Reactions of 1-Phenylpyrazol-4-ylmagnesium Bromide. Part II.[1]

By R. J. Brooklyn and I. L. Finar,* The Northern Polytechnic, Holloway Road, London N.7

1-Phenylpyrazol-4-ylmagnesium bromide reacts with bromine and iodine to give the corresponding 4-halogenopyrazole, and with iodine chloride and iodine bromide to give 4-iodo-1-phenylpyrazole, similar yields of which are obtained by the direct iodination of 1-phenylpyrazole. The reaction of the Grignard reagent with various aldehydes has been examined. The Grignard reagent reacts with certain ethyl esters to yield pyrazolylmethanes, and these have been oxidised to the corresponding carbinols. 1,1'-Diphenyl-4,4'-bipyrazolyl, isolated in the Grignard preparation, has been obtained in high yields by prolonged heating of the Grignard reagent. Though 4-iodo-1-phenylpyrazole and 1-(*p*-bromophenyl)pyrazole form Grignard reagents, 4-chloro-1-phenylpyrazole does not.

Reaction of bromine and iodine with 1-phenylpyrazol-4-ylmagnesium bromide gives 4-bromo- and 4-iodo-1-phenylpyrazole [2] (67·5 and 53·3% respectively). 4-Iodo-1-phenylpyrazole was also obtained by the interaction of the pyrazolyl Grignard reagent with iodine chloride or iodine bromide, and by the direct iodination of 1-phenylpyrazole with iodine chloride [3a] or with iodine–mercuric oxide.[3b] Use of iodine in alkali gave a low yield of iodopyrazole.

Table 1

Yields of 4-iodo-1-phenylpyrazole

Starting material	Iodinating agent	Yield (%)
RMgBr	I_2	53·3
RMgBr	ICl	60·0
RMgBr	IBr	42·4
RH	I_2–NaOH	6·0
RH	I_2–HgO	62·0
RH	ICl	75·4

R = 1-Phenylpyrazol-4-yl.

Attempts to prepare 4-hydroxy-1-phenylpyrazole [4] by the oxidation of the pyrazolyl Grignard reagents with oxygen, even in the presence of an excess of isopropylmagnesium bromide,[5] failed. The magnesium bromide salt of t-butyl hydroperoxide at −70° also failed to effect oxidation,[6] although a small amount of 4-bromo-1-phenylpyrazole (25·3%) was isolated. When a solution of the magnesium bromide salt of t-butyl hydroperoxide was allowed to warm to 0° from −70°, the solution became bright orange; addition of cyclohexene discharged this colour. The salt decomposes to produce bromine, which brominates the pyrazolyl Grignard reagent to give 4-bromo-1-phenylpyrazole. When the reaction was repeated and hydrolysis was affected before the mixture became orange, no 4-bromo-1-phenylpyrazole was obtained.

1-(1-Phenylpyrazol-4-yl)butanol [7] (45·3%) and α-(1-phenylpyrazol-4-yl)benzyl alcohol (I) [7] (47·6%) have been prepared by the equimolar reaction of 1-phenylpyrazol-4-ylmagnesium bromide with n-butyraldehyde and benzaldehyde, respectively. When a solution of compound (I) in ethanol or benzene containing a trace of acid was warmed, α-ethoxy-α-(1-phenylpyrazol-4-yl)-toluene (II) or bis-α-(1-phenylpyrazol-4-yl)benzyl ether (III) were obtained (95·1 and 96·5%, respectively).

$$\mathrm{RCHOH{\cdot}Ph\ (I)} \xrightarrow[\mathrm{EtOH\text{–}H^+}]{} \mathrm{RCHPh{\cdot}OEt\ (II)}$$
$$\mathrm{RCHOH{\cdot}Ph\ (I)} \xrightarrow[\mathrm{C_6H_6\text{–}H^+}]{} \mathrm{(RCHPh)_2O\ (III)}$$

R = 1-phenylpyrazol-4-yl

Reaction of the Grignard reagent with benzaldehyde (2 mol.) gave only 4-benzoyl-1-phenylpyrazole [4] (57·9%), formed by oxidation of the alkoxide complex by excess of benzaldehyde.[8] All attempts to prepare bis-(1-

$$\mathrm{RMgBr + PhCHO \longrightarrow RCHPh{\cdot}OMgBr} \xrightarrow{\mathrm{PhCHO}} \mathrm{RCOPh + PhCH_2{\cdot}OMgBr}$$

