

## Studies on Heterocyclic Chemistry. Part XIX.<sup>1</sup> Synthesis of 4-Aroyl-1-arylpyrazoles from $\alpha$ -Aroyl- $\beta$ -anilinoacrylonitriles and Photochemistry of 4-Carbonyl-substituted Pyrazoles

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4-Aroyl-1-arylpyrazoles are synthesised by the deamination of 5-amino-4-aroyl-1-arylpyrazoles which are obtained by the reaction of  $\alpha$ -aroyl- $\beta$ -anilinoacrylonitriles with arylhydrazines. These ketones and 1-arylpyrazole-4-carbaldehydes, when irradiated with 2537 Å light, undergo ring transposition and photoreduction, producing 1,2-bis-(1-arylimidazol-4-yl)ethane-1,2-diols.

PHOTOREDUCTION of aryl aldehydes, diaryl ketones, and alkyl aryl ketones to give 1,2-diarylethane-1,2-diols has been well studied, the lowest  $n \rightarrow \pi^*$  triplet excited state of these compounds being responsible for the reduction.<sup>2</sup> However, the behaviour of heterocyclic aldehydes and ketones on irradiation has received little attention, and as for aryl ketones,<sup>2</sup> there is a structure-reactivity relationship. Thus, phenyl 3-pyridyl ketones<sup>3,4</sup> and methyl 2-, 3-, and 4-pyridyl ketones<sup>4</sup> can be photo-reduced to the corresponding diols, but 2-thienyl, pyrrol-2-yl, and 2-furyl ketones,<sup>5</sup> and di-4-pyridyl ketone<sup>6</sup> do not afford the corresponding diols. Our continuing interest in the photochemistry of 1,2-azoles<sup>7</sup> prompted us to study the photochemical behaviour of

hydrolysis to 1,5-diphenylpyrazole-4-carboxylic acid. Repetition of their work gave a compound having the same m.p. as that reported, but to which we assign a different structure.

This substance analysed as  $C_{16}H_{13}N_3O$  and the i.r. spectrum ( $CHCl_3$ ) displays  $\nu_{max}$  3480 and 3350 ( $NH_2$ ) and 1620  $cm^{-1}$  ( $C=O$ ) absorptions, but lacks a  $\nu_{max}$  ( $C\equiv N$ ) band. The mass spectrum shows intense  $(M - 77)^+$  and  $m/e$  105 ions besides the molecular ion at  $m/e$  263 and an  $(M - 1)^+$  ion (base peak). From these spectral data and transformation to the known 4-benzoyl-1,5-diphenylpyrazole by means of aprotic deamination in benzene<sup>12a</sup> our product is formulated as 5-amino-4-benzoyl-1-phenylpyrazole (2;  $Ar^1 = Ar^2 = Ph$ ). We

5-Amino-4-aroyl-1-arylpyrazoles (2)

Ar <sup>1</sup>	Ar <sup>2</sup>	M.p. (°C)	Cryst. solvent	Yield (%)	Found (%)			Formula	Required (%)		
					C	H	N		C	H	N
Ph	Ph	181—182	EtOH	80	72.9	4.8	15.8	$C_{16}H_{13}N_3O$	73.0	5.0	16.0
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Ph	215—217	EtOH	88	64.3	3.8	14.1	$C_{16}H_{13}ClN_3O$	64.5	4.1	14.1
2-Furyl	Ph	170—172	MeOH	95	66.6	4.3	16.7	$C_{14}H_{11}N_3O_2$	66.4	4.4	16.6
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	Ph	166—168	EtOH	85	69.8	5.2	14.0	$C_{17}H_{15}N_3O_2$	69.6	5.15	14.3
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	<i>m</i> -MeC <sub>6</sub> H <sub>4</sub>	126—127	AcOEt	70	70.3	5.5	13.7	$C_{16}H_{13}N_3O_2$	70.3	5.6	13.7
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>m</i> -MeC <sub>6</sub> H <sub>4</sub>	169—170	EtOH	85	65.4	4.4	13.4	$C_{17}H_{15}ClN_3O$	65.5	4.5	13.5
Ph	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	202—203	EtOH	85	73.4	5.4	15.1	$C_{17}H_{15}N_3O$	73.6	5.45	15.15
Ph	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	179—180	Cyclohexane	74	64.5	3.8	14.2	$C_{16}H_{12}ClN_3O_2$	64.5	4.1	14.1

4-aroyl-1-arylpyrazoles and 1-arylpyrazole-4-carbaldehydes.

**Synthesis.**—Representative syntheses of aryl pyrazol-4-yl ketones are the Friedel-Crafts acylation of 1-arylpyrazoles,<sup>8</sup> the reaction of 1-arylpyrazol-4-ylmagnesium bromides with acid chlorides,<sup>9</sup> and the reaction of triphenyl- $\beta$ -acylvinylphosphonium salt with diazoalkanes.<sup>10</sup> We now report the preparation of 5-amino-4-aroyl-1-arylpyrazoles and their deamination leading to 4-aroyl-1-arylpyrazoles.

