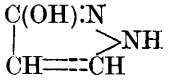
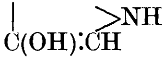
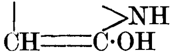
CIX.—*The 4-Hydroxy-1-aryl-5-methylpyrazoles.*

By Frederick Daniel Chattaway and Harry Irving.

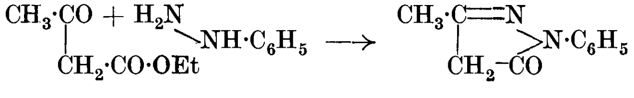
Among derivatives of the three possible hydroxypyrazoles or pyrazolones, those belonging to the 3- and the 5-series have been most studied.


3-Hydroxypyrazole

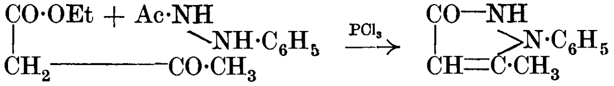

4-Hydroxypyrazole


5-Hydroxypyrazole

The reaction between primary arylhydrazines and β-ketonic esters, discovered by Knorr (*Annalen*, 1888, **238**, 147), gives a general method for the synthesis of members of the 5-series :



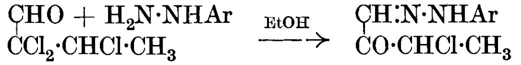
The method of Michaelis (*Annalen*, 1907, **358**, 130 ; *Ber.*, 1907, **40**, 1020), in which phosphorus trichloride brings about the condensation of *as*-acylarylhydrazines and β-ketonic esters, has been used to prepare various members of the corresponding 3-series :



$$\begin{array}{l}\mathrm{CO{\cdot}OEt} + \mathrm{Ac{\cdot}NH} \\ \mid \qquad\qquad\qquad \searrow \mathrm{NH{\cdot}C_6H_5} \\ \mathrm{CH_2}\text{————}\mathrm{CO{\cdot}CH_3}\end{array} \xrightarrow{PCl_3} \begin{array}{l}\mathrm{CO{-}NH} \\ \mid \qquad > \mathrm{N{\cdot}C_6H_5} \\ \mathrm{CH{=}C{\cdot}CH_3}\end{array}$$

No such general method has hitherto been available for the preparation of 4-hydroxypyrazoles and only a few such compounds are known (compare Bertho and Nüssel, *Annalen*, 1927, **457**, 278).

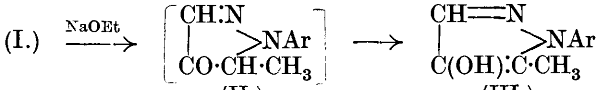
The ease with which the β-chloro-α-ketobutaldehyde arylhydrazones (I) can be obtained (Chattaway and Irving, J., 1930, 87; this vol., p. 751) by the interaction of butyl chloral hydrate and



$$\begin{array}{l}\mathrm{CHO} + \mathrm{H_2N{\cdot}NHAr} \\ \mathrm{CCl_2{\cdot}CHCl{\cdot}CH_3}\end{array} \xrightarrow{EtOH} \begin{array}{l}\mathrm{CH{:}N{\cdot}NHAr} \\ \mathrm{CO{\cdot}CHCl{\cdot}CH_3}\end{array} \quad \text{(I.)}$$

aryl hydrazines in alcohol, now makes possible the synthesis by a general method of a series of derivatives of 4-hydroxypyrazole.

When these ketonic hydrazones (I) are brought into contact with alcoholic sodium ethoxide, a molecule of hydrogen chloride is eliminated and ring closure ensues with the formation of the corresponding 4-hydroxy-1-aryl-5-methylpyrazole (III).



$$\text{(I.)} \xrightarrow{NaOEt} \left[\begin{array}{l}\mathrm{CH{:}N} \\ \mid \qquad > \mathrm{NAr} \\ \mathrm{CO{\cdot}CH{\cdot}CH_3}\end{array}\right] \longrightarrow \begin{array}{l}\mathrm{CH{=}N} \\ \mid \qquad > \mathrm{NAr} \\ \mathrm{C(OH){:}C{\cdot}CH_3}\end{array}$$

(II.) (III.)