R = 1-phenylpyrazol-4-yl

phenylpyrazol-4-yl)methanol by the reaction of 4-formyl-1-phenylpyrazole (1 mol.) with the Grignard reagent (1 mol.), failed, although its transient formation was indicated by the isolation of bis-(1-phenylpyrazol-4-yl) ketone [9] (16·0%), and di[bis-(1-phenylpyrazol-4-yl)methyl] ether (3·8%). The major product from this reaction was tris-(1-phenylpyrazol-4-yl)methane, which is believed to be formed *via* a tertiary alkoxide which is reduced by a hydride-ion transfer mechanism (*cf.* ref. 8*b*).

$$\text{(i)}\ \mathrm{RMgBr + RCHO \longrightarrow R_2CH{\cdot}OMgBr} \xrightarrow{\mathrm{RCHO}}$$
$$\mathrm{RCH_2{\cdot}OMgBr + R_2CO} \xrightarrow{\mathrm{RCHO}} \mathrm{R_3C{\cdot}OMgBr}$$

$$\text{(ii)}\ \mathrm{R_3C{\cdot}OMgBr} + \begin{cases}\mathrm{RCHO}\\ \mathrm{RCH_2{\cdot}OMgBr}\\ \mathrm{R_2CH{\cdot}OMgBr}\end{cases} \longrightarrow \begin{cases}\mathrm{RCO_2MgBr}\\ \mathrm{RCH(OMgBr)_2}\\ \mathrm{R_2C(OMgBr)_2}\end{cases} + \mathrm{R_3CH}$$

R = 1-Phenylpyrazol-4-yl

That one of the three species could effect such a reduction is indicated by the fact that the Grignard reagent reacts with bis-(1-phenylpyrazol-4-yl) ketone alone to give only tris-(1-phenylpyrazol-4-yl)methanol (see ref. 1). Further support for this reduction comes

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[9] I. L. Finar and K. E. Godfrey, *J. Chem. Soc.*, 1954, 2293.

from the reaction of the Grignard reagent (3 mol.) and diethyl carbonate (1 mol), the only product from which was tris-(1-phenylpyrazol-4-yl)methane. Here again the expected product is tris-(1-phenylpyrazol-4-yl)methanol, but, as before, the tertiary alkoxide is probably reduced by the ethoxymagnesium bromide present. Ethoxymagnesium bromide has been reported to reduce benzaldehyde to benzyl alcohol.[10] Reaction of the Grignard reagent (1 mol.) with ethyl benzoate (1 mol.) did not yield either 4-benzoyl-1-phenylpyrazole or αα-bis-(1-phenylpyrazol-4-yl)benzyl alcohol, but gave αα-bis-(1-phenylpyrazol-4-yl)toluene. In this case too, it seems likely that the product is formed as a result of reduction of the alkoxide by ethoxymagnesium bromide. Support for the structure of both substituted methanes is afforded by oxidation with alkaline permanganate to the corresponding tertiary alcohols. Attempts to prepare these substituted methanes *via* hydride-ion transfer reduction of the corresponding tertiary alcohols with formic acid failed, although triphenylmethanol was reduced to triphenylmethane under the same conditions.[11]

Further to the reported reaction of the Grignard reagent with anhydrous cobaltous chloride,[1] a study of the yields of the coupling product, 1,1′-diphenyl-4,4′-bipyrazolyl, obtained by heating the Grignard reagent under reflux for varying periods of time, has cast some doubt on the efficacy of the cobaltous chloride reaction. When the Grignard reagent was prepared in the usual manner and heated under reflux for a further 8 hr., the bipyrazolyl was obtained in yields of 8—28%. When the reflux time was increased to 1 week, the yields were consistently high (55—59%).