Grothaus and Dains<sup>11</sup> studied the reaction of  $\alpha$ -benzoyl- $\beta$ -anilinoacrylonitrile (1;  $Ar^1 = Ph$ ) with phenylhydrazine and obtained a compound with m.p. 182° which they assigned as 1,5-diphenylpyrazole-4-carbonitrile on the basis of nitrogen analysis and alkaline

could not reproduce the work of Grothaus *et al.*,<sup>11</sup> and other  $\alpha$ -aroyl- $\beta$ -anilinoacrylonitriles (1;  $Ar^1 = p$ -ClC<sub>6</sub>H<sub>4</sub>, *p*-MeOC<sub>6</sub>H<sub>4</sub>, or 2-furyl) were always found to give the corresponding 5-amino-4-aroyl-1-arylpyrazoles (Table) when treated with arylhydrazine.  $\alpha$ -Aroyl- $\beta$ -anilinoacrylonitriles (1;  $Ar^1 = Ph$  and *p*-MeOC<sub>6</sub>H<sub>4</sub>) afforded 3-arylpyrazole-4-carbonitriles (4;  $Ar^1 = Ph$  and *p*-MeOC<sub>6</sub>H<sub>4</sub>) as the sole product when treated with hydrazine hydrate.

Deamination of the 5-amino-4-aroyl-1-arylpyrazoles (2;  $Ar^1 = Ar^2 = Ph$ ), (2;  $Ar^1 = p$ -MeOC<sub>6</sub>H<sub>4</sub>,  $Ar^2 = Ph$ ), and (2;  $Ar^1 = Ph$ ,  $Ar^2 = p$ -MeC<sub>6</sub>H<sub>4</sub>) with isopentyl nitrite in tetrahydrofuran<sup>12c</sup> proceeded satisfactorily, yielding the 4-aroyl-1-arylpyrazoles (3;  $Ar^1 =$

<sup>1</sup> Part XVIII, T. Nishiwaki, K. Azechi, and F. Fujiyama, preceding paper.

<sup>2</sup> A. A. Lamola and N. J. Turro, 'Energy Transfer and Organic Photochemistry,' Interscience, New York, 1969, p. 191.

<sup>3</sup> M. R. Kegelman and E. V. Brown, *J. Amer. Chem. Soc.*, 1953, **75**, 4649.

<sup>4</sup> W. L. Bencze, C. A. Burckhardt, and W. L. Yost, *J. Org. Chem.*, 1962, **27**, 2865.

<sup>5</sup> T. S. Cantrell, *J.C.S. Chem. Comm.*, 1972, 155.

<sup>6</sup> F. L. Minn, C. L. Trichilo, C. R. Hurt, and N. Filipescu, *J. Amer. Chem. Soc.*, 1970, **92**, 3600.

<sup>7</sup> T. Nishiwaki, A. Nakano, and H. Matsuoka, *J. Chem. Soc. (C)*, 1970, 1825; T. Nishiwaki and F. Fujiyama, *J.C.S. Perkin I*, 1972, 1456.

<sup>8</sup> I. L. Finar and T. Foster, *J. Chem. Soc. (C)*, 1967, 1494.

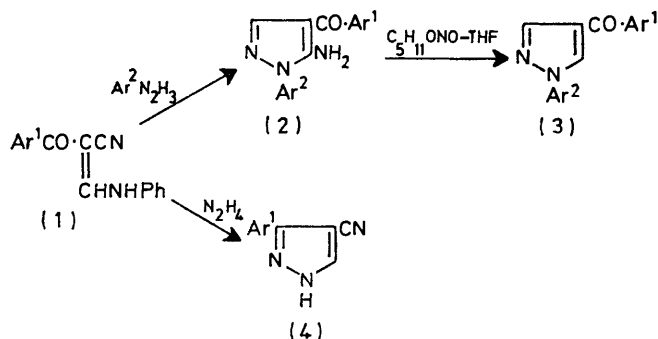
<sup>9</sup> R. J. Brooklyn and I. L. Finar, *J. Chem. Soc. (C)*, 1968, 466.

<sup>10</sup> E. Zbiral and E. Bauer, *Tetrahedron*, 1972, **28**, 4189.

<sup>11</sup> C. E. Grothaus and F. B. Dains, *J. Amer. Chem. Soc.*, 1936, **58**, 1334.

<sup>12</sup> (a) J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257; (b) J. I. G. Cadogan, D. A. Roy, and D. M. Smith, *J. Chem. Soc. (C)*, 1966, 1249; J. I. G. Cadogan and G. A. Molina, *J.C.S. Perkin I*, 1973, 541.

