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A STUDY OF PYRAZOLIN-5-ONE TAUTOMERISM—I

SOME 3-UNSUBSTITUTED 1-ARYL-2-PYRAZOLIN-5-ONES

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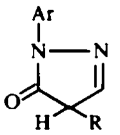
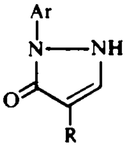
Abstract—The tautomerism of four 1-aryl-2-pyrazolin-5-ones not bearing a 3-substituent has been studied using NMR and IR spectroscopy. In carbon tetrachloride and chloroform solutions compounds without a 4-substituent exist essentially in the CH form (I). However, in the presence of a 4-ethoxycarbonyl substituent the NH form (II) is favoured. Results are also reported for all the compounds studied both in DMSO solution and in the solid state.

INTRODUCTION

THE tautomerism of 1-aryl-2-pyrazolin-5-ones has attracted a considerable amount of interest in recent years.[1–5] Many of the conclusions reached earlier were contradictory but the situation has been reviewed and clarified by Katritzky and Maine.[1] A feature of almost all the compounds studied so far has been the presence of a 3-substituent, although there are reports[6, 7] of an investigation involving 1-phenyl-2-pyrazolin-5-one. We wish to present the results of an examination of four pyrazolones not having a 3-substituent.

Using the nomenclature of Katritzky and Maine, the three possible tautomers may be designated as the CH(I), NH(II) and OH(III) forms according to the position of the labile proton. The CH form may be readily distinguished from the other two by means of NMR spectroscopy, whilst in addition IR spectroscopy may be used to differentiate between the OH and NH forms.


I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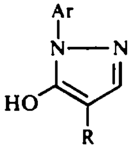
III

RESULTS

NMR spectra. The basis of the use of NMR for determining the tautomeric form of pyrazolin-5-ones is the measurement of the chemical shift of the proton(s) in the 4-position. In the absence of a 4-substituent the CH form (I) will have two protons attached to a saturated C atom, and these will resonate at higher field (ca. $\delta 3{\cdot}5$ ppm) than is the case for the NH (II) or OH (III) forms, when the single 4-H will give rise to a low field signal (ca. δ 5·5 ppm) due to its vinylic nature. Furthermore the multiplicity of the signal due to the 3-H will indicate the number of protons present at the 4-position, a triplet resulting from CH forms and a doublet from NH or OH forms. If a 4-substituent is present, the CH form will still give rise to a high field signal, but the

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NH and OH forms will not have a 4-H and the absence of a high field signal must be taken to indicate the presence of one, or both, of these forms.

It is more difficult to differentiate between the NH and OH forms by NMR, chemical shifts of protons on nitrogen and oxygen being of less structural significance due to the possible intervention of exchange phenomena. However, the presence of the NH form is sometimes indicated by the appearance of a broad low field signal due to NH. IR measurements are of great value in investigating the NH and OH forms (see below).

The NMR spectra of four pyrazoline-5-ones in deuterochloroform solution are summarized in Table 1. From these it will be seen that the two compounds not having a 4-substituent (1 and 2) exist essentially in the CH form in this solvent, whilst compounds having a 4-ethoxycarbonyl substituent (3 and 4) exist as the NH form. The spectra of compounds 1 and 3 have also been measured in carbon tetrachloride (2 and 4 were insoluble) and the results obtained were not significantly different from those found for deuterochloroform solutions.

TABLE 1. NMR SPECTRA OF 1-ARYL-2-PYRAZOLIN-5-ONES IN $CDCl_3$

Compound	Ar	R	Chemical shifts*		$J_{3,4}$	Comments
			H_3	H_4		
1	C_6H_5	H	7·44	3·45	1·3	CH form
2	o-$C_6H_4.NO_2$	H	7·50	3·47	1·4	CH form
3	C_6H_5	CO_2Et	7·75	—	—	NH δ 9·25 (broad)
4	o-$C_6H_4.NO_2$	CO_2Et	7·79	—	—	NH (broad) under aromatic H

* Expressed in ppm downfield from internal TMS.

In order to study the effect of a more polar solvent on the tautomeric equilibria of these compounds the spectra have also been determined in hexadeuterodimethylsulphoxide (DMSO-d_6). The results of these measurements are shown in Table 2 from which it can be seen that none of the compounds studied exist in the CH form in this solvent.