Although the mode of synthesis suggests that the tautomeric keto-form (II) must be first formed, the compounds exhibit only the reactions of the enolic form (III), resembling in this respect 4-hydroxypyrazole itself and 1-phenyl (or methyl)-4-hydroxypyrazole (Wolff, *Annalen*, 1900, **313**, 18).

The 4-hydroxy-1-aryl-5-methylpyrazoles are all colourless, stable, well-crystallised substances, very sparingly soluble in cold water, but readily soluble in most organic solvents. Like the 3- and the 5-hydroxypyrazoles, they possess both basic and acidic properties, dissolving in aqueous ammonia, or dilute aqueous alkalis, or acids and separating unchanged on neutralisation. They can be boiled with concentrated hydrochloric acid or concentrated aqueous alkalis without decomposition, and are unaffected by reducing agents such as sodium amalgam, sodium and boiling alcohol, tin and boiling hydrochloric acid, or hydriodic acid.

They reduce Fehling's solution and ammoniacal silver oxide in the cold and are rapidly oxidised and broken down by cold alkaline potassium permanganate. They do not react with hydroxylamine or with phenylhydrazine.

As hydroxy-compounds, the 4-hydroxy-1-aryl-5-methylpyrazoles yield the corresponding 4-benzoates and 4-*p*-chlorobenzenesulphonates when benzoyl chloride or *p*-chlorobenzenesulphonyl chloride is added to their solution in alkali.

They behave as tertiary bases and combine directly with picric acid, platinic chloride, and methyl iodide.

When the aryl group is substituted by halogens, the basic properties of the corresponding 4-hydroxypyrazoles are diminished and the acidic increased.

The parent substance of the group, 4-*hydroxy*-1-*phenyl*-5-*methylpyrazole*, is of special interest, since it is isomeric with Knorr's 5-hydroxy-1-phenyl-3-methylpyrazole (" pyrazolone "), the first known member of the pyrazole group. It forms a well-characterised *picrate*, a *chloroplatinate*, and a *methiodide*. The last on treatment with moist silver oxide yields the corresponding *quaternary ammonium base*, from which the *hydrochloride* and *chloroplatinate* may be prepared.

EXPERIMENTAL.

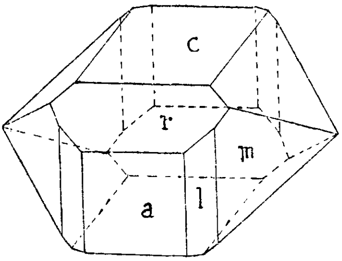
4-*Hydroxy*-1-*phenyl*-5-*methylpyrazole* (III; Ar = C_6H_5).—6 G. of β-chloro-α-ketobutaldehydephenylhydrazone (1 mol.) were added to a solution of 3 g. of sodium (2 mols. + excess) in 100 c.c. of ethyl alcohol. The deep orange solution produced was kept at room temperature for 2 hours, during which sodium chloride separated, and was then very slowly heated to the boiling point of the alcohol and poured into 1000 c.c. of boiling water. The rather turbid brown solution obtained was boiled with animal charcoal, filtered hot, concentrated to 250 c.c., cooled, and neutralised with hydrochloric acid; 4-*hydroxy*-1-*phenyl*-5-*methylpyrazole* then separated as a sand-coloured crystalline precipitate. This was dissolved in 100 c.c. of hot 10% caustic potash solution, boiled with animal charcoal, and reprecipitated from the cooled filtrate by neutralisation with hydrochloric acid. After repetition of this process it was crystallised from boiling alcohol and finally from acetone–light petroleum. Yield, 4 g.

To obtain the 4-hydroxypyrazole it is not, however, necessary to isolate the β-chloro-α-ketobutaldehydephenylhydrazone, as butyl chloral and phenylhydrazine themselves may be used as starting materials.