Ar<sup>2</sup> = Ph), (3; Ar<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, Ar<sup>2</sup> = Ph), and (3; Ar<sup>1</sup> = Ph, Ar<sup>2</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>) in good yield. The ketones (3; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph) and (3; Ar<sup>1</sup> = 2-furyl, Ar<sup>2</sup> = Ph)

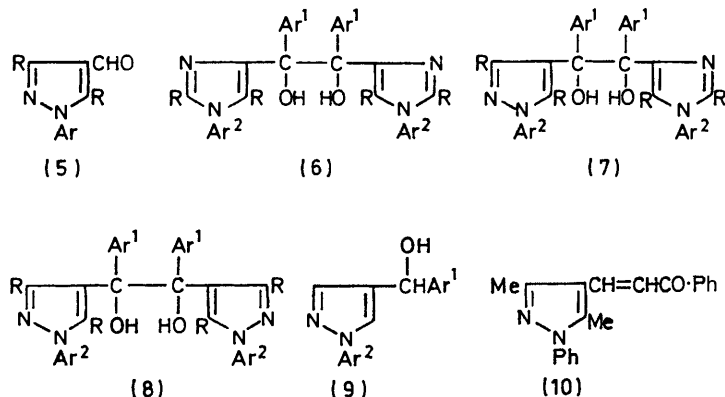


were also obtained by protic deamination of the 5-amino-pyrazoles (2; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph) and (2; Ar<sup>1</sup> = 2-furyl, Ar<sup>2</sup> = Ph), respectively, but aprotic deamination<sup>12c</sup> is a more convenient procedure as regards manipulation.

**Photochemistry.**—Irradiation of the 4-aryl-1-arylpyrazoles (3; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph) and (3; Ar<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, Ar<sup>2</sup> = Ph) and of the 1-arylpyrazole-4-carbaldehydes (5; Ar = Ph, R = H), (5; Ar = Ph, R = Me), and (5; Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>, R = Me) with 2537 Å light in propan-2-ol or ether afforded the 1,2-bis-(1-arylimidazol-4-yl)ethane-1,2-diols (6) in low yield and uncharacterisable oil(s).

H) and (6; Ar<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, Ar<sup>2</sup> = Ph, R = H) consist of only a complex aromatic multiplet but the spectrum of the diol (6; Ar<sup>1</sup> = R = H, Ar<sup>2</sup> = Ph) has signals at  $\tau$  5.26 (CH), 4.70 (exch., OH), 2.67 (1H, d, *J* 1.5 Hz), and 2.33 (1H, d, *J* 1.5 Hz), in addition to a multiplet of benzene protons. The peak at  $\tau$  2.33 is assigned to 2-H of the imidazole ring by reference to the spectra of 1-arylimidazoles.<sup>14</sup> The 4-substituted 1-aryl-imidazole structure is proposed on the basis of a coupling constant.<sup>15</sup> The spectra of the diols (6; Ar<sup>1</sup> = H, Ar<sup>2</sup> = Ph, R = Me) and (6; Ar<sup>1</sup> = H, Ar<sup>2</sup> = *p*-ClC<sub>6</sub>H<sub>4</sub>, R = Me) each exhibit two Me singlets, eliminating an unsymmetrical structure (7). Other unsymmetrical diol structures containing at least one pyrazole ring having a hydroxy-group at C(3) or C(5) are also eliminated because the spectra of the diols (6; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph, R = H), (6; Ar<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, Ar<sup>2</sup> = Ph, R = H), and (6; Ar<sup>1</sup> = R = H, Ar<sup>2</sup> = Ph) have no signals at a higher field than  $\tau$  3.2 where the C(4) protons of the pyrazole ring should be observed.<sup>16</sup>

The 1,2-bis-(1-arylpyrazol-4-yl)ethane-1,2-diol structure (8) is ruled out by comparison of the u.v. spectrum of the diol (6; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph, R = H) [ $\lambda_{\max}$  (EtOH) 211 and 264 nm (log  $\epsilon$  4.52 and 4.49)] with that of phenyl-(1-phenylpyrazol-4-yl)methanol (9; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph) [ $\lambda_{\max}$  (EtOH) 249 and 279 nm (log  $\epsilon$  4.20 and 4.29)]; if the product under consideration had the structure (8);



The high resolution mass spectra of the diol (6) display no molecular ion peak, but presence of weak ( $M + 2$ )<sup>+</sup> and ( $M - H_2O$ )<sup>+</sup> ions and the ions (a) and (b) of moderate intensity in the region  $m/e > M^+/2$ , which are explained in terms of the pinacol-pinacolone rearrangement in a mass spectrometer,<sup>13</sup> establish the molecular formulae. A strong  $\nu_{\max}$  (OH) absorption is found in the i.r. spectra, and the mass spectra have an  $M^+/2$  ion as the base peak, in agreement with the general fragmentation patterns of ethane-1,2-diols.<sup>13</sup>

N.m.r. spectra of the diols (6; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph, R =

Ar<sup>1</sup> = Ar<sup>2</sup> = Ph, R = H), its u.v. spectrum would closely resemble that of the compound (9; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph). The spectrum of the diol (6; Ar<sup>1</sup> = R = H, Ar<sup>2</sup> = Ph) (see Experimental section) also differs from that of (1-phenylpyrazol-4-yl)methanol (9; Ar<sup>1</sup> = H, Ar<sup>2</sup> = Ph) [ $\lambda_{\max}$  (EtOH) 258 nm (log  $\epsilon$  4.01)].

