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TAUTOMERISM OF 4-HYDROXYPYRAZOLES AND 4-HYDROXYISOXAZOLES—I

SPECTROSCOPIC EVIDENCE

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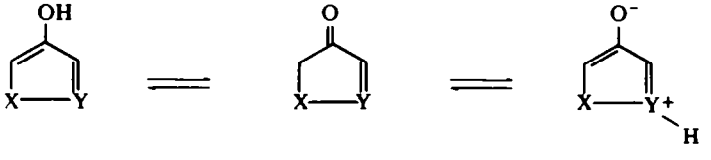
Abstract—4-Hydroxy-3,5-diphenylpyrazole, 4-hydroxy-1-methyl-3,5-diphenylpyrazole and 4-hydroxy-3,5-diphenylisoxazole have been shown to exist as enolic tautomers. UV, IR, and PMR data of these compounds and several related compounds are presented.

INTRODUCTION

A GOOD understanding of the factors affecting tautomeric equilibria of heterocyclic systems is of vital importance in the study of living processes, since potentially tautomeric heterocycles are known to occur abundantly in nature. Yet at present, predictions of relative stabilities of heterocyclic tautomers are very unreliable. One reason for this is that reliable data on equilibria have only started really accumulating since the advent of quantitative spectroscopic techniques. Before that time, conclusions were based on chemical proof which was generally invalid, since fast tautomerization could not be completely discounted. One area in which spectroscopic data are noticeably[1] absent is the group of five-membered heterocyclic aromatic systems which have a potential keto group flanked by a carbon atom on each side. As a result of this particular structural type being neglected, the published data present a somewhat unbalanced picture possibly leading to misleading generalizations. The enol and keto tautomers of the type in question are represented by the general formulae I and II. If we allow X and Y to be first period elements of the periodic table only, then we find that the possibilities are virtually limited to four, namely

FIG A



	X	Y
a	NH	CH
b	O	CH
c	NH	N
d	O	N

I (a, b, c and d) II (a, b, c and d) III (c and d)

3-hydroxypyrrole (Ia), 3-hydroxyfuran (Ib), 4-hydroxypyrazole (Ic) and 4-hydroxyisoxazole (Id). Each of these systems is much less accessible synthetically than the position isomers with the potential keto group flanked by a heteroatom, and has consequently not been studied at all extensively. For example it is well-known[1] that

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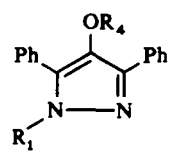
the amount of information published on 3- and 5-hydroxypyrazoles (pyrazolones) is vast, whereas 4-hydroxypyrazoles have been almost overlooked. Concerning the tautomeric behaviour of the latter system, chemical evidence[2,3] and a little spectroscopic evidence[4,5] indicate the enol structure, but not conclusively.

The purpose of the work presented in this paper is to help fill this particular gap. New results are also reported on the similarly substituted isoxazoles. Spectroscopic evidence favouring the enolic structure for the latter system is however available from the work of Cabiddu and Ricca[6] and Desimoni, Grünanger and Servi.[7,*] A further point of interest connected with the 4-hydroxypyrazole and 4-hydroxyisoxazole systems is the fact that they are potentially capable of existing as zwitterionic tautomers (IIIc and IIId), whereas Ia and Ib are not.

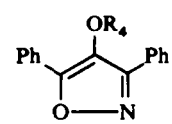
RESULTS AND DISCUSSION

The tautomeric structures of representatives (IV and V) of the title systems were deduced largely by the usual method of comparing the spectra of the potentially tautomeric compound with those of model compounds of fixed structure.

FIG B



IV

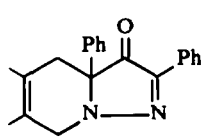


V

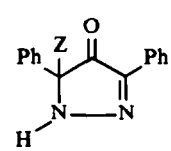
	R_1	R_4
a	H	H
b	H	Me
c	H	COMe
d	Me	H
e	Me	Me
f	Me	COMe

In the pyrazole series, model compounds having the keto structure are available. VI,[8] VIIa,[9] and VIIb[10] were chosen for comparison, since they bear Ph groups in appropriate positions, and their spectra are self consistent. Model enolic and zwitterionic pyrazoles were prepared by methylation of 4-hydroxy-1-methyl-3,5-diphenylpyrazole (IVd) to give the O-methylated product, IVe, under alkaline conditions