IR spectra. In using IR spectroscopy to differentiate between the tautomeric forms two spectral regions are of particular interest, namely 3500–1750 cm^{-1} and 1750–1500 cm^{-1}. In the first region NH or OH and their related vibrations absorb although it is difficult to differentiate between the OH and NH forms in this region. In the second region the most significant vibration is the CO stretching mode and its presence and observed frequency, or its absence, are of primary importance in determining the tautomeric form. The region 1600–1500 cm^{-1} is also important because, apart from the vibrations of the Ph ring in 1-aryl-2-pyrazolin-5-ones, the presence of C=N or C=C stretching vibrations indicates which tautomer is present. In practice, whereas it is possible to give a resonable assignment to all the absorption bands in this region

TABLE 2. NMR SPECTRA OF 1-ARYL-2-PYRAZOLIN-5-ONES IN DMSO-d_6

Compound	Ar	R	Chemical shifts*		$J_{3,4}$	Comments
			H_3	H_4		
1	C_6H_5	H	7·56	5·70	2·0	NH or OH
2	o-$C_6H_4.NO_2$	H	7·49	5·54	2·0	NH or OH
3	C_6H_5	CO_2Et	7·85	—	—	NH or OH
4	o-$C_6H_4.NO_2$	CO_2Et	7·89	—	—	NH or OH
5†	C_6H_5	H	—	5·38	—	OH

* Expressed in ppm downfield from external TMS.
† 1-Phenyl-3-methyl-2-pyrazolin-5-one.

for pyrazolin-5-ones in the CH form,[1] we believe that because of the sensitivity of νC=C and νC=N to frequency and intensity changes depending on the environment it is not possible to give unequivocal assignments to the IR spectra obtained from NH or OH tautomers. We have based the IR spectroscopic evidence on the position of the CO frequency and the band shape in the 1600–1500 cm^{-1} region. In the CH form the unperturbed CO frequency is to be expected near 1740 cm^{-1} in 5-membered ring systems.[8] In the NH form the CO absorption should be lowered to about 1680 cm^{-1} since it has the configuration of an α,β-unsaturated ketone[9] in this tautomer.

The IR spectra of solutions of compound 1 in $CHCl_3$ and DMSO are shown in Fig. 1. Spectrum (a) was run as a weak solution in a cell of 1·0 mm thickness and because of this comparatively large path length the absorption of the solvent has blanked out certain regions of the spectrum. Nevertheless the presence of a flat background (3500–2000 cm^{-1}) together with a CO absorption doublet at 1723 cm^{-1} (average) indicates the presence of the CH form. The multiplicity of this band and its occurrence at lower frequencies than expected are due to H-bonding to the solvent. Fermi resonance has also been proposed as a cause of multiplicity in some compounds containing a single CO group.[10, 11] Figs 1 (b) and 1 (c) show the spectra obtained from solutions of compound 1 in 0·1 mm path-length cells; these solutions are more concentrated than that whose spectrum is shown in Fig. 1 (a). Fig. 1 (c) is the result obtained from a more concentrated solution than Fig. 1 (b). As the concentration is increased three new bands appear and grow in intensity. The broad absorption with a max near 2700 cm^{-1} is assigned to a very strongly H-bonded NH or OH vibration, and the other two bands are found at 1558 cm^{-1} and 1529 cm^{-1}. The bands found at 1596 and 1499 cm^{-1} are assigned to the Ph ring vibrational modes.

Undoubtedly some OH or NH form accompanies the CH tautomer, but with only a small amount of the second form present it is difficult to decide to which tautomer it corresponds. The absence of even a weak second CO absorption near 1670 cm^{-1} is indicative of the absence of the NH form. Furthermore the spectrum of compound 1 in DMSO (Fig. 1 (d)) has virtually no CO absorption (very weak 1720 cm^{-1}) and the

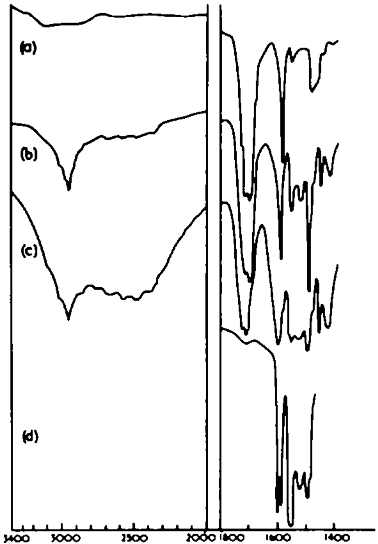


FIG. 1 IR Spectra of 1-phenyl-2-pyrazolin-5-one in (a) $CHCl_3$, 1·0 mm cell, (b) $CHCl_3$, 0·1 mm cell, (c) as (b) but more concentrated (d) DMSO.