The proposed structure also agrees with the mass spectral fragmentations. Abundant ions (*d*) at  $m/e$  116 (C<sub>8</sub>H<sub>6</sub>N only) for the diols (6; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph, R = H) and (6; Ar<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, Ar<sup>2</sup> = Ph, R = H) and at  $m/e$  130 (C<sub>9</sub>H<sub>8</sub>N only) for the diol (6; Ar<sup>1</sup> = H, Ar<sup>2</sup> =

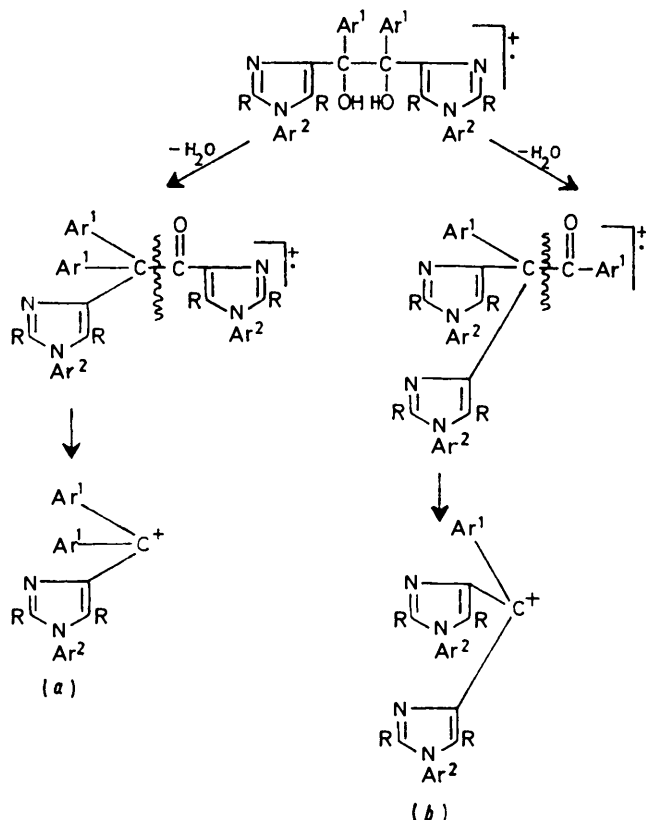
<sup>13</sup> P. Funke, K. G. Das, and A. K. Bose, *J. Amer. Chem. Soc.*, 1964, **86**, 2527; K. G. Das, C. A. Chinchwadkar, and P. S. Kulkarni, *Chimia (Switz.)*, 1968, **22**, 88; J. Kossanyi, J. P. Morizur, B. Furth, J. Wiemann, A. M. Duffield, and C. Djerassi, *Org. Mass Spectrometry*, 1968, **1**, 777.

<sup>14</sup> C. G. Begg, M. R. Grimmett, and P. D. Wethey, *Austral. J. Chem.*, 1973, **26**, 2435.

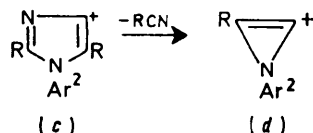
<sup>15</sup> H. R. Matthews and H. Rapoport, *J. Amer. Chem. Soc.*, 1973, **95**, 2297.

<sup>16</sup> T. J. Batterham, 'N.m.r. Spectra of Simple Heterocycles,' Wiley, New York, 1973, p. 178.

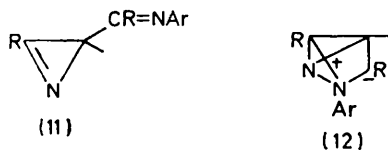
Ph, R = Me) must have been generated by loss of RCN<sup>17</sup> from the 1-arylimidazolyl ion (c). A weak peak at *m/e*



145 for the diol (6; Ar<sup>1</sup> = H, Ar<sup>2</sup> = Ph, R = Me) is C<sub>10</sub>H<sub>11</sub>N only and includes atoms at N(1), C(2), and C(5) of the proposed structure.



