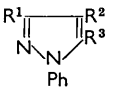
534. *The Preparation and Some Reactions of 4-Formyl-1-phenylpyrazoles.*

By I. L. Finar and M. Manning.

Various pyrazoles have been formylated, and in each case there has been isolated an intermediate, the composition of which supports the mechanism of formylation proposed by Smith [1] and Silverstein *et al.*[2] The aldehydes have been oxidised to the corresponding acids and the influence of alkyl and aryl substituents on the reactivity of the aldehydic group has been investigated in a series of condensations with aniline, malonic acid, acetophenone, and *o*-phenylenediamine. Six bipyrazolyls have also been prepared.

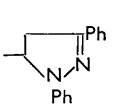
Phosphoryl chloride and dimethylformamide have been used by Finar and Lord to formylate 1-phenylpyrazole,[3a] 1-methylpyrazole,[3a] and 1,1′,3-triphenyl-4′,5-bipyrazolyl [3b] in the 4-position. Formylations have now been carried out with the substituted pyrazoles (I; $R^2 = H$, i—vi) to give the pyrazole-4-aldehydes (II; $R^2 = CHO$, i—vi). There is a slight decrease in yield with increasing size of substituent (Table 1).

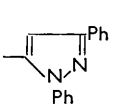


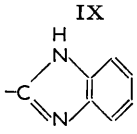
I; $R^2 = H$	i	ii	iii	iv	v	vi
R^1	Me	H	Me	Me	Ph	Ph
R^3	H	Me	Me	Ph	Me	Ph

I	II	III	IV	V	VI
$R^2 = H$	CHO	CO_2H	$CH{=}CH{\cdot}CO_2H$	CH=NPh	CH=CH·COPh

VII VIII IX

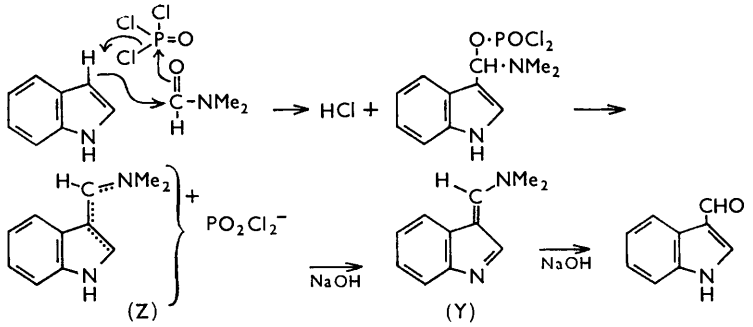






Smith,[1] who studied the formylation of indole with phosphoryl chloride and dimethylformamide, believed that the reaction proceeded through the mesomeric cation (Z) as intermediate which, on hydrolysis, gives 3-formylindole. He proposed the mechanism (A). This was supported by the isolation of the free base (Y). Silverstein *et al.*,[2] investigating

Scheme (A)

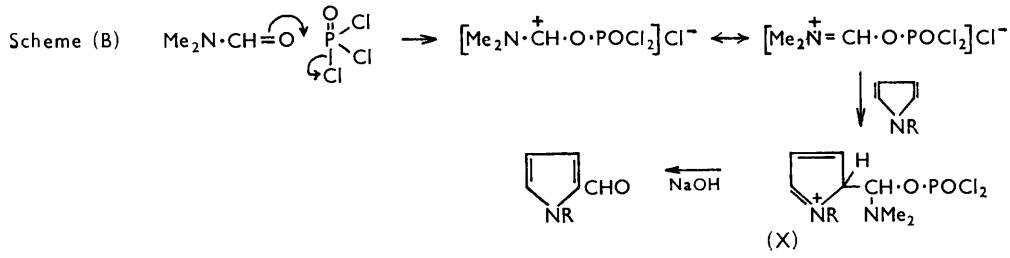


the formylation of pyrroles, proposed an attack by the initial 1 : 1 phosphoryl chloride–dimethylformamide complex at position 2 of the pyrrole nucleus, to give the intermediate (X), which is hydrolysed to the aldehyde (scheme B). Bosshard and Zollinger [4] prepared this 1 : 1 complex and showed that it formylated *NN*-dimethylaniline.

