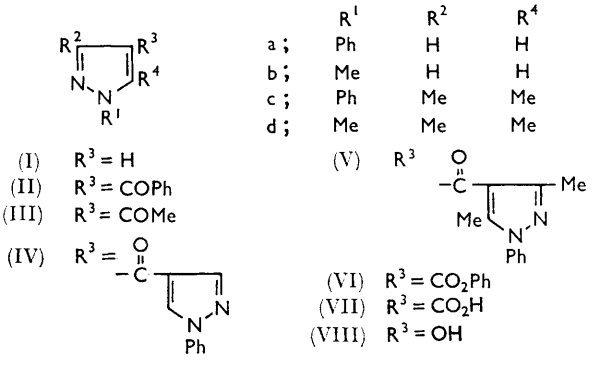
Preparation and Properties of Some Pyrazolyl Ketones

By **I. L. Finar** and **T. Foster**, The Northern Polytechnic, Holloway, London N.7

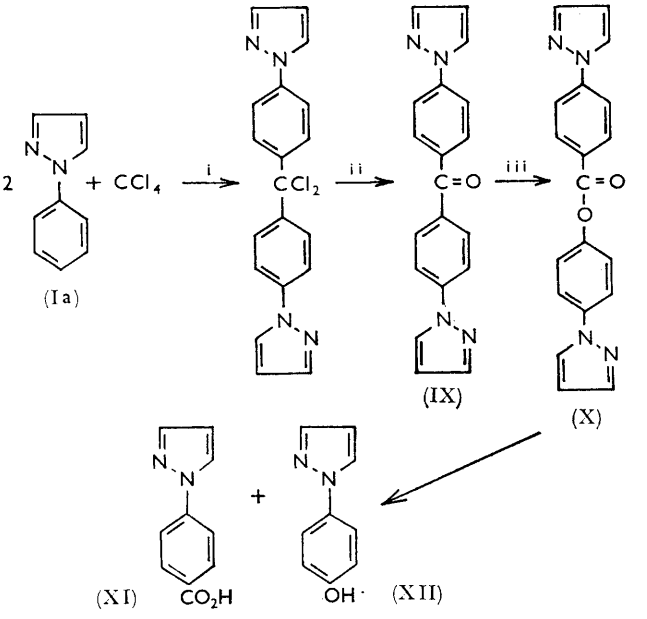
Friedel–Crafts acylation reactions of some *N*-methyl and *N*-phenylpyrazoles have been investigated and some phenyl pyrazolyl ketones and dipyrazolyl ketones have been prepared. Substitution occurred at the 4-position in the pyrazole nucleus, an exception being the reaction of 1-phenylpyrazole with carbon tetrachloride under Friedel–Crafts conditions. The 1 : 1 aluminium chloride–1-phenylpyrazole complex has been isolated and brominated in neutral solution, and 1-phenylpyrazole has been brominated in strongly acidic solution. Some pyrazole ketones have been converted to esters by the Baeyer–Villiger oxidation with peracetic acid, and migration aptitude has been correlated with the electron-releasing properties of some substituted pyrazole nuclei. The infrared absorption spectra of some pyrazoles have been examined.

Owing to the ability of pyrazoles to complex with aluminium chloride,[1] Friedel–Crafts acylations in the pyrazole series usually proceed with difficulty and have only been successfully carried out with those pyrazoles containing electron-releasing groups or *N*-aryl substituents, or both, in the ring.[1-7] In all cases acylation occurred in position 4 of the pyrazole ring.



Lord [7] prepared 4-benzoyl-1-phenylpyrazole (IIa) by reaction between approximately equimolecular amounts of 1-phenylpyrazole (Ia),[8] benzoyl chloride, and aluminium chloride, at 95—100° in nitrobenzene. Attempts to improve the yield of (IIa) obtained by this method, by varying the proportions and nature of the catalyst, use of different solvents, etc., were unsuccessful. Use of carbon tetrachloride as solvent, and mixing the reactants at low temperature gave no ketone, but when an excess of aluminium chloride was used and the reactants were mixed below 0° in carbon tetrachloride and set aside at room temperature for several hours (cf. ref. 1), *ca.* 1% of a ketone was obtained. Analysis indicated that benzoylation had not taken place, and the same ketone was obtained by carrying out the above reaction in the absence of benzoyl chloride. The Baeyer–Villiger oxidation of the ketone with peracetic acid and hydrolysis of the ester so obtained gave 1-(*p*-carboxyphenyl)pyrazole [9] (XI) and 1-(*p*-hydroxyphenyl)pyrazole (XII). The latter has been synthesised by alkaline fusion, at 300°, of 1-(*p*-sulphonyl)pyrazole.[10] The identity of the oxidation products was confirmed by means of their infrared spectra. Thus, the ketone is di-*p*-(1-pyrazolyl)phenyl ketone (IX),[11] and the ester is *pp*′-di(1-pyrazolyl)phenyl benzoate (X).