The transposition of the pyrazoles (3) and (5) probably occurs through photo-induced ring contraction and ring enlargement *via* the arylimino-2*H*-azirine derivative (11)



as an intermediate<sup>18a</sup> or the ammonium ylide intermediate (12).<sup>19</sup> To obtain some insight into the intermediacy of the azirine (11), the pyrazole (5; Ar = Ph, R = H) was irradiated in a mixture of propan-2-ol and

<sup>17</sup> J. H. Bowie, R. G. Cooks, S.-O. Lawesson, and G. Schroll, *Austral. J. Chem.*, 1967, **20**, 1613.

<sup>18</sup> (a) H. Tiefenthaler, W. Dörscheln, H. Göth, and H. Schmidt, *Helv. Chim. Acta*, 1967, **50**, 2244; (b) J. P. Ferris and L. E. Orgel, *J. Amer. Chem. Soc.*, 1966, **88**, 1074; (c) P. Beak and W. Messer, *Tetrahedron*, 1969, **25**, 3287.

<sup>19</sup> H. C. Van der Plas, 'Ring Transformations of Heterocycles,' Vol 1, Academic Press, New York, 1973, p. 262.

formic acid; the azirine is expected to be hydrolysed under these conditions, yielding product(s) other than the imidazole (6; Ar<sup>1</sup> = R = H, Ar<sup>2</sup> = Ph). However, formic acid quenched the reaction, up to 95% of the starting material being recovered.

Occurrence of the transposition reported here appears to be dependent on the solvent used; the reactions of the pyrazole (5; Ar = Ph, R = H) in benzene and of the pyrazole (5; Ar = Ph, R = Me) in acetonitrile do not proceed to an appreciable extent. The ready transposition of the pyrazoles (3) and (5) in ether and alcohol is of interest when compared with the related ketones 1-phenyl-3-(1-phenyl-3,5-dimethylpyrazol-4-yl)prop-2-enone (10) and 4-benzoyl 3,5-diphenylisoxazole,<sup>20</sup> which do not undergo transposition or stereoisomerisation (confirmed by n.m.r. spectrum) when irradiated in ether.

It is not clear at present which of the two processes, transposition or photoreduction, precedes, but presumably photoreduction will follow transposition to 1-aryl-imidazole-4-carbaldehyde; if the reduction precedes, the diols (7) and (8) might be isolated.

It is known that carbonyl compounds are photoreduced by amines through a charge-transfer complex.<sup>21</sup> To compare with the foregoing photoreduction, the pyrazole (5; Ar = Ph, R = Me) was irradiated in a mixture of acetonitrile (or benzene) and triethylamine. Although a large excess of the amine quenched the reaction, the reduction proceeds in the presence of *ca.* 10 equiv. of the amine, affording the diol (6; Ar<sup>1</sup> = H, Ar<sup>2</sup> = Ph, R = Me) in low yield.

#### EXPERIMENTAL

Petroleum refers to the fraction of b.p. 70–110° unless otherwise stated. High resolution mass spectra were registered by 'element map' technique. N.m.r. spectra were recorded at 60 MHz. The light source used throughout this work is a Riko low pressure mercury lamp (30 W). Phenyl-(1-phenylpyrazol-4-yl)methanol (9; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph) and (1-phenylpyrazol-4-yl)methanol (9; Ar<sup>1</sup> = H, Ar<sup>2</sup> = Ph) were prepared as described.<sup>22</sup> 1-Phenyl-3-(1-phenyl-3,5-dimethylpyrazol-4-yl)prop-2-enone (10) was prepared as reported,<sup>23</sup>  $\tau$  (CDCl<sub>3</sub>) 7.57 (s, Me), 7.50 (s, Me), 2.85 (1H, d, *J* 12 Hz), 2.57 (10H, s), and 2.34 (1H, d, *J* 12 Hz).

$\alpha$ -Aroyl- $\beta$ -anilinoacrylonitriles (1).—The following compounds were prepared by heating aroylacetonitrile (0.01 mol) and *NN'*-diphenylformamidine (0.01 mol) in xylene or chlorobenzene (20 ml) for 2 h at 120–130° and diluting the mixture with petroleum;  $\alpha$ -*p*-chlorobenzoyl- (1; Ar<sup>1</sup> = *p*-ClC<sub>6</sub>H<sub>4</sub>), m.p. 146–148° (from ethanol) (Found: C, 68.1; H, 4.0. C<sub>16</sub>H<sub>11</sub>ClN<sub>2</sub>O requires C, 68.0; H, 3.9%);  $\alpha$ -2-furoyl- (1; Ar<sup>1</sup> = 2-furyl), m.p. 131–132° (from petroleum) (Found: C, 70.8; H, 4.1. C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> requires C, 70.6; H, 4.2%);  $\alpha$ -*p*-methoxybenzoyl- (1; Ar<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>), m.p. 115–117° (from methanol) (Found: C, 73.6; H, 4.9. C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> requires C, 73.4; H, 5.1%).