pattern of the absorption bands in the region 1600–1500 cm^{-1} is very similar to that of Fig. 1 (c). Thus the OH form is present in DMSO together with a very small amount of CH form whereas in chloroform the CH form is predominant, with a lesser amount of OH form. These changes are to be expected due to the differences in polarity of the two solvents. The presence of the second tautomer in compound 1 has not been observed previously,[5, 6] but Elguero *et al.* report the presence of 55% CH + 45% OH tautomers in dioxan solution.[5]

Fig. 2 shows the IR spectra of 1-phenyl-3-methyl-2-pyrazolin-5-one (compound 5)

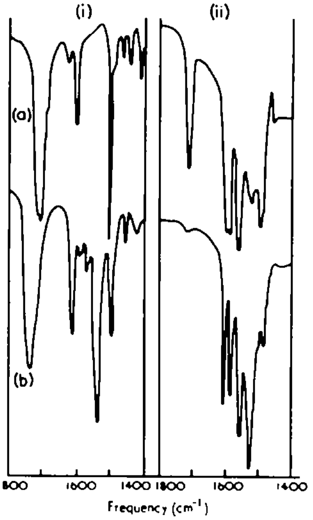
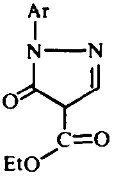


FIG. 2 IR spectra of (a) 1-phenyl-3-methyl-2-pyrazolin-5-one and (b) Compound 2 in $CHCl_3$ (i) and DMSO (ii).

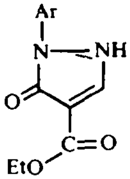
and compound 2 in $CHCl_3$ and DMSO solutions examined in the 1800–1400 cm^{-1} region. The existence of the CH form of 1-phenyl-3-methyl-2-pyrazolin-5-one in chloroform is well established.[1, 5, 6] Similar results were obtained for compound 2 after assignments of the very strong band found at 1535 cm^{-1} to the $C—NO_2$ asymmetric stretching vibration. The effect of the electron-attracting *o*-nitrophenyl ring raises the CO frequency of the pyrazolone ring to 1735 cm^{-1} in chloroform. Some additional weak bands were observed near 1600 cm^{-1} together with a weak broad absorption near 3000 cm^{-1} corresponding to the presence of a very small amount of another tautomer.

In DMSO the pattern of absorption bands obtained from compound 2 is in good agreement with that obtained from compound 1 if the additional $\nu C—NO_2$ is taken into account. However the results obtained from 1-phenyl-3-methyl-2-pyrazolin-5-one in DMSO indicate the presence of substantial amounts of CH and OH forms because the spectral pattern is similar to that obtained from compounds 1 and 2, and in addition a strong CO absorption is found at 1710 cm^{-1}. A value of 74% ± 5% OH form in DMSO for this compound has been reported.[12] The IR absorption frequencies of these compounds are reported in Table 3.

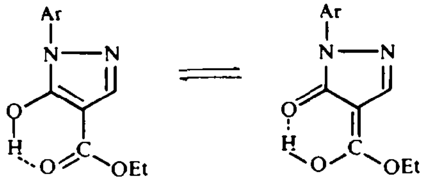
The tautomeric possibilities existing in the case of compounds 3 and 4 are interesting:



CH
IV



NH
V



OH
VIa

VIb

The IR spectra of compounds 3 and 4 in $CHCl_3$ and DMSO are shown in Fig. 3. For compound 3 in $CHCl_3$ solution, a broad band is observed with a max near 3210 cm^{-1} and is assigned to a H-bonded NH or OH group. This band shifted in the expected ratio (1·36) after deuteration whereas no other significant shifts in the spectrum were observed. Two CO frequencies were observed at 1730 cm^{-1} and 1669 cm^{-1}. The spectrum obtained in the region 1600–1500 cm^{-1} is very simple comprising three main bands, two attributable to Ph ring vibrations (1610, 1504 cm^{-1}) and a strong absorption at 1580 cm^{-1}. This evidence, together with the NMR data, indicates that the NH tautomer is present in $CHCl_3$ solution. A similar IR spectrum was obtained in CCl_4 except for sharper bands and some frequency shifts due to the absence of any H-bonding in this solvent. In the NH form both the ring and ester CO groups are α,β-unsaturated. The higher of the two frequencies is the ester CO, which is not greatly affected by α,β-unsaturation, whilst the strong band is due to the ring CO. The difference in intensities may be due to the fact that the ring CO group is *s-trans* to the C═C whereas the ester CO group is in the *s-cis* configuration. Furthermore both CO groups are α,β to a double bond and a heteroatom, and this is known to produce unusually intense νC═C bands compared with νC═O bands.[13] Thus the band at 1582 cm^{-1} is assigned to νC═C of the pyrazolone ring. Similar results were obtained for compound 4.