The benzoyl ketones (IIc) and (IId) were prepared from (Ic) [12] and (Id), but benzoylation of (Ib) [13] and acetylation of (Ia) and (Ib) were unsuccessful. Compound (IIa) was also prepared (in low yield) by reaction of 1-phenylpyrazole-4-carbonyl chloride with benzene, but 4-benzoyl-1-methylpyrazole could not be prepared by



the corresponding reaction with 1-methylpyrazole-4-carbonyl chloride.

The dipyrazolyl ketones (IVa)—(IVc) were prepared by the Friedel–Crafts reaction between 1-phenylpyrazole-

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[6] I. I. Grandberg, G. I. Sharov, V. S. Troitskaya, and V. G. Vinokurov, *Zhur. obshchei Khim.*, 1962, **32**, 3582.
[7] G. H. Lord, Ph.D. Thesis, London University, 1958.
[8] I. L. Finar and R. J. Hurlock, *J. Chem. Soc.*, 1954, 3024.
[9] L. Balbiano, *Gazzetta*, 1889, **19**, 119, 128.
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[11] M. Gomberg and R. L. Jickling, *J. Amer. Chem. Soc.*, 1915, **37**, 2577.
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4-carbonyl chloride and the respective pyrazoles (Ia)—(Ic). Compound (IVb) was also prepared by reaction between 1-methylpyrazole-4-carbonyl chloride and 1-phenylpyrazole (Ia); the former compound failed to react with 1-methylpyrazole (Ib). Compound (Vc) was prepared by the reaction between 3,5-dimethyl-1-phenylpyrazole-4-carbonyl chloride and 3,5-dimethyl-1-phenylpyrazole, but no ketone was obtained from the reaction between the former and 1-methylpyrazole.

The yields of ketone are low, varying from 13 to 33% (Table 1). Interpretation of the results is difficult since the substrate is a mixture of the pyrazole–aluminium chloride complex and its dissociation products. The equilibrium position depends on the stability of the complex, and this stability depends on steric factors and the basicity of the pyrazole. Preliminary molecular orbital calculations by Finar [14] have shown that the basicity increases with the number of groups in the pyrazole ring, and consequently stability of the complex will be expected to increase in the same order, but at the same time will be decreased by the steric effect of a substituent at position 3.

TABLE 1

Dipyrazolyl ketones

Pyrazole acid	Pyrazole	Ketone	M. p.	Yield (%)	Found (%)			Formula	Required (%)		
					C	H	N		C	H	N
(VIIa)	(Ic)	(IVc)	146°	23	73·8	5·5	16·2	$C_{21}H_{18}N_4O$	73·7	5·3	16·4
(VIIa)	(Ib)	(IVb)	171	13	66·4	4·5	22·7	$C_{14}H_{12}N_4O$	66·7	4·8	22·2
(VIIb)	(Ia)	(IVb)	171	33							
(VIIc)	(Ic)	(Vc)	160—161	19	74·3	5·7	15·3	$C_{23}H_{22}N_4O$	74·6	5·9	15·1