5-Amino-4-*aroyl*-1-arylpyrazoles (2).—The  $\alpha$ -*aroyl*- $\beta$ -anilinoacrylonitrile (1) (0.01 mol) and phenylhydrazine (0.01 mol) were heated in ethanol (20 ml) for 1–2 h and the

<sup>20</sup> T. Nishiwaki, unpublished work.

<sup>21</sup> S. G. Cohen, A. Parola, and G. H. Parson, *Chem. Rev.*, 1973, **73**, 141.

<sup>22</sup> I. L. Finar and G. H. Lord, *J. Chem. Soc.*, 1959, 1819.

<sup>23</sup> I. L. Finar and M. Manning, *J. Chem. Soc.*, 1961, 2733.

ketone (2) was collected. The reaction with *m*-tolylhydrazine was carried out similarly. 5-Amino-4-benzoyl-1-*p*-tolylpyrazole (2; Ar<sup>1</sup> = Ph, Ar<sup>2</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>) and 5-amino-4-benzoyl-1-*p*-chlorophenylpyrazole (2; Ar<sup>1</sup> = Ph, Ar<sup>2</sup> = *p*-ClC<sub>6</sub>H<sub>4</sub>) were obtained by heating a mixture of  $\alpha$ -benzoyl- $\beta$ -anilinoacrylonitrile (1; Ar<sup>1</sup> = Ph) (0.01 mol), *p*-tolylhydrazine hydrochloride or *p*-chlorophenylhydrazine hydrochloride (0.01 mol), sodium acetate (0.01 mol), ethanol (20 ml), and water (10 ml) for 2 h and diluting the mixture with water. Physical constants and analyses of the 5-amino-4-aryloxy-1-arylpyrazoles (2) are collected in the Table.

4-Benzoyl-1,5-diphenylpyrazole.—A mixture of the amino-ketone (2; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph) (0.70 g), isopentyl nitrite (1 ml), and dry benzene (20 ml) was heated under reflux for 2 h. The solvent was removed under reduced pressure and the residue was washed with ether. Two recrystallisations from petroleum gave the ketone as needles (0.23 g, 27%), m.p. 142—143° (lit.,<sup>24</sup> 144—145°).

4-Benzoyl-1-phenylpyrazole (3; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph).—(a) A solution of the amino-ketone (2; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph) (3.24 g) in dry tetrahydrofuran (100 ml) was added during 1 h to a boiling solution of isopentyl nitrite (10 ml) and dry tetrahydrofuran (20 ml) and heating was continued for a further 3 h. The solvent was removed under reduced pressure and 4-benzoyl-1-phenylpyrazole (2.60 g, 84%) crystallised from petroleum as needles, m.p. 123—124° (lit.,<sup>8</sup> 124—125°),  $\nu_{\max}$  (CHCl<sub>3</sub>) 1640 cm<sup>-1</sup> (C=O).

(b) Isopentyl nitrite (3 ml) was slowly added into a solution of the aminopyrazole (1.26 g), dioxan (20 ml), and hydrochloric acid (3 ml). The mixture was set aside for 15 min in an ice-bath and then copper powder (1.0 g) was added. After evolution of a gas, the mixture was diluted with water and extracted with ether. The extracts were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to give the ketone (0.42 g, 35%).

4-*p*-Methoxybenzoyl-1-phenylpyrazole (3; Ar<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, Ar<sup>2</sup> = Ph).—This compound was prepared in 93% yield by aprotic deamination of the amino-ketone (2; Ar<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, Ar<sup>2</sup> = Ph) as above and crystallised from petroleum as needles, m.p. 118—119° (Found: C, 73.4; H, 5.1; N, 9.8. C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> requires C, 73.4; H, 5.1; N, 10.1%),  $\nu_{\max}$  (CHCl<sub>3</sub>) 1640 cm<sup>-1</sup> (C=O).

4-Benzoyl-1-*p*-tolylpyrazole (3; Ar<sup>1</sup> = Ph, Ar<sup>2</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>).—This compound was prepared in 90% yield by aprotic deamination of the amino-ketone (2; Ar<sup>1</sup> = Ph, Ar<sup>2</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>) as described above and crystallised from petroleum as rods, m.p. 121—122° (Found: C, 77.8; H, 5.4; N, 10.6. C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O requires C, 77.8; H, 5.4; N, 10.7%),  $\nu_{\max}$  (CHCl<sub>3</sub>) 1640 cm<sup>-1</sup> (C=O).