By use of the entrainment method,[1,12] dispersion with dry benzene, and carbonation with dry ice to estimate the Grignard reagent as the carboxylic acid, 4-iodo-1-phenylpyrazole and 1-(*p*-bromophenyl)pyrazole [13] have been converted into the corresponding Grignard reagents in yields of 80 and 62·3%, respectively. The estimated yield of the latter reagent is probably low in view of the recovery of 1-phenylpyrazole (20%) and it seems probable that carbonation was not totally effective because the Grignard reagent could not be dispersed completely. 4-Chloro-1-phenylpyrazole [14] failed to yield a Grignard reagent.

A new route to *pp*′-di(pyrazol-1-yl)benzophenone [4] (VI) has been found; *p*-(pyrazol-1-yl)benzoic acid [13] is converted into *p*-(pyrazol-1-yl)benzoyl chloride (IV), which is treated with *p*-(pyrazol-1-yl)phenylmagnesium bromide (V). The low yield of ketone (16%) is attributed to the incomplete dispersion of *p*-(pyrazol-1-yl)-phenylmagnesium bromide.

$$\underset{\text{(IV)}}{\text{RCOCl}} + \underset{\text{(V)}}{\text{RMgBr}} \longrightarrow \underset{\text{(VI)}}{\text{R}_2\text{CO}}$$

R = *p*-(pyrazol-1-yl)phenyl

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EXPERIMENTAL

4-Iodo-1-phenylpyrazole.—(*a*) The ethereal solvate of 1-phenylpyrazol-4-ylmagnesium bromide [1] (0·02 mole) in dry benzene (50 ml.) was added dropwise during 1 hr. to a stirred solution of iodine chloride (3·25 g., 0·02 mole) in dry ether (50 ml.) under reflux. The mixture was stirred under reflux for a further 7 hr., then cooled and hydrolysed with 2N-hydrochloric acid. The ether layer was separated, washed with water and 0·1N-sodium thiosulphate solution, dried (Na_2SO_4), and evaporated. The solid residue gave 4-iodo-1-phenylpyrazole (3·29 g., 60%), m.p. 75° [from ethanol (charcoal)].

Similar reaction with iodine or iodine bromide gave 4-iodo-1-phenylpyrazole (2·88 g., 53·3% or 2·29 g., 42·4%, respectively).

(*b*) To 1-phenylpyrazole (3·6 g., 0·025 mole) was added a solution of iodine (6·35 g., 0·025 mole) in 20% aqueous sodium hydroxide, and the mixture was heated and stirred for 90 min. The precipitate obtained when the solution was cooled gave 4-iodo-1-phenylpyrazole (0·41 g., 6%) (from ethanol). The filtrate was extracted with ether and the extracts were washed with 0·1N-sodium thiosulphate solution and water, dried (Na_2SO_4), and evaporated, to give 1-phenylpyrazole (2·75 g., 76·4%).

(*c*) A mixture of iodine (12·7 g., 0·05 mole) and yellow mercuric oxide (8·9 g., 0·041 mole) was added in portions to a warmed, stirred solution of 1-phenylpyrazole (7·2 g., 0·05 mole) in dry benzene (50 ml.) during 0·5 hr., and the mixture was stirred and warmed for a further 1·5 hr., then cooled. The precipitate was washed with ether and the ether extracts were combined and evaporated to leave a brown solid which gave 4-iodo-1-phenylpyrazole (8·36 g., 62%) [from ethanol (charcoal)].

(*d*) A solution of iodine chloride (8·13 g., 0·05 mole) and 1-phenylpyrazole (7·2 g., 0·05 mole) in glacial acetic acid (100 ml.) was stirred and heated for 1·5 hr., then poured into ice-cold water. Work-up as in (*a*) gave 4-iodo-1-phenylpyrazole (10·2 g., 75·4%).

Reaction of 1-Phenylpyrazol-4-ylmagnesium Bromide with Oxygen in the presence of Isopropylmagnesium Bromide.—To the ethereal solvate of 1-phenylpyrazol-4-ylmagnesium bromide (0·02 mole), filtered free of magnesium, was added the ethereal solvate of isopropylmagnesium bromide (0·03 mole), and the mixture was cooled to −20°. Dry oxygen was bubbled through for 6 hr. with stirring, and the solution was then hydrolysed with an excess of 2N-hydrochloric acid. The ether layer was removed and extracted with 10% aqueous sodium hydroxide, but acidification of the alkaline extracts yielded no 4-hydroxyl-1-phenylpyrazole. Evaporation of the organic layer yielded 1,1′-diphenyl-4,4′-bipyrazolyl (0·41 g., 14·3%), m.p. 209—210°, and 1-phenylpyrazole (2·21 g., 77%).