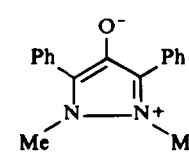
FIG C



VI



VII



VIII

	Z
a	Me
b	OH

and the N_2-methylated product VIII under neutral conditions. O-methylation is expected with alkali since an anion bearing a high concentration of negative charge on the oxygen atom is the reacting species. The structures of IVe and VIII are assigned unambiguously since in the PMR spectra, the former shows two Me peaks and the

* We thank Dr A. R. Katritzky, School of Chemical Sciences, University of East Anglia, Norwich, England, for sending us a preprint of the paper "The tautomerism of heteroaromatic compounds with five-membered rings XI, 4-hydroxy-isoxazoles-4-isoxazolones", G. Bianchi, M. J. Cook and A. R. Katritzky, to be published in Tetrahedron, in which more substantial spectroscopic evidence is presented favouring the enolic structure.

latter only one peak. Enolic models IVb, IVc, IVe and IVf were also prepared and their structures assigned with confidence based on their spectra and methods of preparation.

In the isoxazole series, zwitterionic and ketonic models are not available with appropriately placed Ph groups. Attempts* were made to prepare a zwitterionic model analogous to those which were used to prepare VIII, namely from 4-hydroxy-3,5-diphenylisoxazole and dimethylsulfate, and from 2-acetoxy-1,3-diphenyl-1,3-propanedione and N-methylhydroxylamine hydrochloride, but they were not successful. Two model enolic structures were prepared[11] by methylation and acetylation of 4-hydroxy-3,5-diphenylisoxazole Va to give Vb and Vc. These structures, rather than zwitterionic structures were assigned partly on the grounds that their UV spectra lacked a long-wavelength band in the same region as the anion band (360 nm), expected for the zwitterion by analogy to the pyrazole analogue. Other evidence was the fact that the methylation of Va was carried out under alkaline conditions which should lead to preferential attack at the C_4 oxygen.

The ketonic models in the pyrazole series show normal carbonyl bands in the IR, exemplified by VI, which absorbs at 1680 cm^{-1} (nujol), and there is no reason to believe that the analogous isoxazolones should not absorb at similar wavenumbers. The spectra of IVa, IVd and Va exhibit no carbonyl bands either in solution or in the solid state, and hence the keto structure is discredited. Instead, the enolic structure is indicated by the observance of free OH bands in dilute (0·03 M) $CHCl_3$ solutions of the pyrazole IVd (3576 cm^{-1}) and the isoxazole Va (3564 cm^{-1}).† Both free (3456 cm^{-1}) and bonded (3232 cm^{-1}) NH bands were observed for the fixed enol IVb. IVa was not sufficiently soluble in non-hydrogen bonding solvents to be studied.

The UV spectra (Table 1) provide the strongest evidence for the enolic structure. In the pyrazole series the spectra of the neutral tautomeric compounds IVa and IVd closely resemble those of the fixed enolic species IVb, c, e and f rather than the ketonic models‡ or the zwitterion VIII, which all show conspicuous long wavelength bands. All the spectra of pyrazoles in Table 1 are completely self-consistent if we use the peak interpretation given in Table 2. In the isoxazole series the UV spectrum of the tautomeric compound Va resembles that of the enolic model Vb, and to a lesser extent Vc, and does not show a long wavelength band expected for the zwitterion, hence indicating the enolic structure also. Va is noticeably ionized in 95% EtOH solutions corresponding to an apparent pK_a of 8·3,§ but the spectrum of the unionized compound may be obtained in acidified solutions (see Table 1).

The PMR spectra (Table 3) are also in agreement with enolic structures. Notably, the CH ring proton of the keto structures is not observed in IVa, IVd or Va. Also IVa shows two exchangeable protons at 8·40 ppm and *ca.* 7·50 ppm, clearly incompatible with the zwitterionic structure. The OH protons in all three compounds (IVa, IVd

* We thank Dr M. J. O'Hare for this work.

† The small difference in the free OH stretching band may be attributed to a decrease in electron density when the NMe of IVd is replaced by the more electronegative O. The absorption band of 1-acetyl-4-hydroxy-3,5-diphenylpyrazole (3556 cm^{-1}) supports the theory.