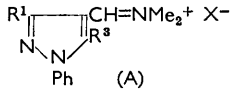
[1] Smith, *J.*, 1954, 3842.
[2] Silverstein, Ryskiewicz, Willard, and Koehler, *J. Org. Chem.*, 1955, **20**, 668.
[3] Finar and Lord, (*a*) *J.*, 1957, 3314; (*b*) *J.*, 1959, 1819.
[4] Bosshard and Zollinger, *Helv. Chim. Acta*, 1959, **42**, 1659.

The present work has resulted in the isolation of the cation (corresponding to Z), as the dichlorophosphate or hexachloroplatinate (Table 2). Chlorine and phosphorus analyses are in agreement with the general structure (A*a*) where X = PO_2Cl_2, for the six substituted pyrazolyl intermediates. On the other hand, the intermediate obtained in the formylation of 1-phenylpyrazole was shown to have structure (A*b*), where X = Cl. These intermediates (A*a*, i-vi; and A*b*, vii) were obtained by triturating the reaction mixture

Scheme (B)



with either absolute alcohol or dry propanol, cooled to about −80°, and washing the precipitate with ether.



	a	*b*	*c*
X =	PO_2Cl_2	Cl	$\frac{1}{2}PtCl_6$

The intermediates dissolve readily in water and liberate the respective aldehydes when these solutions are kept. Dimethylamine hydrochloride was isolated from each intermediate by precipitation with dry ether from cooled, previously refluxed ethanolic solutions.

Further evidence for the ionic nature of the intermediates was as follows. Precipitates were obtained by treating the aqueous solutions with aqueous chloroplatinic acid, picric acid, or sodium tetraphenylborate. Estimation of chlorine in the chloroplatinates agreed with the structures (A*c*). The quantitative formation of the picrate [A*d*; X = $O{\cdot}C_6H_2(NO_2)_3$] and the tetraphenylborate (A*e*; X = BPh_4) from some of these intermediates supports their structures.

The substituted formyl compounds, on oxidation, gave the corresponding carboxylic acids (III; Table 3). These formyl compounds also condensed with malonic acid [5] to form β-1-phenyl-4-pyrazolylacrylic acids (IV; Table 4).

Only the 3- and the 5-methyl-1-phenylpyrazole-aldehydes formed anils [6] (V) under the conditions used. Ketones (VI; Table 5) were prepared by condensing the aldehydes with acetophenone and these were condensed with phenylhydrazine to give the pyrazolines (VII; Table 6). All the pyrazolines were oxidised to the corresponding pyrazoles (VIII; Table 7) by potassium permanganate in pyridine.

4-Formyl-1-phenylpyrazole and the six substituted formyl compounds have also been condensed with *o*-phenylenediamine,[7] giving the corresponding 2-pyrazol-4′-ylbenzimidazoles (IX; Table 8).

Experimental

Preparation of the 1-(*Substituted Phenyl*)*pyrazoles*.—Pyrazoles (I; R^2 = H; i[8], ii[8], iii[9], iv[10], v[11], vi[12], vii[13]) were prepared by condensation of phenylhydrazine with the appropriate β-diketone in glacial acetic acid.

[5] Finar and Godfrey, *J.*, 1954, 2293.
[6] Finar and Utting, *J.*, 1959, 4015.
[7] Weidenhagen, *Ber.*, 1936, **69**, 2263.
[8] Finar and Hurlock, *J.*, 1958, 3259.
[9] Knorr, *Ber.*, 1887, **20**, 1103.
[10] Drumm, *Proc. Roy. Irish Acad.*, 1931, **40**, *B*, 106.
[11] Minunni, Lazzarini, and d'Urso, *Gazzetta*, 1925, **55**, 502.
[12] Knorr and Laubmann, *Ber.*, 1888, **21**, 1205.
[13] Finar and Hurlock, *J.*, 1957, 3024.