Bromination of 1-phenylpyrazole (Ia) with molecular bromine, in neutral [9] and acidic [15,16] solvents, results in initial 4-substitution, further substitution occurring at the *p*-position of the phenyl ring, the product often being a mixture of 4-bromo-1-phenylpyrazole (XIII) and 4-bromo-1-(*p*-bromophenyl)pyrazole (XIV). Lynch and co-workers [17] treated (Ia) with bromine in the presence of silver sulphate, in concentrated sulphuric acid (*i.e.*, "positive bromination" [18]) and obtained only 1-(*p*-bromophenyl)pyrazole, (XV) and suggested that the difference in orientation of substitution was due to protonation of (Ia) in this medium. This does not agree with the results of Miller [15] and Brain.[16] In the present work bromination of the aluminium chloride complex of (Ia) (which was isolated and shown to be a 1 : 1 complex) with molecular bromine in carbon tetrachloride gave only (XIII) in the cold and a mixture of (XIII) and (XIV) on heating, the yields obtained being similar to those obtained by bromination of (Ia) itself under similar conditions. Bromination of (Ia) in concentrated sulphuric acid gave mainly (XIII) plus a small amount of (XIV); attempts to repeat Lynch's work gave a mixture of (XIV) and (XV), the latter being the predominant product.

Initial *p*-substitution has only been found to occur under conditions for "positive bromination," *i.e.*, when the brominating species is the Br^+ cation. Preliminary calculations [14] indicate that the 4-position of the pyrazole ring is still the position of highest electron density in the protonated pyrazole (XVII), and hence it appears likely that the difference in orientation of substitution in this case is due to a difference in the nature of the attacking species. Calculation of the localisation energy (in β units) for electrophilic substitution at the 4- and *p*-positions in 1-phenylpyrazole and the protonated molecule has shown that in both cases the value for the 4-position is lower than that for the *p*-position. It has also been found that the potential energy of a unit positive charge (*e.g.*, the Br^+ cation) at a point 3 Å perpendicular to position 4 is greater than that of a corresponding point for the *p*-position. The difference (converted into β units), when added to the localisation energy for the 4-position, now makes the value greater than that for the *p*-position, and so attack by a positive ion would be expected to occur at the *p*-position. If we treat molecular bromine as an uncharged species then bromination can be expected to occur preferentially in the 4-position in both 1-phenylpyrazole and the protonated molecule.[14]

Oxidation of aryl ketones with peracetic acid gives an ester which may be hydrolysed to an acid and a phenol.[19] Hence, oxidation of the ketones prepared in the present work appeared to offer a new route to 4-hydroxypyrazoles which are difficult to prepare by other methods.[20–22] Peracetic acid oxidation of the phenyl pyrazolyl ketones (IIa), (IIc), and (IId) gave the phenyl esters (VIa), (VIc), and (VId) of the corresponding pyrazole-4-carboxylic acids, which gave phenol and the pyrazole acids (VIIa), (VIIc), and (VIId) on hydrolysis. Oxidation of 4-acetyl-1-phenylpyrazole (IIIa) gave the acid (VIIa), hydrolysis of the methyl ester occurring under the reaction conditions. Similarly, oxidation of the dipyrazolyl ketones (IVa), (IVb), and Vc) resulted in hydrolysed

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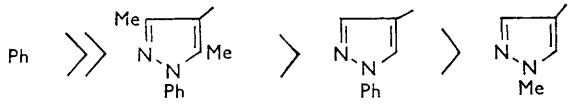
products, but in these cases reaction was not complete even after one week. Oxidation of the symmetrical ketones (IVa) and (Vc) gave the corresponding pyrazole-4-carboxylic acids (VIIa) and (VIIc) and 4-hydroxypyrazoles (VIIIa) and (VIIIc) in reasonable yield. Oxidation of (IVc) gave 4-hydroxy-3,5-dimethyl-1-phenylpyrazole (VIIIc) and 1-phenylpyrazole-4-carboxylic acid (VIIa) and 1-methyl-1′-phenyldi(4-pyrazolyl) ketone gave low yields of 4-hydroxy-1-phenylpyrazole (VIIIa) and 1-methylpyrazole-4-carboxylic acid (VIIb). According to the proposed mechanism [19] of this oxidation, it is the more electron-releasing group which migrates and gives a phenol on hydrolysis. Hence the order of electron-releasing power is,



Examination of the infrared spectra (in Nujol) of all the ketones prepared showed that the carbonyl stretching frequencies occurred in the range 1640—1610 cm.$^{-1}$. All these frequencies are considerably lower than the "normal" range for diaryl ketones (1670—1660 cm.$^{-1}$),[23] suggesting considerable conjugation of the carbonyl group with the pyrazole ring.

