.5 g, 60%), m.p. 210 °C;

$\nu_{max.}$ (Nujol): 3 160 cm^{-1} (NH); δ (^1H, $CDCl_3$) 12.63 (br s, NH), 8.66 (s, CH), 7.2 (q, 2 × C_6H_4), 7.5 (m, Ph), and 3.75 (s, 2 × OCH_3); $\lambda_{max.}$ (MeCN) 250 (ε 19 590), 298 (33 790), and 345 nm (38 850) (Found: C, 73.3; H, 5.31; N, 13.35. $C_{25}H_{22}N_4O_2$ requires C, 73.2; H, 5.4; N, 13.65%).

5,7-*Bis*(*p-methoxybenzylideneamino*)-3-*oxo*-2,6-*diphenyl*-3H-4λ^5-*pyrazolo*[1,2-a]*pyrazolylium*-1-*olate*.—A stirred solution of the di-imine (21) (0.2 g) in dry THF (4 ml) was cooled to 15 °C and (chlorocarbonyl)phenylketen [17] (22) (0.3 g) was added during 3 min. The stirring was continued for 10 min, and the precipitated product was collected and resuspended in 5% aqueous sodium hydrogen carbonate (10 ml). The mixture was stirred for 30 min and the *paraionic compound* (23) was obtained (0.1 g, 40%), m.p. 218 °C (decomp.); $\nu_{max.}$ (Nujol) 1 670 cm^{-1} (C=O); $\lambda_{max.}$ (MeCN) 275 (ε 43 750), 322 (31 250), and 383 nm (30 500) (Found: C, 73.5; H, 4.7; N 10.5. $C_{34}H_{26}N_4O_4$ requires C, 73.6; H, 4.7; N, 10.1%).

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