Formylation to yield the Pyrazole-4-aldehydes [3] (II).—To a stirred mixture of 3-methyl-1,5-diphenylpyrazole (23·4 g., 0·1 mole) and dimethylformamide (14·6 g., 0·2 mole) at 95—100° was added phosphoryl chloride (19·4 g., 0·125 mole) dropwise during 45 min. Heating and stirring were maintained for a further 2 hr. The mixture was cooled to 0°, the pH adjusted to 4—6 by addition of aqueous sodium hydroxide, and after 6 hr. the aldehyde was collected and recrystallised twice from ethanol to give colourless prisms of *4-formyl-3-methyl-1,5-diphenylpyrazole* (62%), m. p. 136—137° (Found: C, 78·0; H, 5·4; N, 10·5. $C_{17}H_{14}N_2O$ requires C, 77·9; H, 5·3; N, 10·7%).

The other formyl derivatives were prepared in a similar manner (Table 1).

TABLE 1. *4-Formyl-1-phenylpyrazoles* (II; R^2 = CHO).

				Yield	Found (%)				Required (%)		
No.	R^1	R^3	M. p.	(%)	C	H	N	Formula	C	H	N
i	Me	H	60—61° [a]	74	71·1	5·4	15·1	$C_{11}H_{10}N_2O$	71·1	5·4	15·1
ii [d]	H	Me	75·5—76·5 [b]	75							
iii [d]	Me	Me	123—124 [a]	70							
v [d]	Ph	Me	101—101·5 [a]	63							
vi	Ph	Ph	160·5—161·5 [c]	57	81·5	5·1	8·6	$C_{22}H_{16}N_2O$	81·5	4·9	8·6

[a, b, c] Recrystallised from (*a*) aqueous ethanol, (*b*) ligroin, and (*c*) aqueous acetic acid. [d] Rojahn and Farr, *Annalen*, 1923, **434**, 261.

Formylation to Isolate the Intermediates (Aa) *and* (Ab) (Table 2).—(1) *As solids.* To 3-methyl-1-phenylpyrazole (15·8 g., 0·1 mole) and dimethylformamide (14·6 g., 0·2 mole), stirred at 70—80°, was added phosphoryl chloride (19·4 g., 0·125 mole) dropwise during 30 min. Heating and stirring were continued for a further 1 hr. The solid product obtained on gradual cooling to room temperature was brought to −30° and triturated with absolute ethanol (40 c.c.) cooled to −80° and collected under anhydrous conditions. It was further washed with cooled absolute ethanol and washed well with dry ether to give, after drying *in vacuo* over phosphorus pentoxide, colourless crystals of the *salt* (A*a* i) (26 g.), m. p. 172—173° (Table 2).

Similarly were obtained the *salts* (A*a* ii) and (A*b* vii) (Table 2).

(2) *As oils.* 3-Methyl-1,5-diphenylpyrazole was formylated as in (1) above. A portion of the viscous product was cooled to −30° and dissolved in a minimum amount of absolute ethanol (cooled to −80°). An excess of dry ether was added and the precipitated oil collected by decantation. The process was repeated on the oil until the final dry ethereal washings became colourless. After drying overnight *in vacuo* over phosphorus pentoxide the red oily *dichlorodioxophosphate* (A*a* iv) was analysed for chlorine and phosphorus (Table 2).

Similarly were obtained the *salts* (A*a* iii), (A*a* v), and (A*a* vi) (Table 2).

TABLE 2. *NN-Dimethyl-N-(1-phenylpyrazol-4-ylmethylene)immonium chlorides and dichlorodioxophosphates and the corresponding hexachloroplatinates* B_2PtCl_6 (A).