A solution of 30 g. of butyl chloral hydrate (1 mol.) and 17 g. of phenylhydrazine (1 mol.) in 150 c.c. of ethyl alcohol was maintained at 10° for 12 hours and poured into 1500 c.c. of cold water. A viscid black mass then separated which, in the course of a few hours, on repeated trituration, became comparatively solid and granular. It was dissolved in 150 c.c. of alcohol and 20 g. (2 mols. + excess) of powdered potassium hydroxide were slowly added in small portions (½ hour). As the potassium hydroxide dissolved, heat was evolved and potassium chloride separated. When all had been added, the mixture was warmed gradually on a water-bath, until the alcohol was boiling vigorously, and poured in a thin stream into 1500 c.c. of boiling water. A tarry by-product which separated in considerable amount was filtered off, the alkaline solution of 4-hydroxy-1-phenyl-5-methylpyrazole thus obtained was concentrated, and the pyrazole isolated as described above. Yield, 7—8 g.

4-Hydroxy-1-phenyl-5-methylpyrazole dissolves readily in cold chloroform, and in hot benzene, alcohol, acetone and acetic acid: it is sparingly soluble in boiling water, ether, and light petroleum. It separates from acetone or acetone–light petroleum in colourless prisms with domed ends, m. p. 136·5—137·5° (Found: C, 68·9; H, 5·75; N, 16·0. $C_{10}H_{10}ON_2$ requires C, 68·9; H, 5·8; N, 16·0%). With ferric chloride it gives a transient blue coloration, which quickly fades and is replaced by a permanent bright yellow.

FIG. 1.



The crystals belong to the monoclinic system (type—digonal equatorial) and are of prismatic habit. The axial elements are $a : b : c = 1·3383 : 1 : 0·78035$; $\beta = 95°\ 57'$. The forms observed were *a*{100}, *l*{210}, *m*{110}, *c*{001}, *r*{201}, *q*{011}, and less frequently *p*{$\bar{1}$11}.

The interfacial angles are given in the accompanying table :—

Angle.	No.	Limits.	Mean observed.	Calc.
110 : 100	19	52° 58′—53° 16′	53° 5′	*
001 : 011	15	37° 41′—38° 8′	37° 49′	*
001 : $\bar{1}$00	6	95° 54′—96° 3′	95° 57′	*
201 : 001	6	45° 57′—46° 2′	46° 0′	45° 59½′
210 : 110	6	19° 18′—19° 39′	19° 30′	19° 26′
001 : 210	3	84° 58′—85° 4′	84° 59′	85° 1′
001 : 110	8	86° 11′—86° 38′	86° 27′	86° 26′
110 : 11$\bar{1}$	6	47° 30′—47° 59′	47° 51′	47° 57′
100 : 11$\bar{1}$	7	69° 11′—69° 57′	69° 30′	69° 42′
11$\bar{1}$: 01$\bar{1}$	7	24° 50′—25° 55′	25° 10′	25° 0′
201 : 110	6	61° 12′—61° 53′	61° 43′	61° 45′
110 : 011	2	57° 19′—57° 23′	57° 21′	57° 22′
201 : 210	2	48° 34′—49° 2′	48° 48′	48° 51′
210 : 01$\bar{1}$	2	74° 14′—74° 35′	74° 24′	74° 24′

There is a perfect cleavage parallel to *a*{100}. The double refraction is weak and negative: the axial angle is very wide.

The *hydrochloride* separated as a colourless crystalline powder when dry hydrogen chloride was passed into a solution of the hydroxy-pyrazole in benzene. After being dried over sulphuric acid in a desiccator filled with hydrogen chloride, it melted at 83° (decomp.) (Found : Cl, 16·9. $C_{10}H_{10}ON_2,HCl$ requires Cl, 17·3%). When exposed to the air it loses hydrogen chloride and it is very soluble in, and hydrolysed by, water.

On the addition of chloroplatinic acid to a solution of 4-hydroxy-1-phenyl-5-methylpyrazole in concentrated hydrochloric acid, the *chloroplatinate* separated. It crystallised from concentrated hydrochloric acid in slender, pale orange prisms which, dried to constant weight over quicklime in a vacuum desiccator, melted at 205° (decomp.) (Found : Pt, 25·8. $C_{20}H_{22}O_2N_4Cl_6Pt$ requires Pt, 25·75%).