In DMSO (Fig. 3) only one CO absorption was observed in the spectra obtained from compounds 3 and 4. The band shapes in the region 1600–1500 cm^{-1} are similar

TABLE 3. IR ABSORPTION FREQUENCIES OF 1-ARYL-2-PYRAZOLIN-5-ONES IN $CHCl_3$ AND DMSO

Compound	νOH	Assignment[1] region 1800–1500 cm^{-1}					Solvent	Comments	Tautomer
		ν C=O	ν C=N	Phenyl	Phenyl	Phenyl			
5†		1706 1710 1706 s	1616 ~1622* 1620 w	1597 1600 1596 m	1566 — —	1502 1500 1499 m	$CHCl_3$ $CHCl_3$ $CHCl_3$	Ref. 1 Ref. 6 This work	CH CH CH
2	~3000 vw	1735 s	1609 m	1590 w 1580 w	1567 w 1535 vs‡	1492 m	$CHCl_3$	—	CH + small amount OH or NH
1		1720 1707 } d, s		1595 ms		1498 m	$CHCl_3$	Weak solution, 1·0 mm cell	CH
	~2700 w, b	1720 1707 } d, s		1595 s	1558 ms 1529 ms	1498 s	$CHCl_3$	0·1 mm cell	CH + OH
	N.I.	1710 vw		1597 1587 } d, s	1558 1551 } d, s 1522 ms	1494 ms	DMSO		OH
2	N.I.		1607 m	1586 m	1563 m 1532 vs‡	1494 m	DMSO	—	OH
5†	N.I.	1710 s		1596 1590 } d, s	1562 s 1525 m	1497 s	DMSO	—	OH

Notes: [1] Normal CH vibrations in region 3150–2800 cm^{-1} not reported.

[2] Normal overtone and combination bands associated with phenyl substitution not reported (2000–1800 cm^{-1}).

[3] Intensities, v—very strong, s—strong, m—medium, w—weak, b—broad, d—doublet, sh—shoulder.

[4] N.I.—region not investigated.

* Value not reported in Reference 6 but clearly present and estimated from their published spectrum.

† 1-Phenyl-3-methyl-2-pyrazolin-5-one.

‡ ν_{asym} C—NO_2.

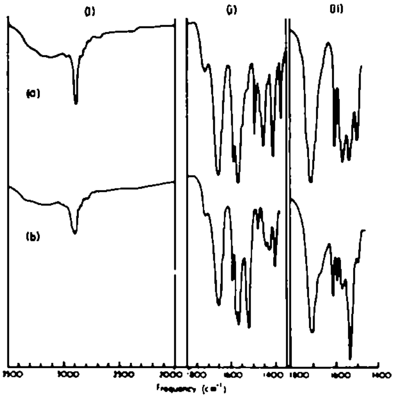


FIG. 3 IR spectra of compounds 3 and 4 in $CHCl_3$ (i) and DMSO (ii).

to those observed for compounds 1 and 2 in DMSO. The intense CO absorption is assigned to the ester CO group and the compounds are present in the OH form. There is no evidence of chelation, i.e. intramolecular H-bonding, probably because the OH group is H-bonded to the solvent. If the ester group was enolised the pyrazolone ring CO group would be found at lower frequencies (ca. 1670 cm^{-1}). There is some evidence in the spectrum of compound 4 to suggest that other forms may also be present.