			Compound			Found (%)		Required (%)	
No.	R^1	R^3	(A)	Formula	M. p.	Cl	P	Cl	P
			b [1, 2]	$C_{12}H_{14}ClN_3$	85—86 [6]	15·0	—	15·1	—
—	H	H	*c* [3]	$C_{24}H_{28}Cl_6N_6Pt$	228 *	26·3	—	26·3	—
			a [1, 3]	$C_{13}H_{16}Cl_2N_3O_2P$	172—173 [6]	20·4	8·8	20·4	8·9
i	Me	H	*c* [3]	$C_{26}H_{32}Cl_6N_6Pt$	240—242	25·3	—	25·4	—
			a [3, 4]	$C_{13}H_{16}Cl_2N_3O_2P$	118—119 [7]	20·1	8·6	20·4	8·9
ii	H	Me	*c* [3]	$C_{26}H_{32}Cl_6N_6Pt$	207—209 *	25·1	—	25·4	—
			a [2]	$C_{14}H_{18}Cl_2N_3O_2P$	Oil	19·3	8·2	19·6	8·6
iii	Me	Me	*c*	—	—	—	—	—	—
			a [2, 5]	$C_{19}H_{20}Cl_2N_3O_2P$	Oil	16·4	7·2	16·7	7·3
iv	Me	Ph	*c* [3]	$C_{38}H_{40}Cl_6N_6Pt$	201—203 *	21·4	—	21·5	—
			a [2, 5]	$C_{19}H_{20}Cl_2N_3O_2P$	Oil	16·5	7·0	16·7	7·3
v	Ph	Me	*c* [3]	$C_{38}H_{40}Cl_6N_6Pt$	215—217 *	21·2	—	21·5	—
			a [2, 5]	$C_{24}H_{22}Cl_2N_3O_2P$	Oil	14·4	6·1	14·6	6·4
vi	Ph	Ph	*c* [3]	$C_{48}H_{44}Cl_6N_6Pt$	170 *	18·8	—	19·1	—

* With decomp. [1] Chloroplatinic acid, picric acid, and sodium tetraphenylborate gave quantitative precipitates. [2] Unstable *in vacuo*. [3] Stable *in vacuo*. [4] Picrate and tetraphenylborate unstable *in vacuo*. [5] The reagents of note (1) gave oily precipitates. [6, 7] Triturating solvents were (6) propanol at −80° and (7) ethanol at −80°.

Isolation of Dimethylamine Hydrochloride.—Solutions of the reaction intermediates (A*a*) or (A*b*) in absolute ethanol, when refluxed for 30 min. and then cooled to −80° and treated with an excess of dry cooled ether, deposited dimethylamine hydrochloride, m. p. 174—175°.

Oxidations to the Carboxylic Acids (III).—(*a*) The aldehydes (II; R^2 = CHO; i—v) were oxidised by refluxing, aqueous, alkaline potassium permanganate. The corresponding *4-carboxylic acid* was obtained in each case (Table 3). All the acids were recrystallised from aqueous ethanol.

(*b*) A pyridine solution of 4-formyl-1,3,5-triphenylpyrazole was refluxed with alkaline potassium permanganate for 20 min. Working up gave 1,3,5-triphenylpyrazole-4-carboxylic acid [14] (73%), m. p. 238—239°.

TABLE 3. *1-Phenylpyrazole-4-carboxylic acids* (III).

No.	R^1	R^3	M. p.	Yield (%)
i [a]	Me	H	196—197°	94
ii [a]	H	Me	166—167	82
iii [9]	Me	Me	200—201	90
iv [b]	Ph	Ph	205—206	87
v [c]	Ph	Me	193—194	85

[a] Bulow, *Ber.*, 1900, **33**, 3269. [b] Knorr and Blank, *Ber.*, 1885, **18**, 312. [c] *Idem, ibid.*, p. 933.