When warmed with an equivalent amount of picric acid in alcoholic solution, 4-hydroxy-1-phenyl-5-methylpyrazole formed a well-characterised *picrate*. This separated from boiling alcohol, in which it was moderately easily soluble, in deep golden-yellow prisms with domed ends, m. p. 154—154·5° (Found : N, 17·3. $C_{10}H_{10}ON_2,C_6H_3O_7N$ requires N, 17·4%).

1-*Phenyl*-5-*methylpyrazolyl* 4-*benzoate* gradually separated as a white solid when 1·5 g. of benzoyl chloride (1 mol. + excess) was added to a vigorously shaken solution of 0·5 g. of 4-hydroxy-1-phenyl-5-methylpyrazole in 10 c.c. of 10% aqueous potassium hydroxide. It is easily soluble in boiling alcohol, from which it separates in colourless compact prisms, m. p. 91·5° (Found : N, 10·1. $C_{17}H_{14}O_2N_2$ requires N, 10·1%).

1-*Phenyl*-5-*methylpyrazolyl* 4-p-*chlorobenzenesulphonate*, prepared similarly from the 4-hydroxy-pyrazole and *p*-chlorobenzenesulphonyl chloride, crystallised from boiling alcohol, in which it was readily soluble, in very slender, colourless prisms, m. p. 87° (Found : N, 8·2; Cl, 10·15. $C_{16}H_{13}O_3N_2ClS$ requires N, 8·0; Cl, 10·2%).

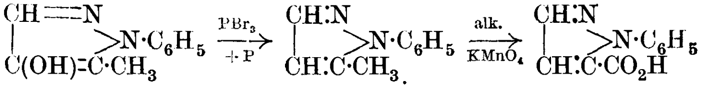
4-*Hydroxy*-1-*phenyl*-5-*methylpyrazole methiodide.* 3 G. of 4-hydroxy-1-phenyl-5-methylpyrazole (1 mol.) and 10 g. of methyl iodide (1 mol. + large excess) were heated in a sealed tube for 5 hours at 100°. The *methiodide*, which separated as a crystalline mass on cooling, was washed with ether till colourless. It is very easily soluble in water and warm alcohol, sparingly soluble in boiling benzene, acetone, or ether, and separates from alcohol–ether in short colourless prisms, m. p. 201—202° (decomp.) (Found : I, 40·3. $C_{10}H_{10}ON_2,CH_3I$ requires I, 40·2%).

4-*Hydroxy*-1-*phenyl*-1(or 2) : 5-*dimethylpyrazolinium hydroxide.* Moist silver oxide was added in slight excess to a solution of 2 g. of 4-hydroxy-1-phenyl-5-methylpyrazole methiodide in 10 c.c. of warm water, and the filtered solution was concentrated over sulphuric acid in a vacuum desiccator; after 3 days a colourless crystalline crust of the *quaternary ammonium base* remained. It is very easily soluble in boiling chloroform and cold water, but sparingly in ether and light petroleum. It crystallises from hot chloroform in very large rhombic tablets which darken at 145° and melt at 150—155° (decomp.) (Found: N, 13·4. $C_{10}H_{10}ON_2,CH_3{\cdot}OH$ requires N, 13·6%). Its aqueous solution is strongly alkaline; it reduces ammoniacal silver oxide and gives a blood-red coloration with ferric chloride.

The *methochloride* was obtained as a mass of compact colourless prisms with domed ends when 1·5 g. of the ammonium base were exactly neutralised with dilute hydrochloric acid, the solution concentrated on a water-bath until crystals began to separate, and the remainder of the water removed over quicklime in a vacuum. It is very soluble in boiling water, alcohol, benzene and chloroform, but very sparingly soluble in boiling ether. It separates from ether–chloroform in slender colourless prisms, m. p. 225° (decomp.) (Found: Cl, 15·9. $C_{10}H_{10}ON_2,CH_3Cl$ requires Cl, 15·8%).

Chloroplatinic acid was added to a solution of the quaternary base (1 g.) in a little hot concentrated hydrochloric acid. On cooling, the *chloroplatinate* separated as an orange crystalline mass. It crystallised from boiling dilute hydrochloric acid in very thin, flattened prisms of a dull orange colour. Dried to constant weight in a vacuum desiccator, it darkened from 140° and melted at 190—195° (decomp.) [Found: Pt, 24·6. $(C_{10}H_{10}ON_2{\cdot}CH_3)_2PtCl_6$ requires Pt, 24·8%].