Tautomerism in the solid state. Fig. 4 illustrates the spectra obtained from compounds 1–4 together with 1-phenyl-3-methyl-2-pyrazolin-5-one. The latter compound and compounds 1 and 2 have two broad absorptions near 2500 cm^{-1} and 1800 cm^{-1} whilst a CO band is absent. This suggests that the OH form is present. Furthermore the pattern of the spectra is reasonably consistent with that observed in DMSO. Katritzky and Maine[1] have suggested that strong H-bonding occurs in the solid

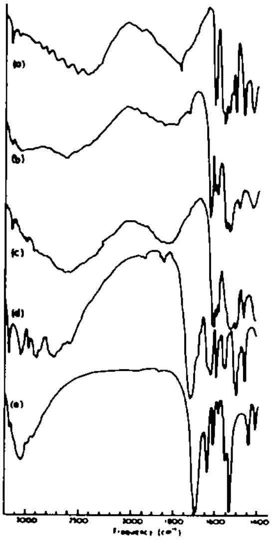
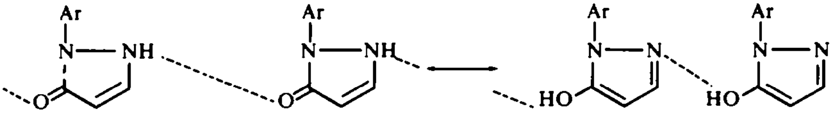


FIG. 4 IR spectra of compounds 1–4 (a, b, d, e) and 1-phenyl-3-methyl-2-pyrazolin-5-one (c) in the solid state.

state which together with proton transfer renders the intermolecularly H-bonded OH and NH forms indistinguishable (VIIa and b).



VIIa VIIb

In certain compounds containing NH and OH groups Bellamy and Rogasch,[14] have assigned the broad band found in the 3000–2500 cm^{-1} region as due to co-operative proton transfer. The multiplicity of this band may be due to Fermi resonance of the OH or NH absorptions, with overtone and combination bands from lower frequency fundamentals,[14] although various other possibilities have been proposed.[15] On deuteration of this band the ratio of frequencies νNH/νND was frequently less than the theoretical value (1·4). In some compounds a second band observed by Tarte[16] near 1900 cm^{-1} was assigned either to overtones of bands absorbing near 1000 cm^{-1} or to δOH shifted to higher frequencies because of very strong H-bonding. Neither of these possibilities is satisfactory and at present the origin of these bands remains obscure.[17]

We have therefore assigned the broad band found in the region 3000–2500 cm^{-1} to OH...N type H-bonding since the spectra observed are consistent with the OH tautomer, but the possibility exists that proton transfer could occur.

The spectra obtained from compounds 3 and 4 do not contain a broad absorption in the 2000–1750 cm^{-1} region. The H-bonding is very strong in compound 3, but is less strong in compound 4 as evidenced by the higher frequency of the broad absorptions (near 3000 cm^{-1}). This may be due to electron withdrawal from the pyrazolone ring by the *o*-nitrophenyl substituent. When compound 3 was deuterated a frequency shift of about 1·30–1·26 was observed in the solid state whereas when measured in CCl_4 (NH form) a value of 1·36 was obtained.

Only one CO absorption is obvious (~1700 cm^{-1}) and the spectra are different from those obtained in $CHCl_3$ indicating that the NH form is not present. The spectra of these compounds examined in DMSO were assigned to the OH form and the only difference observed in the solid state in the 1750–1500 cm^{-1} region is one additional band found at 1620 cm^{-1} (compound 3) and 1637 cm^{-1} (compound 4). This could be due to an intramolecularly H-bonded keto group forming a conjugate chelate system. A possible structure which would fit the spectroscopic evidence is the tautomeric equilibrium VIa ⇌ VIb.

The absorption frequencies of these compounds in various media are listed in Table 4.

DISCUSSION

From previous work[1] it might be anticipated that the pyrazolones studied would exist as the CH form in non-polar solvents. The NMR (Table 1) and IR (Table 3) results confirm that this is so only in the case of compounds 1 and 2; compounds 3 and 4, which both have a 4-ethoxycarbonyl substituent, exist predominantly in the NH form. Compound 1 changes over to the OH form in chloroform solution if its con-