Knoevenagel Reaction,[5] *yielding Acrylic Acids* (IV).—4-Formyl-3-methyl-1,5-diphenylpyrazole (2·62 g., 0·01 mole) and malonic acid (2·08 g., 0·02 mole) were warmed on a steam-bath with pyridine (6 c.c.) and piperidine (13 drops) for 2 hr., then refluxed for 2 hr., poured on ice, and basified with sodium hydroxide. Unchanged aldehyde was collected (0·8 g.). The aqueous filtrate was extracted with ether (2 × 100 c.c.) and acidified, and the precipitate was collected and recrystallised twice from aqueous acetic acid to give colourless prisms of β-(*3-methyl-1,5-diphenylpyrazol-4-yl)acrylic acid* (2·1 g., 69%), m. p. 245—246° (Found: C, 75·1; H, 5·2; N, 9·2. $C_{19}H_{16}N_2O_2$ requires C, 75·0; H, 5·3; N, 9·2%).

The other *acrylic acids* were obtained in a similar manner (Table 4).

TABLE 4. β-(*1-Phenylpyrazol-4-yl)acrylic acids* (IV).

				Yield	Found (%)				Required (%)		
No.	R^1	R^3	M. p.	(%)	C	H	N	Formula	C	H	N
i	Me	H	166·5—167° [a]	88	68·6	5·4	12·0	$C_{13}H_{12}N_2O_2$	68·4	5·3	12·3
ii	H	Me	199—200 [a]	88	68·3	5·4	12·1	$C_{13}H_{12}N_2O_2$	68·4	5·3	12·3
iii	Me	Me	163—164 [a]	66	69·6	8·1	16·4	$C_{14}H_{14}N_2O_2$	69·4	8·3	16·6
v	Ph	Me	211·5—212·5 [a]	43	75·1	5·1	9·1	$C_{19}H_{16}N_2O_2$	75·0	5·3	9·2
vi	Ph	Ph	246—247·5 [b]	30	78·4	4·9	7·6	$C_{24}H_{18}N_2O_2$	78·7	4·9	7·6

[a, b] Recrystallised from (*a*) aqueous ethanol and (*b*) aqueous acetic acid.

Preparation of Anils [6] (V).—4-Formyl-5-methyl-1-phenylpyrazole (3·72 g., 0·02 mole) and aniline (1·8 g., 0·02 mole) in absolute ethanol (20 c.c.) were warmed on a steam-bath for 30 min., then cooled, and the precipitate was recrystallised twice from ethanol to give N-(*5-methyl-1-phenyl-4-pyrazolylmethylidene)aniline*, as white leaflets (5·0 g., 95%), m. p. 108·5—109·5° (Found: C, 78·1; H, 6·0; N, 16·0. $C_{17}H_{15}N_3$ requires C, 78·2; H, 5·7; N, 16·1%).

In the same way was obtained N-(*3-methyl-1-phenyl-4-pyrazolylmethylidene)aniline* from methanol as rhombs (92%), m. p. 75·5—76·5° (Found: C, 78·1; H, 5·5; N, 16·2. $C_{17}H_{15}N_3$ requires C, 78·2; H, 5·7; N, 16·1%).

Preparation of Acrylophenones [3b] (VI).—(1) 4-Formyl-3-methyl-1-phenylpyrazole (5·58 g., 0·03 mole) in ethanol (60 c.c.) was added dropwise with stirring to a cooled solution of sodium hydroxide (3·6 g., 0·09 mole) in water (25 c.c.), ethanol (10 c.c.), and acetophenone (3·6 g., 0·03 mole) at 0—10°. The mixture was stored for 12 hr. and the solid then collected, washed with water, and recrystallised twice from aqueous ethanol, to give needles of β-(*3-methyl-1-phenylpyrazol-4-yl)acrylophenone* (7·1 g., 82%), m. p. 137—137·5° (Found: C, 79·1; H, 5·6; N, 9·4. $C_{19}H_{16}N_2O$ requires C, 79·2; H, 5·6; N, 9·7%).

The ketones (ii—v) (Table 5) were obtained in a similar manner.

[14] Seidel, *J. prakt. Chem.*, 1898, **58**, 153.