Reduction of 4-Hydroxy-1-phenyl-5-methylpyrazole: Formation of 1-Phenyl-5-methylpyrazole.—Although ordinary reducing agents had no action upon 4-hydroxy-1-phenyl-5-methylpyrazole, it could be reduced to 1-phenyl-5-methylpyrazole as follows.



$$\begin{array}{l}\mathrm{CH{=\!=}N}\\ |\qquad >\mathrm{N{\cdot}C_6H_5}\\ \mathrm{C(OH){=}C{\cdot}CH_3}\end{array}\xrightarrow[+P]{PBr_3}\begin{array}{l}\mathrm{CH{:}N}\\ |\qquad >\mathrm{N{\cdot}C_6H_5}\\ \mathrm{CH{:}C{\cdot}CH_3}\end{array}\xrightarrow[KMnO_4]{alk.}\begin{array}{l}\mathrm{CH{:}N}\\ |\qquad >\mathrm{N{\cdot}C_6H_5}\\ \mathrm{CH{:}C{\cdot}CO_2H}\end{array}$$

12 G. of 4-hydroxy-1-phenyl-5-methylpyrazole were heated with 25 g. of phosphorus tribromide (b. p. 171°) and 3 g. of yellow phosphorus in a sealed tube at 200—220° for 24 hours. When cold, the viscid reddish-black contents of the tube were washed out with water, made strongly alkaline, and steam-distilled. The 1-phenyl-5-methylpyrazole in the distillate, partly as oily drops, was extracted with ether, dried over potassium carbonate, and fractionated at the ordinary pressure; it distilled almost completely at 255—265°. On refractionation the main fraction (4·2 g.) had b. p. 261°/761 mm. (Stoermer and Martinsen, *Annalen*, 1907, **352**, 333, give b. p. 263·5°/762 mm.). Its identity was confirmed by the preparation of the chloroplatinate, m. p. 197—199° (decomp.),

the picrate, m. p. 97°, and the ethiodide, m. p. 208—209° (Found : I, 40·6. Calc. : I, 40·4%).

1·4 G. of the reduction product (1 mol.), 2·8 g. of potassium permanganate (1 mol.), and 0·6 g. of potassium hydroxide were refluxed with 40 c.c. of water for 8 hours. After separation of the manganese dioxide formed, the colourless filtrate was concentrated to about 15 c.c. and acidified with hydrochloric acid; 1-phenylpyrazole-5-carboxylic acid then separated. After two recrystallisations from boiling water it melted at 183—183·5° (compare Claisen and Roosen, *Annalen*, 1894, **278**, 292), alone or mixed with the acid prepared by the similar oxidation of authentic 1-phenyl-5-methylpyrazole (Stoermer and Martinsen, *loc. cit.*).

When heated in a sealed tube with 2—10 mols. of phosphorus oxychloride at temperatures ranging from 100° to 300° and for periods of 5—30 hours, 4-hydroxy-1-phenyl-5-methylpyrazole did not yield any recognisable amount of 4-chloro-1-phenyl-5-methylpyrazole, and from the black coked product only traces of the initial material could be isolated. Wolff and Fertig (*Annalen*, 1900, **313**, 21) used this procedure to establish the constitution of 4-hydroxy-1-phenylpyrazole, which gave 4-chloro-1-phenylpyrazole in "extraordinarily bad yield."

4-*Hydroxy*-1-*aryl*-5-*methylpyrazoles*.—A series of 4-hydroxy-1-aryl-5-methylpyrazoles has been made by the action of alcoholic sodium ethoxide upon the corresponding arylhydrazone of β-chloro-α-ketobutaldehyde (compare p. 788), or by treating the crude condensation product of butyl chloral hydrate and the appropriate arylhydrazine in alcohol, with alcoholic potash (compare p. 788). The latter procedure is specially applicable where the purification of the ketonic hydrazone presents some difficulty—as with those derived from phenyl- and the three tolyl-hydrazines.