The spectra of the 4-substituted derivatives of 1-phenylpyrazole all showed a band in the region 964—953 cm.$^{-1}$, which is not present in the spectrum of 1-phenylpyrazole itself, in accordance with the previous suggestion [17,7] that such a band is indicative of 4-substitution in 3,5-unsubstituted 1-phenylpyrazole.

The spectra of the *p*-substituted 1-phenylpyrazoles (XII), (XIV), and (XV) showed a band in the region 830—810 cm.$^{-1}$,[23] as expected for a *p*-substituted phenyl ring. However, the spectra of 1-(*p*-carboxyphenyl)-pyrazole (XI) and di-*p*-(1-pyrazolylphenyl) ketone (IX) showed a band outside this region, *viz.*, 868 and 864 cm.$^{-1}$, respectively, possibly due to the electron-withdrawing effects of the carbonyl groups in these two compounds.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 137 Infracord spectrophotometer either in Nujol or as liquid films where applicable.

Preparation of the Pyrazoles (I).—Pyrazoles (Ia) and (Ic) were prepared by the condensation of phenylhydrazine with 1,1,3,3-tetraethoxypropane [8] and acetylacetone,[12] respectively. Pyrazoles (Ib) and (Id) were prepared by methylation of pyrazole [13] and 3,5-dimethylpyrazole,[24] respectively.

Preparation of 4-Benzoylpyrazoles (II).—To a stirred mixture of 1-phenylpyrazole (5·0 g., 0·035 mole) and anhydrous aluminium chloride (5·55 g., 0·042 mole), in nitrobenzene (10 ml.) at 95—100°, was added benzoyl chloride (5·35 g., 0·038 mole), over 5 min.; heating and stirring were continued for 3 hr. The mixture was poured on ice, acidified with conc. hydrochloric acid and steam-distilled; solid material was collected, digested with hot 2N-sodium hydroxide, and recrystallised from aqueous ethanol to give needles of 4-benzoyl-1-phenylpyrazole (2·6 g., 30%), m. p. 124—125° (lit.,[25] m. p. 126—126·5°).

Similarly prepared were 4-benzoyl-3,5-dimethyl-1-phenylpyrazole [(IIc) 15%], m. p. 98—99° (lit.,[26] m. p. 99—100°) and 4-benzoyl-1,3,5-trimethylpyrazole [(IId),[1] 9%], b. p. 120—121°/0·05 mm. Compound (IIa) was also prepared in 13% yield by a similar reaction using 1-phenylpyrazole-4-carbonyl chloride and benzene.

*Preparation of Di-*p*-(1-pyrazolylphenyl) Ketone* (IX).—To a stirred mixture of aluminium chloride (18·4 g., 0·14 mole) in carbon tetrachloride (100 ml.), cooled to −5 to −10°, was added 1-phenylpyrazole (5·0 g., 0·035 mole) over 5 min.; the mixture was kept at room temperature for 14 hr. Hydrolysis and evaporation of the solvent gave a tarry solid; repeated recrystallisation from aqueous ethanol gave white plates of the *ketone* (0·07 g., 1%), m. p. 230·5—231° (Found: C, 72·4; H, 4·6; N, 17·6. $C_{19}H_{14}N_4O$ requires C, 72·6; H, 4·5; N, 17·9%).

Preparation of Dipyrazolyl Ketones (IV).—The pyrazole-4-carboxylic acids (VIIa), (VIIb), and (VIIc) were prepared by oxidation of the corresponding 4-formyl compounds. A mixture of 1-phenylpyrazole-4-carboxylic acid (4·7 g., 0·025 mole) and thionyl chloride (5·95 g., 0·05 mole) was kept at 50° for 1 hr. The excess of thionyl chloride was distilled off to leave the acid chloride as a solid which was dissolved in nitrobenzene (20 ml.). Aluminium chloride (4·0 g., 0·03 mole) and 1-phenylpyrazole (3·6 g., 0·025 mole) were added and the mixture was heated at 95—100° for 3 hr. Work-up followed by recrystallisation of the solid from benzene gave white plates of di-(1-phenyl-4-pyrazolyl) ketone (2·2 g., 28%), m. p. 220—221° (lit.,[27] 221°).