2-Furyl-1-phenylpyrazole (3; Ar<sup>1</sup> = 2-furyl, Ar<sup>2</sup> = Ph).—Isopentyl nitrite (1 ml) was slowly added to an ice-cooled mixture of the amino-ketone (2; Ar<sup>1</sup> = 2-furyl, Ar<sup>2</sup> = Ph) (0.33 g), dioxan (10 ml), and 50% sulphuric acid (5 ml). The solution was set aside for 15 min, mixed with copper powder (0.5 g), and heated on a steam-bath for 30 min. Dilution with water, extraction with ether, and evaporation of the dried (Na<sub>2</sub>SO<sub>4</sub>) extracts gave the furyl ketone (0.12 g, 37%). Crystallisation from aqueous methanol gave light yellow needles, m.p. 101—102° (Found: C, 70.65; H, 4.2; N, 11.8. C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> requires C, 70.6; H, 4.2; N, 11.8%),  $\nu_{\max}$  (CHCl<sub>3</sub>) 1625 cm<sup>-1</sup> (C=O).

3-Phenylpyrazole-4-carbonitrile (4; Ar<sup>1</sup> = Ph).—This compound was obtained in 80% yield as reported<sup>11</sup> and had m.p. 130—132° (lit.,<sup>11</sup> 134°),  $\nu_{\max}$  (CHCl<sub>3</sub>) 3180 (NH) and 2240 cm<sup>-1</sup> (C≡N).

3-*p*-Methoxyphenylpyrazole-4-carbonitrile (4; Ar<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>).—This compound was obtained in 95% yield by using the reported method<sup>11</sup> and crystallised from aqueous methanol as needles, m.p. 144—145° (Found: C, 66.4; H, 4.6; N, 21.3. C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>O requires C, 66.3; H, 4.55; N, 21.1%),  $\nu_{\max}$  (Nujol) 3100 (NH) and 2240 cm<sup>-1</sup> (C≡N).

1,2-Diphenyl-1,2-bis-(1-phenylimidazol-4-yl)ethane-1,2-diol (6; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph, R = H).—A solution of the phenyl ketone (3; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph) [ $\lambda_{\max}$  (cyclohexane) 239 and 278 nm (log  $\epsilon$  4.25 and 4.32)] (0.80 g) in propan-2-ol (300 ml) was irradiated for 4 h. The solvent was removed under reduced pressure and the residue was chromatographed on alumina. Elution with ether gave the starting material (0.29 g) and elution with ether-methanol (3:1) afforded the ethanediol (0.04 g, 8% yield based on unrecovered starting material). Crystallisation from ethyl acetate-petroleum gave rectangular plates, m.p. 206—208° (Found: C, 76.6; H, 5.4; N, 11.1. C<sub>32</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub> requires C, 77.1; H, 5.3; N, 11.2%),  $\nu_{\max}$  (Nujol) 3150 cm<sup>-1</sup> (OH). Prolonged irradiation (14 h) did not increase the yield, whereas irradiation of the ketone in ether for 5 h gave the diol (6; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph, R = H) in 4% yield (based on unrecovered starting material).

1,2-Bis-*p*-methoxyphenyl-1,2-bis-(1-phenylimidazol-4-yl)-ethane-1,2-diol (6; Ar<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, Ar<sup>2</sup> = Ph, R = H).—A solution of the *p*-methoxyphenyl ketone (3; Ar<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, Ar<sup>2</sup> = Ph) [ $\lambda_{\max}$  (cyclohexane) 280 and 286 nm (log  $\epsilon$  4.51 and 4.51)] (1.36 g) in ether (300 ml) was irradiated for 6 h and the mixture was treated as described above. Elution with ether gave the starting material (0.58 g) and elution with ether-methanol (3:1) gave the ethanediol (0.105 g, 13% yield based on unrecovered starting material). Crystallisation from ethyl acetate-petroleum gave rods, m.p. 203—204° (Found: C, 73.1; H, 5.5; N, 10.1. C<sub>34</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub> requires C, 73.1; H, 5.4; N, 10.0%),  $\nu_{\max}$  (Nujol) 3270 cm<sup>-1</sup> (OH),  $\lambda_{\max}$  (EtOH) 230 and 263 nm (log  $\epsilon$  4.49 and 4.77).

1,2-Bis-(1-phenylimidazol-4-yl)ethane-1,2-diol (6; Ar<sup>1</sup> = R = H, Ar<sup>2</sup> = Ph).—A solution of 1-phenylpyrazole-4-carbaldehyde<sup>25</sup> (5; Ar = Ph, R = H) [ $\lambda_{\max}$  (cyclohexane) 271 nm (log  $\epsilon$  4.23)] (0.80 g) in propan-2-ol (300 ml) was irradiated for 5 h. The solvent was evaporated under reduced pressure and trituration of the residue with ether (20 ml) gave the ethanediol (0.07 g, 9%). Crystallisation from aqueous methanol gave needles, m.p. 232—233° (decomp.) (Found: C, 67.6; H, 5.1; N, 15.75. C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>·0.5H<sub>2</sub>O requires C, 67.6; H, 5.4; N, 15.8%),  $\nu_{\max}$  (Nujol) 3250 cm<sup>-1</sup> (OH),  $\lambda_{\max}$  (EtOH) 262 nm (log  $\epsilon$  4.51). The filtrate was chromatographed on alumina and the column was eluted with ether, ether-ethyl acetate (3:1), and ether-methanol (5:1), successively. An uncharacterised oil was obtained from the last eluate. Irradiation of the aldehyde (1.00 g) in benzene (300 ml) for 3 h resulted in the recovery of 93% of the starting material.