Reaction of 1-Phenylpyrazol-4-ylmagnesium Bromide with the Magnesium Bromide Salt of t-Butyl Hydroperoxide.—The ethereal solvate of 1-phenylpyrazol-4-ylmagnesium bromide (0·02 mole) was added to a stirred, freshly prepared ethereal solution of the magnesium bromide salt of t-butyl hydroperoxide (0·031 mole), during 1 hr. at −70°. The mixture was stirred at −70° for a further 3 hr. and then at 0° for 1 hr.; it was then hydrolysed with an excess of 2N-hydrochloric acid. When warmed to 0° the green mixture

[13] B. M. Lynch, M. A. Khan, and Y-Y Hung, *Canad. J. Chem.*, 1961, **41**, 1540.
[14] W. J. Barry, I. L. Finar, and G. V. Khatkhate, *J. Chem. Soc.* (*C*), 1968, 1120.

became bright orange. Treatment of the separated organic layer as before gave no 4-hydroxy-1-phenylpyrazole. Evaporation of the ether layer left a brown, oily solid, which was extracted with 10N-hydrochloric acid. The residue was extracted with ether and the combined extracts were evaporated to leave the bipyrazolyl (0·29 g., 10%) and a brown solid, 4-bromo-1-phenylpyrazole (1·13 g., 25·3%), m.p. 79—80° [from ethanol (charcoal)]. Basification of the acid extract gave a brown oil which was extracted with ether. The extracts were combined, dried (Na_2SO_4), and evaporated to give 1-phenylpyrazole (1·51 g., 52·4%).

When hydrolysis was performed before the mixture changed colour, only the bipyrazolyl (0·26 g., 9%), and 1-phenylpyrazole (2·31 g., 80·2%) were isolated.

1-(*1-Phenylpyrazol-4-yl*)*butanol*.[7]—A solution of n-butyraldehyde (1·3 g., 0·018 mole) in dry benzene (25 ml.) was added dropwise during 1 hr. to a stirred solution of the ethereal solvate of 1-phenylpyrazol-4-ylmagnesium bromide (0·02 mole) in dry benzene (100 ml.) under reflux. The mixture was stirred and heated for a further 7 hr., then cooled and hydrolysed with 2N-hydrochloric acid. The organic layer was removed and the aqueous layer extracted with ether (2 × 20 ml.). The extracts were combined with the benzene layer, washed (water), and dried (Na_2SO_4). Evaporation in stages gave the bipyrazolyl (0·26 g., 9·1%), then another solid which gave 1-(1-phenylpyrazol-4-yl)-butanol (1·76 g., 45·3%), m.p. 73—74° [from aqueous ethanol (charcoal)]. Evaporation of the mother liquor gave 1-phenylpyrazole (0·64 g., 22·2%).

Similarly prepared were α-(1-phenylpyrazol-4-yl)benzyl alcohol [7] (47·6%), m.p. 119—120° (from ethanol), from benzaldehyde (0·018 mole) and the Grignard reagent (0·02 mole), and 4-benzoyl-1-phenylpyrazole [4] (57·9%), m.p. 124—125° (from ethanol) from benzaldehyde (0·04 mole) and the Grignard reagent (0·02 mole).

α-*Ethoxy*-α-(1-*phenylpyrazol-4-yl*)*toluene*.— α-(1-Phenylpyrazol-4-yl)benzyl alcohol (1·0 g., 0·004 mole) was dissolved in absolute ethanol (30 ml.) and 2N-hydrochloric acid (1 drop) was added. The solution was warmed for 5 min., then cooled and evaporated to give a white solid, which gave the *pyrazolyltoluene* (1·06 g., 95·1%), m.p. 88° (from ethanol) (Found: C, 77·5; H, 6·5; N, 9·9. $C_{18}H_{18}N_2O$ requires C, 77·7; H, 6·5; N, 10·1%).