The yields of the 4-hydroxy-pyrazoles are usually good and reach 90% in the case of 4-hydroxy-1-(2′ : 4′-dichlorophenyl)-5-methylpyrazole.

4-*Hydroxy*-1-o-*tolyl*-5-*methylpyrazole* (III; Ar = C_7H_7) crystallises from boiling alcohol, in which it is moderately easily soluble, in colourless prisms, m. p. 157·5° (Found: N, 15·05. $C_{11}H_{12}ON_2$ requires N, 14·9%), and its *methiodide* from alcohol–ether in irregular colourless prisms, m. p. 198° (decomp.) (Found : I, 38·7. $C_{12}H_{15}ON_2I$ requires I, 38·5%).

4-*Hydroxy*-1-m-*tolyl*-5-*methylpyrazole* separates from benzene–light petroleum in colourless prisms, m. p. 120° (Found: N, 14·8%), and the corresponding p-*tolyl* compound in colourless prisms with domed ends, m. p. 125° (Found : N, 14·9%).

4-*Hydroxy*-1-p-*chlorophenyl*-5-*methylpyrazole* separates from boiling benzene, in which it is moderately easily soluble, in compact colourless prisms with domed ends, m. p. 141—142° (Found : Cl, 17·1. $C_{10}H_9ON_2Cl$ requires Cl, 17·0%). The *picrate* crystallises from boiling alcohol, in which it is moderately easily soluble, in bright yellow, compact prisms, m. p. 125—126° (Found : Cl, 8·0. $C_{10}H_9ON_2Cl,C_6H_3O_7N_3$ requires Cl, 8·1%). The hydrochloride separates from concentrated hydrochloric acid, in which it is readily soluble, in colourless prisms, m. p. 99—102° (decomp.). The *methiodide* crystallises from boiling alcohol, in which it is easily soluble, in colourless rhombic tablets, m. p. 196—197° (slight decomp.) (Found : Cl + I, 46·5. $C_{10}H_9ON_2Cl,CH_3I$ requires Cl + I, 46·4%).

1-p-*Chlorophenyl-5-methylpyrazolyl 4-benzoate* separates from boiling alcohol, in which it is very easily soluble, in very slender, colourless, flattened prisms, m. p. 95—96° (Found : Cl, 11·25. $C_{17}H_{13}O_2N_2Cl$ requires Cl, 11·3%).

4-*Hydroxy*-1-p-*bromophenyl-5-methylpyrazole* crystallises from 50% alcohol, or boiling benzene, in which it is moderately easily soluble, in colourless prisms, m. p. 143° (Found : Br, 31·6. $C_{10}H_9ON_2Br$ requires Br, 31·6%). The 4-*benzoate* separates from boiling alcohol, in which it is easily soluble, in fine colourless prisms, m. p. 108·5—109° (Found : Br, 22·6. $C_{17}H_{13}O_2N_2Br$ requires Br, 22·4%).

4-*Hydroxy*-1-(2′ : 4′-*dichlorophenyl*)-5-*methylpyrazole* separates from boiling alcohol, in which it is readily soluble, in large colourless compact crystals resembling octahedra, m. p. 184° (Found : C, 49·0; H, 3·4; N, 11·3; Cl, 29·2. $C_{10}H_8ON_2Cl_2$ requires C, 49·3; H, 3·3; N, 11·5; Cl, 29·2%). It is almost insoluble in boiling water, but readily soluble in hot acetic acid, chloroform, benzene, and alcohol. The crystals (from alcohol) belong to the orthorhombic system (class—holohedral), and the axial elements are $a : b : c = 1·1250 : 1 : 1·0649$. The forms observed were $m\{110\}$, $q\{011\}$, $s\{201\}$, and $o\{111\}$. There is no good cleavage. The crystals show strong positive double refraction with a wide axial angle. The optic axes lie in the plane {100}, and the acute bisectrix is perpendicular to {001}. The interfacial angles are given in the following table :—