Preparation of the 1-Phenylpyrazole–Aluminium Chloride Complex.—To a stirred mixture of 1-phenylpyrazole (2·88 g., 0·02 mole) in carbon tetrachloride (20 ml.) was added aluminium chloride (2·67 g., 0·02 mole). After stirring for 10 min. at room temperature the solid was filtered off, under anhydrous conditions, washed with carbon tetrachloride and dried, giving the *complex* as a red-brown solid (5·48 g.) (Found: Al, 9·9; Cl, 37·9. $C_9H_8N_2,AlCl_3$ requires Al, 9·7; Cl, 38·4%).

Bromination of the Complex.—An authentic sample of 4-bromo-1-(*p*-bromophenyl)pyrazole was prepared by bromination [16] of 1-(*p*-bromophenyl)pyrazole, the latter being obtained by the condensation of *p*-bromophenylhydrazine with 1,1,3,3-tetraethoxypropane.[17]

(*a*) A cooled solution of bromine (3·84 g., 0·024 mole) in carbon tetrachloride was added to a cooled suspension of the 1-phenylpyrazole–aluminium chloride complex (5·55 g., 0·02 mole) in carbon tetrachloride. The mixture was kept at room temperature for 24 hr. and poured on crushed ice; collection and recrystallisation of the solid from aqueous ethanol gave white needles of 4-bromo-1-phenylpyrazole (1·5 g., 33%), m. p. 80—81° (lit.,[16] m. p. 82—83°). A similar experiment in the absence of aluminium chloride gave 27% of 4-bromo-1-phenylpyrazole.

(*b*) The experiment in (*a*) was repeated, but the reaction mixture was heated for 6 hr. at 95—100°. Fractional

[23] C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic Press, New York, 1963.
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[27] I. L. Finar and K. E. Godfrey, *J. Chem. Soc.*, 1954, 2293.

crystallisation of the crude product gave 4-bromo-1-phenylpyrazole (2·9 g., 65%), m. p. 80—81°, and 4-bromo-1-(*p*-bromophenyl)pyrazole (0·9 g., 15%), m. p. 84—84·5° (lit.,[16] m. p. 84·5—85°; the infrared spectrum was identical with that of an authentic sample). A similar experiment with 1-phenylpyrazole itself yielded 63% of the mono- and 20% of the di-bromopyrazole.

Bromination of 1-Phenylpyrazole in Concentrated Sulphuric Acid.—(*a*)* To a cooled solution of 1-phenylpyrazole (5·4 g., 0·038 mole) in sulphuric acid (30 ml., *d* 1·84), was added, dropwise, a solution of bromine (6·0 g., 0·038 mole) in sulphuric acid (10 ml., *d* 1·84). The mixture was mechanically shaken for 3 hr. and then poured on ice. Solid material was collected and fractionally crystallised from aqueous ethanol, giving 4-bromo-1-phenylpyrazole (57%), and 4-bromo-1-(*p*-bromophenyl)pyrazole (5%).

(*b*)† Bromine (14·4 g., 0·09 mole) and silver sulphate (17·0 g., 0·055 mole) were added to a mixture of 1-phenylpyrazole (10·8 g., 0·075 mole) in sulphuric acid (90 ml., *d* 1·84) and water (10 ml.), and the mixture was shaken for 3 hr. Silver bromide was filtered off and the mixture was worked-up. Fractional crystallisation of the crude product from aqueous ethanol gave white plates of 1-(*p*-bromophenyl)pyrazole (7 g., 42%), m. p. 69—70° (lit.,[17] m. p. 70°; the infrared spectrum was identical with that of an authentic sample) and 4-bromo-1-phenylpyrazole (4·5 g., 20%)

Peracetic Acid Oxidations of Pyrazolyl Ketones.—Peracetic acid (40%) was from Laporte Ltd.; analysis showed it to be a 39% w/v peracetic acid solution.