TABLE 5. β-(1-*Phenylpyrazol-4-yl*)*acrylophenones* (VI).

				Yield	Found (%)				Required (%)		
No.	R^1	R^3	M. p.	(%)	C	H	N	Formula	C	H	N
ii	H	Me	110·5—111°	88	79·5	5·7	9·5	$C_{19}H_{16}N_2O$	79·2	5·6	9·7
iii	Me	Me	102—102·5	96	79·7	6·1	9·2	$C_{20}H_{18}N_2O$	79·5	6·0	9·4
iv	Me	Ph	169—170	88	82·4	5·6	7·9	$C_{25}H_{20}N_2O$	82·7	5·5	7·7
v	Ph	Me	139·5—140·5	98	82·6	5·6	7·8	$C_{25}H_{20}N_2O$	82·7	5·5	7·7

(2) Because of the insolubility of 4-formyl-1,3,5-triphenylpyrazole in ethanol the acrylophenone was prepared as follows. The aldehyde (3·24 g., 0·01 mole) and absolute ethanol (100 c.c.) were placed in a stout-walled conical flask. A cooled solution of sodium hydroxide (1·2 g., 0·03 mole in 15 c.c. of water) and acetophenone (1·2 g., 0·01 mole) were then added and the stoppered flask agitated for 40 hr. The flocculent white product was collected, washed with water, and recrystallised twice from ethanol, to give light green needles of β-(1,3,5-*triphenylpyrazol-4-yl*)*acrylophenone* (3·8 g., 89·2%), m. p. 185·5—186° (Found: C, 84·5; H, 5·0; N, 6·6. $C_{30}H_{22}N_2O$ requires C, 84·5; H, 5·2; N, 6·6%).

Preparation of Pyrazolylpyrazolines (VII).—Phenylhydrazine (2·2 g., 0·02 mole) in glacial acetic acid (15 c.c.) was added quickly to a hot solution of β-(3,5-dimethyl-1-phenylpyrazol-4-yl)acrylophenone (6·04 g., 0·02 mole) in absolute ethanol (100 c.c.). The mixture was heated for 1 hr. on a steam-bath. The crystals which separated were collected, washed with a little aqueous ethanol, and recrystallised twice from aqueous ethanol, to give green needles of 5-(3,5-*dimethylpyrazol-4-yl*)-1,3-*diphenyl-2-pyrazoline* (6·2 g., 79%), m. p. 126·5—127·5° (Found: C, 79·5; H, 6·4; N, 13·9. $C_{26}H_{24}N_4$ requires C, 79·6; H, 6·1; N, 14·1%).

The other *pyrazolines* were obtained in a similar manner (Table 6). All six gave the Knorr pyrazoline test and all showed a blue fluorescence under ultraviolet light.

TABLE 6. 1,5-*Diphenyl-5-*(*pyrazol-4-yl*)*-2-pyrazolines* (VII).

				Yield	Found (%)				Required (%)		
No.	R^1	R^3	M. p.	(%)	C	H	N	Formula	C	H	N
i	Me	H	135—136° [a]	76	79·6	5·8	14·6	$C_{25}H_{22}N_4$	79·4	5·8	14·8
ii	H	Me	132—133 [a]	79	79·6	5·6	14·6	$C_{25}H_{22}N_4$	79·4	5·8	14·8
iv	Me	Ph	190—191 [a]	75	82·0	6·0	11·9	$C_{31}H_{26}N_4$	82·1	5·7	12·1
v	Ph	Me	184—185 [a]	84	81·9	5·9	11·9	$C_{31}H_{26}N_4$	82·1	5·7	12·1
vi	Ph	Ph	212—213 [b]	62	83·4	5·3	10·9	$C_{36}H_{28}N_4$	83·7	5·4	10·9

[a] Recrystallised from aqueous ethanol. [b] Purified by trituration with boiling ethanol.