Bis-α-(1-*phenylpyrazol-4-yl*)*benzyl Ether*.—Trifluoroacetic acid (1 drop) was added to a solution of α-(1-phenylpyrazol-4-yl)benzyl alcohol (1·0 g., 0·004 mole) in dry benzene (30 ml.) and the solution was warmed for 5 min., then cooled and evaporated. The solid residue gave the *ether* (0·91 g., 96·5%), m.p. 183·5—184·5° (from benzene) (Found: C, 79·2; H, 5·5; N, 11·75. $C_{32}H_{27}N_4O$ requires C, 79·7; H, 5·4; N, 11·6%).

Reaction of 1-*Phenylpyrazol-4-ylmagnesium Bromide with* 4-*Formyl*-1-*phenylpyrazole*.—A solution of 4-formyl-1-phenylpyrazole (3·09 g., 0·018 mole) in dry benzene (100 ml.) was added dropwise during 1 hr. to a stirred solution of 1-phenylpyrazol-4-ylmagnesium bromide (0·02 mole) in dry benzene (100 ml.) under reflux. The mixture was worked up as for the preparation of α-(1-phenylpyrazol-4-yl)benzyl alcohol. The precipitate obtained on hydrolysis with 10% aqueous ammonium chloride was fractionally crystallised to give bis-(1-phenylpyrazol-4-yl) ketone (0·45 g., 16·0%), m.p. 220—221°, and the bipyrazolyl (0·2 g., 6·9%). Evaporation of the dried organic extract gave a solid, which gave *tris*-(1-*phenylpyrazol-4-yl*)*methane* (1·29 g.), m.p. 223—224° (from benzene) (Found: C, 76·2; H, 5·1; N, 18·8. $C_{28}H_{22}N_6$ requires C, 76·0; H, 5·0; N, 19·0%). Further evaporation yielded another solid, which gave *di*[*bis*-(1-*phenylpyrazol-4-yl*)*methyl*] *ether* (0·45 g., 6·1%), m.p. 188—189° (from benzene) (Found: C, 74·5; H, 4·9; N, 18·6. $C_{38}H_{30}N_8O$ requires C, 74·3; H, 4·9; N, 18·2%).

Reaction of 1-*Phenylpyrazol-4-ylmagnesium Bromide with Diethyl Carbonate*.—A solution of diethyl carbonate (1·18 g., 0·01 mole) in dry benzene (100 ml.) was added to a stirred solution of the ethereal solvate of 1-phenylpyrazol-4-ylmagnesium bromide (0·03 mole) in dry benzene (100 ml.) under reflux during 1 hr. The mixture was stirred and heated under reflux for a further 7 hr. Work-up gave the bipyrazolyl (0·4 g., 9·4%) and tris-(1-phenylpyrazol-4-yl)methane (2·28 g.), m.p. 223—224° (from benzene). Similarly, reaction of the pyrazolyl Grignard reagent (1 mol.) with ethyl benzoate (2 mol.) gave αα-*bis*-(1-*phenylpyrazol-4-yl*)*toluene*, m.p. 110·5—111° (Found: C, 79·8; H, 5·2; N, 14·8. $C_{25}H_{20}N_4$ requires C, 79·8; H, 5·3; N, 14·9%).

Tris-(1-*phenylpyrazol-4-yl*)*methanol*.— Tris-(1-phenylpyrazol-4-yl)methane (0·5 g., 0·001 mole) was dissolved in pyridine (10 ml.) and a solution of 4% alkaline potassium permanganate (50 ml.) was added. The mixture was heated under reflux on a steam-bath for 30 min., cooled, flushed with sulphur dioxide, and filtered. The filtrate was poured into a large excess of water and the solid deposited gave tris-(1-phenylpyrazol-4-yl)methanol (0·41 g., 80·2%), m.p. 188° (from ethanol). Similarly, αα-bis-(1-phenylpyrazol-4-yl)toluene gave αα-bis-(1-phenylpyrazol-4-yl)-benzyl alcohol (76·0%), m.p. 159—159·5°.