(a) *Oxidation of alkyl and aryl pyrazolyl ketones* (II), (III), and (IX). To a cooled solution of 4-benzoyl-1-phenylpyrazole (2·5 g., 0·01 mole) in glacial acetic acid (25 ml.) and concentrated sulphuric acid (15 ml.), was added peracetic acid (3·9 ml., 0·02 mole), in a rapid stream of drops, and the mixture was kept at room temperature for 2 hr., after which time analysis[19] of an aliquot indicated that reaction was complete. The mixture was poured on crushed ice, and the solid material was collected and recrystallised from aqueous ethanol, giving white needles of phenyl 1-phenylpyrazole-4-carboxylate (2·1 g., 79%), m. p. 114—114·5° (Found: C, 73·0; H, 4·6; N, 10·5. $C_{16}H_{12}N_2O_2$ requires C, 72·7; H, 4·5; N, 10·6%). The ester was heated under reflux with 2N-sodium hydroxide for 1 hr., the solution acidified with dilute hydrochloric acid and extracted with ether. The ether extracts were extracted with 10% sodium carbonate and dried (Na_2SO_4). Evaporation of the solvent gave phenol (0·4 g., 59%). The sodium carbonate extract was acidified and the solid was collected and recrystallised from aqueous ethanol, giving 1-phenylpyrazole-4-carboxylic acid (1·1 g., 63%), m. p. 220—221° (lit.,[27] m. p. 221°).

(b) *Preparation of* 1-(p-*hydroxyphenyl*)*pyrazole* (XII). To a stirred mixture of potassium hydroxide (5 g.) and sodium hydroxide (2 g.), at 190°, was added 1-(*p*-sulphophenyl)pyrazole (1·12 g., 0·005 mole) (prepared by the condensation between *p*-sulphophenylhydrazine and 1,1,3,3-tetraethoxypropane[10]); the temperature was raised to 330° when vigorous effervescence ensued; when this had ceased the mixture was cooled and dissolved in water. The solution was acidified with 2N-hydrochloric acid and extracted with ether; the extracts were dried, the solvent evaporated, and the residue was recrystallised from aqueous ethanol, giving white needles of 1-(*p*-hydroxyphenyl)pyrazole (0·6 g., 73%), m. p. 107—108° (Found: C, 67·1; H, 5·1; N, 17·3. $C_9H_8N_2O$ requires C, 67·5; H, 5·0; N, 17·5%).

(c) *Oxidation of dipyrazolyl ketones.* The oxidations were carried out as in (a) above, but the reaction did not go to completion after 7 days' standing at room temperature. The crude product was heated under reflux with 2N-sodium hydroxide, the unchanged ketone filtered off, and the solution was worked-up as in (a) to give the pyrazole-4-carboxylic acid and 4-hydroxypyrazole.

TABLE 2

Baeyer–Villiger oxidation of alkyl and aryl pyrazolyl ketones

Ketone	Ester	M. p.	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N	Acid	M. p.	Yield (%)	Yield of phenol (%)
(IIc)	(VIc)	91—91·5°	80	74·3	5·4	9·7	$C_{18}H_{16}N_2O_2$	74	5·5	9·6	(VIIc)	200—201° [a]	72	50
(IId)	(VId)	63—64	83	68·1	6·0	12·0	$C_{13}H_{14}N_2O_2$	67·8	6·1	12·2	(VIId)	219—220 [b]	61	56
(IIIa)											(VIIa)	220—221	79	
(IX)	(X)	239—240	77	69·5	4·3	17·2	$C_{19}H_{14}N_4O_2$	69·1	4·2	17·0	(XI)	265	65	(XII) 58 [b]

[a] Lit.,[28] m. p. 200—201°. [b] Lit.,[29] m. p. 217°.

TABLE 3

Baeyer–Villiger oxidation of dipyrazolyl ketones

Ketone	Acid	M. p.	Yield (%)	4-Hydroxypyrazole	M. p.	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N
(IVa)	(VIIa)	220—221°	38	(VIIIa)	119—120° [b]	44							
(IVb)	(VIIb)	204·5—205·5 [c]	16	(VIIIa)	119—120 [b]	17							
(IVc)	(VIIa)	220—221 [a]	51	(VIIIc)	128—129	49	70·5	6·3	15·1	$C_{11}H_{12}N_2O$	70·2	6·4	14·9
(Vc)	(VIIIc)	200—201 [d]	52	(VIIIc)	128—129	50							

[c] Lit.,[27] m. p. 220—221°. [b] Lit.,[20] m. p. 119—120°. [c] Lit.,[13] m. p. 205—206°. [d] Lit.,[28] m. p. 200—201°.

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* Cf. ref. 15.
† Cf. ref. 17.

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