TABLE 4. IR ABSORPTION FREQUENCIES OF 1-ARYL-2-PYRAZOLIN-5-ONES

Compound	ν_{OH} or ν_{NH} 3500–2000 cm^{-1}	Region 2000–1750 cm^{-1}	Region 1750–1500 cm^{-1}										Comments
1	~2500 m, b	~1770 m, b					1601 1592 ms, d	1565 sh	1557 s	1537 sh	1517 sh	1500 ms	Solid
2	~2600 m, b	~1840 m, b					1616 ms	1595 m	1583 m	1540 s‡	1526 s		Solid
3	~3230 mw, b	—	1730 m, sh		1669 vs		1600 s		1580 vs	1540 sh	1504 m		CHCl$_3$
	N.I.	N.I.		1700 vs			1596 m		1560 s	1531 s	1494 m		DMSO
	~2900 m, b	~1740 m, b	1720 vs		1622 m		1599 m		1560 m, b	1510 sh	1502 s		Solid
4	~3250 w, b	—	1732 m, sh		1670 s		1610 m	1590 1581 s, d		1536 s‡		1497 mw	CHCl$_3$
	N.I.	N.I.		1700 s, b			1607 m	1586 mw		1563 m	1532 vs‡	1494 mw	DMSO
	3040 s, b	—		1692 vs		1637 ms	1609 m	1583 mw		1550 ms	1530 vs‡		Solid
5†	~2500 m, b	~1760 m, b					1606 s	1590 sh		1581 sh	1525 s	1499 m	Solid*

Notes: (1)–(4) apply, see Table 3.

* good agreement with Ref. 1.

† 1-phenyl-3-methyl-2-pyrazolin-5-one

‡ ν_{asym} C—NO$_2$.

centration is raised much above 5%; compound **2** is not sufficiently soluble to be examined in this way.

It is reasonable to expect that the CH forms of compounds **3** and **4** would be less energetically favourable than either of the other tautomers, since in both these cases the ester CO group would be conjugated with the heterocyclic ring. The preference of the NH rather than the OH form is less readily understood, since it would be expected that the OH tautomer could form a stable intramolecular H-bond (VI). The OH form usually predominates under such conditions,[1, 18] although in the case of 1-phenyl-4-phenylazopyrazolin-5-ones in chloroform solution the 4-phenylhydrazone structure occurs and this forms a chelate with the CO group.[19, 20] If a species such as VI was present in solution it would be expected that a low field NMR signal would be observed[21] for the enolic proton; careful examination of the spectra of compounds **3** and **4** failed to reveal the presence of such a signal.

It has previously been reported[1] that 4-substituted pyrazolones undergo changes in chloroform solution. freshly prepared solutions containing about 50% of the NH form which over a period of several days reverts to give 100% CH form. No such equilibration has been observed for compounds **3** and **4**, the IR and NMR spectra of which remain unchanged for periods of more than a week. Compounds **1** and **2**, which more readily undergo tautomeric changes, are also quite stable in solution and the occurrence of the small ring coupling constants in their NMR spectra, which are comparable[22-24] with those found in pyrazoles, is an indication that rapid exchange in solution does not take place. The sole exception to this behaviour occurs with concentrated (10%) solutions of compound **1** in deuterochloroform, when a poorly resolved NMR spectrum results due to chemical exchange and, on the basis of IR data, the OH tautomer is present in addition to the CH form.

A summary of the conclusions reached in this study is presented in Table 5.

TABLE 5. TAUTOMERIC FORMS OF SOME 1-ARYL-2-PYRAZOLIN-5-ONES

Compound	Ar	R	$CHCl_3$	DMSO	Solid
1	C_6H_5	H	CH (+ OH > 5% solns)	OH	OH/NH
2	o-$C_6H_4 . NO_2$	H	CH (+ small amount NH or OH)	OH	OH/NH
3	C_6H_5	CO_2Et	NH	OH	OH tautomeric equilibrium
4	o-$C_6H_4 . NO_2$	CO_2Et	NH	OH (+ other form?)	OH tautomeric equilibrium
5*	C_6H_5	H	CH	OH + CH	OH/NH

* 1-Phenyl-3-methyl-2-pyrazolin-5-one.

EXPERIMENTAL

NMR spectra were determined for 2–5% solns at 100 MHz using a Varian HA-100 spectrometer, and IR spectra were recorded on a Perkin-Elmer 257 instrument. Solid state IR spectra were determined as dispersions in mineral oil and in hexachlorobutadiene. Similar results were obtained from samples pressed in KBr.

4-Ethoxycarbonyl-1-phenyl-2-pyrazolin-5-one and 1-phenyl-2-pyrazolin-5-one were prepared from 1,1,3,3-tetraethoxycarbonylpropene[25] and phenylhydrazine according to the procedure of Ruhemann and Morrell.[26] 4-Ethoxy-carbonyl-2-(2′-nitrophenyl)-2-pyrazolin-5-one was prepared by condensation of ethyl methoxymethylene malonate[27] and *o*-nitrophenylhydrazine followed by ring closure using NaOMe. 1-(2′-Nitrophenyl)-2-pyrazolin-5-one was prepared from the 4-ethoxycarbonyl derivative by hydrolysis and decarboxylation.

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