Angle.	No.	Limits.	Mean observed.	Calc.
$110 : 1\bar{1}0$	6	96° 43′— 96° 50′	96° 44′	*
$201 : 20\bar{1}$	4	55° 57′— 56° 1′	55° 59′	56° 0′
$110 : 0\bar{1}1$	3	122° 31′—123° 11′	122° 50′	122° 54′
$111 : \bar{1}1\bar{1}$	3	74° 32′— 75° 38′	75° 5′	75° 14′
$111 : \bar{1}\bar{1}1$	8	119° 27′—110° 24′	119° 36′	*
$110 : 111$	17	35° 27′— 35° 40′	35° 13′	35° 15′
$110 : 1\bar{1}1$	6	84° 35′— 85° 3′	84° 33′	84° 31′
$011 : 111$	12	32° 46′— 33° 16′	32° 54′	32° 52′
$110 : 201$	6	53° 49′— 54° 18′	54° 5′	54° 5′

1-(2′ : 4′-Dichlorophenyl)-4-hydroxy-5-methylpyrazole does not form a picrate or a methiodide. It dissolves readily in boiling concentrated hydrochloric acid and on cooling the *hydrochloride* separates as large, colourless, compact, rhombic plates, m. p. 96° (decomp.) (Found : Cl, 37·9. $C_{10}H_8ON_2Cl_2$,HCl requires Cl, 38·1%). The 4-*benzoate*, prepared by the Schotten–Baumann reaction, crystallises from boiling alcohol, in which it is readily soluble, in very thin, colourless, apparently square, rectangular platelets, m. p. 112·5—113° (Found : Cl, 20·4. $C_{17}H_{12}O_2N_2Cl_2$ requires Cl, 20·4%).

4-*Hydroxy*-1-(2′ : 4′-*dibromophenyl*)-5-*methylpyrazole* separates from boiling alcohol, in which it is moderately easily soluble, in large, colourless, compact crystals, m. p. 186° (Found : Br, 48·2. $C_{10}H_8ON_2Br_2$ requires Br, 48·2%). The 4-*benzoate* crystallises from boiling alcohol, in which it is readily soluble, in very slender, colourless prisms, m. p. 112—113° (Found : Br, 41·1. $C_{17}H_{12}O_2N_2Br_2$ requires Br, 41·2%).

For comparison with 4-hydroxy-1-(2′ : 4′-dichlorophenyl)-5-methylpyrazole the isomeric 1-(2′ : 4′-*dichlorophenyl*)-5-*methyl*-3-*pyrazolone* was prepared by the method of Michaelis (*Annalen*, 1907, **358**, 130) by condensing 29 g. of β-acetyl-2 : 4-dichlorophenylhydrazine (1 mol.) and 17·2 g. of acetoacetic ester (1 mol.) with 40 g. (2½ mols.) of phosphorus trichloride. It crystallised from boiling alcohol, in which it was moderately easily soluble, in colourless flattened prisms, m. p. 208—209° (Found : Cl, 29·0. $C_{10}H_8ON_2Cl_2$ requires Cl, 29·2%).

The 3-pyrazolone dissolves readily in warm 10% caustic soda solution and on cooling the *sodium* salt separates in very slender, colourless needles, m. p. 55° (decomp.) (Found : Na, 8·6. $C_{10}H_7ON_2Cl_2Na$ requires Na, 8·7%).

1-(2′ : 4′-*Dichlorophenyl*)-5-*methylpyrazolyl* 3-*benzoate*, prepared by the Schotten–Baumann reaction, separates from boiling alcohol, in which it is very readily soluble, in colourless hair-like prisms, m. p. 98—99° (Found : Cl, 20·5. $C_{17}H_{12}O_2N_2Cl_2$ requires Cl, 20·4%).

4-*Bromo*-1-(2′ : 4′-*dichlorophenyl*)-5-*methyl*-3-*pyrazolone*, prepared by the action of bromine (1 mol.) upon a solution of the 3-pyrazolone (1 mol.) in acetic acid at the ordinary temperature, crystallises from boiling alcohol, in which it is rather sparingly soluble, in compact colourless tablets, m. p. 241—242° (decomp.) (Found : Cl + Br, 47·0. $C_{10}H_7ON_2Cl_2Br$ requires Cl + Br, 46·85%).

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[*Received, February* 12*th*, 1931.]