1,2-Bis-(2,5-dimethyl-1-phenylimidazol-4-yl)ethane-1,2-diol (6; Ar<sup>1</sup> = H, Ar<sup>2</sup> = Ph, R = Me).—A solution of 3,5-dimethyl-1-phenylpyrazole-4-carbaldehyde<sup>23</sup> (5; Ar = Ph, R = Me) [ $\lambda_{\max}$  (cyclohexane) 263 nm (log  $\epsilon$  4.22),  $\tau$  (CDCl<sub>3</sub>) 7.43 (s, 2 Me), 2.50 (5H, s), and -0.08 (1H, s)] (1.00 g) in ether (300 ml) was irradiated for 4 h. The solvent was evaporated and the residue was washed with ether, giving the ethanediol (0.065 g, 7% yield based on unrecovered start-

<sup>24</sup> K. v. Auwers and H. Mauss, *J. prakt. Chem.*, 1927, **117**, 311.

<sup>25</sup> I. L. Finar and G. H. Lord, *J. Chem. Soc.*, 1957, 3314.

ing material). Crystallisation from aqueous ethanol gave plates, m.p. 242—244° (Found: C, 71.4; H, 6.65; N, 13.8.  $C_{24}H_{26}N_4O_2$  requires C, 71.6; H, 6.5; N, 13.9%),  $\nu_{\max}$  (Nujol) 3250  $cm^{-1}$  (OH),  $\lambda_{\max}$  (EtOH) 250 nm ( $\log \epsilon$  4.32),  $\tau$  [(CD<sub>3</sub>)<sub>2</sub>SO] 7.90 (s, 2 Me), 7.87 (s, 2 Me), 5.23 (2H, s), and 2.55 (10H, s) (an OH proton was not observed). Evaporation of the filtrate and washings afforded the starting material (0.085 g). Irradiation of the aldehyde (1.00 g) in acetonitrile (300 ml) and triethylamine (2.0 ml) for 4 h and evaporation of the solvent under reduced pressure gave the diol (0.06 g, 8% yield based on unrecovered starting material). Alumina chromatography of the filtrate with ether and then ether-ethyl acetate (3 : 1) as eluant gave the starting material (0.25 g). When this aldehyde was irradiated in acetonitrile for 4 h, the starting material was recovered in 90% yield.

1-*p*-Chlorophenyl-3,5-dimethylpyrazole-4-carbaldehyde (5; Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>, R = Me).—This compound was prepared in 63% yield by the method described<sup>23</sup> and crystallised from aqueous ethanol as *needles*, m.p. 128—131° (Found: C,

61.2; H, 4.8; N, 11.8.  $C_{12}H_{11}ClN_2O$  requires C, 61.4; H, 4.7; N, 11.9%),  $\nu_{\max}$  (CHCl<sub>3</sub>) 2820 and 2740 (CH) and 1670  $cm^{-1}$  (C=O),  $\lambda_{\max}$  (EtOH) 228 and 261 nm ( $\log \epsilon$  4.39 and 4.58),  $\tau$  (CDCl<sub>3</sub>) 7.45 (s, Me), 7.42 (s, Me), 2.53 (4H, s), and -0.06 (1H, s).

1,2-Bis-(1-*p*-chlorophenyl-2,5-dimethylimidazol-4-yl)ethane-1,2-diol (6; Ar<sup>1</sup> = H, Ar<sup>2</sup> = *p*-ClC<sub>6</sub>H<sub>4</sub>, R = Me).—A solution of the aldehyde (5; Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>, R = Me) (1.00 g) and ether (300 ml) was irradiated for 4 h and the mixture was treated as described for the diol (6; Ar<sup>1</sup> = H, Ar<sup>2</sup> = Ph, R = Me). The *ethanediol* (0.10 g, 10%) crystallised from aqueous ethanol as *needles*, m.p. 249—250° (Found: C, 60.9; H, 5.4; N, 11.7.  $C_{24}H_{24}Cl_2N_4O_2$  requires C, 61.15; H, 5.1; N, 11.9%),  $\nu_{\max}$  (Nujol) 3250  $cm^{-1}$  (OH),  $\lambda_{\max}$  (EtOH) 257 nm ( $\log \epsilon$  4.40),  $\tau$  [(CD<sub>3</sub>)<sub>2</sub>SO] 7.83 (s, 2 Me), 7.76 (s, 2 Me), 5.23 (2H, s), 4.90 (2H, s, exch.), and 2.43 (8H, s). This diol was obtained in very low yield when the aldehyde was irradiated in propan-2-ol.

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