Preparation of Bipyrazolyls (VIII).—A mixture of 5-(3,5-dimethylpyrazol-4-yl)-1,3-diphenyl-2-pyrazoline (1 g.), powdered potassium permanganate (1·5 g.), pyridine (15 c.c.), and water (5 c.c.) was kept at room temperature for 30 min., then refluxed for 15 min. The product recrystallised from ethanol to give colourless rhombs of 3,5-*dimethyl*-1,1′,3′-*triphenyl*-4,5′-*bipyrazolyl* (98%), m. p. 169—170° (Found: C, 79·9; H, 5·7; N, 14·5. $C_{26}H_{22}N_4$ requires C, 80·0; H, 5·6; N, 14·4%).

The other *bipyrazolyls* were obtained in a similar manner (Table 7).

TABLE 7. 1,1′,3′-*Triphenyl*-4,5′-*bipyrazolyls* (VIII).

				Yield	Found (%)				Required (%)		
No.	R^1	R^3	M. p.	(%)	C	H	N	Formula	C	H	N
i	Me	H	101·5—102·5° [a]	98	79·6	5·3	14·6	$C_{25}H_{20}N_4$	79·9	5·3	14·9
ii	H	Me	123—124 [b]	98	79·7	5·4	15·0	$C_{25}H_{20}N_4$	79·9	5·3	14·9
iv	Me	Ph	176—177 [b]	98	82·3	5·4	12·2	$C_{31}H_{24}N_4$	82·3	5·3	12·4
v	Ph	Me	193—194 [b]	95	82·1	5·1	12·2	$C_{31}H_{24}N_4$	82·3	5·3	12·4
vi	Ph	Ph	175—176 [b]	95	84·3	5·1	10·9	$C_{36}H_{26}N_4$	84·1	5·1	10·9

[a, b] Recrystallised from (*a*) aqueous methanol and (*b*) aqueous ethanol.

Preparation of Benzimidazoles [7] (IX).—To a solution of *o*-phenylenediamine (1·08 g., 0·01 mole) and cupric acetate monohydrate (4 g., 0·02 mole) in water (30 c.c.) was added 4-formyl-3-methyl-1-phenylpyrazole (1·86 g., 0·01 mole) in warm ethanol (20 c.c.), and the mixture was heated slowly on a steam-bath. The cuprous salt soon began to separate and when the solution had completely lost its blue colour it was cooled and the precipitate was collected and

decomposed in hot ethanolic suspension with hydrogen sulphide. The filtrate was boiled (to remove hydrogen sulphide), then cooled and the precipitate collected to give, after two recrystallisations from aqueous ethanol, white plates of 2-(3-*methyl*-1-*phenylpyrazol*-4-*yl*)-*benzimidazole* (2·2 g., 80%), m. p. 236·5—237·5° (Found: C, 74·6; H, 5·1; N, 20·3. $C_{17}H_{14}N_4$ requires C, 74·5; H, 5·1; N, 20·4%).

The other benzimidazoles were prepared in a similar manner (Table 8).

TABLE 8. 2-(1-*Phenylpyrazol*-4-*yl*)*benzimidazoles* (IX).

				Yield	Found (%)				Required (%)		
No.	R^1	R^3	M. p.	(%)	C	H	N	Formula	C	H	N
ii	H	Me	202—203°	84	74·6	5·1	20·1	$C_{17}H_{14}N_4$	74·5	5·1	20·4
iii	Me	Me	264—265	76	74·8	5·6	19·2	$C_{18}H_{16}N_4$	75·0	5·6	19·4
iv	Me	Ph	213—214	70	78·7	5·2	15·9	$C_{23}H_{18}N_4$	78·9	5·1	16·0
v	Ph	Me	247—248	75	78·7	5·1	16·0	$C_{23}H_{18}N_4$	78·9	5·1	16·0
vi	Ph	Ph	288—289	49	81·7	4·7	13·5	$C_{28}H_{20}N_4$	81·6	4·9	13·6
vii	H	H	249—250	90	73·6	4·6	21·2	$C_{16}H_{12}N_4$	73·8	4·6	21·5

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