Attempted Reduction of Tris-(1-*phenylpyrazol-4-yl*)-*methanol*.—A solution of tris-(1-phenylpyrazol-4-yl)methanol (0·5 g., 0·001 mole) in 94·4% formic acid (30 ml.) was shaken in a stoppered, covered flask for 2 weeks, then poured into water. The solid deposited gave starting material (0·41 g., 80·2%) (from ethanol). Similar treatment of triphenylmethanol gave triphenylmethane (82%), m.p. 93—94°.

TABLE 2

Effect of prolonged heating on 1-phenylpyrazol-4-ylmagnesium bromide

Reflux time	Yield of bipyrazolyl (%)	Yield of 1-phenylpyrazole (%)
8 hr.	8·0	83·1 [a]
8 hr.	12·0	68·2
8 hr.	27·5	61·0 [b]
8 hr.	28·0	60·1 [c]
5 days	59·1	13·2
5 days	55·7	16·1 [d]

[a] Reaction performed under nitrogen. [b] Excess of magnesium filtered off before addition of dry benzene. [c] The upper colourless ether layer was decanted at the end of the Grignard preparation. [d] Excess of magnesium removed by addition of a calculated amount of ethylene dibromide.

Effect of Prolonged Heating on 1-*Phenylpyrazol-4-ylmagnesium Bromide*.—The ethereal solvate of 1-phenylpyrazol-4-ylmagnesium bromide (0·02 mole) was prepared *via* the entrainment technique during 5·5 hr., including 0·5 hr. reflux after completion of addition. Dry benzene (100 ml.) was added to disperse the Grignard reagent, and the solution was then stirred under reflux. After cooling and hydrolysis with 2N-hydrochloric acid, the organic layer was evaporated to leave the bipyrazolyl and 1-phenylpyrazole. The results of a number of experiments are given in Table 2.

p-(*Pyrazol*-1-*yl*)*benzoic Acid*.—A solution of 1-(*p*-bromophenyl)pyrazole (4·46 g., 0·02 mole) and ethylene dibromide

(11·28 g., 0·06 mole) in dry ether (50 ml.) was added dropwise during 5 hr. to dry magnesium (2·43 g., 0·1 mole) under dry ether (50 ml.). The mixture was heated under reflux and stirred throughout, and for a further 0·5 hr. after completion of the addition. Dry benzene (200 ml.) was added, the mixture was cooled, and carbonation was effected by the addition of small pieces of solid carbon dioxide (2 g.) with rapid stirring. The mixture was hydrolysed with 2N-hydrochloric acid and the organic layer was extracted with 10% aqueous sodium hydroxide. Acidification of the alkaline extract yielded a white precipitate which, on re-extraction, gave *p*-(pyrazol-1-yl)benzoic acid (2·34 g., 62·3%), m.p. 266—268° (lit.,[13] 268—270°). Evaporation of the organic layer gave 1-phenylpyrazole (0·57 g., 20·1%).

p-(*Pyrazol-1-yl*)*benzoyl Chloride*.—This was prepared by heating an excess of thionyl chloride (2·38 g., 0·02 mole) with *p*-(pyrazol-1-yl)benzoic acid (1·69 g., 0·009 mole) on a water-bath (50°) for 1 hr.

pp′-*Di*(*pyrazol-1-yl*)*benzophenone*.—A solution of *p*-(pyrazol-1-yl)benzoyl chloride (0·009 mole) in dry benzene (50 ml.) was added dropwise during 10 min. to the ethereal solvate of 1-(*p*-bromophenyl)magnesium bromide (0·01 mole) in dry benzene (100 ml.). The mixture was stirred and heated under reflux for 8 hr., then cooled and hydrolysed with 10% aqueous sodium hydroxide. The solid was collected and added to the brown, oily solid obtained from the evaporation of the organic layer. This mixture was extracted by heating under reflux with 11% ethanolic sodium hydroxide for 2 hr. The mixture was cooled and the solid gave *pp′*-di(pyrazol-1-yl)benzophenone (0·45 g., 15·8%), m.p. 230—231° [from aqueous ethanol (charcoal)] (lit.,[4] 230·5—231°). Extraction of the alkaline filtrate with ether and evaporation of the extract gave 1-phenylpyrazole (0·81 g., 56·7%). Acidification of the alkaline filtrate gave *p*-(pyrazol-1-yl)benzoic acid (0·93 g., 55·3%).

[9/211 *Received, February 5th,* 1969]