‡ VI, λ_{max} (95% EtOH), 270 (ε 17,200), 392 (8200) nm.[8] VIIa λ_{max} (EtOH), 264 (ε 12,600), 382 (4700) nm.[9] VIIb λ_{max} (95% EtOH), 254 (ε 19,100), 370 (3210) nm.[10].

§ This value is only approximate since trace impurities could greatly modify it.

and Va) are hidden under the aromatic multiplet, but they may be shifted out and integrated by using a water-miscible solvent and adding a little D_2O. The NH peaks in IVa, IVb and IVc occur at lower field, and the chemical shift is highly solvent

TABLE 1. UV DATA[a]

Compound No.	Substituent		λ_{max} nm (ε)		
	R_1	R_4	Neutral	Acidic[b]	Basic[c]
IVa	H	H	252 (22700) 276 (sh) (17100) 295 (sh) (10000)	225 (18800)[d] 290 (19200)	257 (19700) 358 (14300)
IVb	H	Me	255 (28100) 291 (sh) (6000)	229 (18600)[d] 278 (20700) 291 (sh) (17800)	—
IVc	H	COMe	251 (29900)	[e]	—
IVd	Me	H	245 (21500) 276 (sh) (15200) 290 (sh) (10600)	223 (sh) (17900) 288 (16700)	251 (18700) 344 (13100)
IVe	Me	Me	251 (24100)	227 (sh) (14230)[d] 278 (18340)	—
IVf	Me	COMe	247 (27800)	[e]	—
VIII	—	—	226 (14200) 248 (sh) (6740) 356 (11400)	220 (13200) 283 (14100)	226 (14700) 248 (sh) (6850) 356 (11600)
Va	H	H	223 (sh) (20400) 240 (sh) (13800) 283 (sh) (15600) 288 (14400) 296 (14900) 360 (4430)	[f]	226 (21500) 286 (5300) 360 (15800)
Va	H	H	219 (20200)[g] 240 (sh) (13800) 283 (sh) (18200) 288 (18800) 296 (sh) (17800)	[f]	—
Vb	H	Me	220 (sh) (18700) 237 (16500) 275 (22100) 280 (22500) 287 (sh) (19000) 293 (sh) (15200)	[e]	—

TABLE 1—*continued*

Compound No.	Substituent		λ_{max} nm (ε)		
	R_1	R_4	Neutral	Acidic[b]	Basic[c]
Vc	H	COMe	218 (sh) (17700) 237 (16700) 269 (23200)	[e]	——

sh Shoulder

[a] Determined on a Unicam SP 800 spectrophotomer in 95% EtOH at 25°.

[b] 95% EtOH—0·2N HCl.

[c] 95% EtOH—0·1 N NaOH.

[d] 20% EtOH—2N HCl.

[e] 95% EtOH—0·5N HCl. (There was almost no change in spectrum compared with neutral solution).

[f] In 95% EtOH—0·2N HCl: the spectrum is identical with the one run in 95% EtOH—0·02N HCl.

[g] In 95% EtOH—0·2N HCl. The spectrum is that of the neutral species.

TABLE 2. INTERPRETATION OF THE UV DATA OF THE 4-HYDROXYPYRAZOLES GIVEN IN TABLE 1

Neutral	Zwitterion	Cation	Anion
245–255 nm (ε 21,500–29,900)	226 nm (ε 14,700) 356 nm (ε 11,600)	220–229 nm (ε 13,200–18,800) 278–290 nm (ε 14,100–20,700)	251–257 nm (ε 18,700–19,700) 344–358 nm (ε 13,100–14,300)

TABLE 3. PMR DATA[a]

Cpd No.	Solvent	R_1		R_4		Aromatic
IVa	$CD_3SO_2CD_3$	H	8·40 (br)	H	*ca.* 7·50[b]	7·32–7·67 (6H); 7·94–8·11 (4H)
IVb	$CDCl_3$	H	10·87 (br)	Me	3·63	7·28–7·53 (6H); 7·83–8·00 (4H)
IVc	$CDCl_3$	H	10·68 (br)	COMe	2·26	7·30–7·50 (6H); 7·60–7·77 (4H)
IVd	$CDCl_3$	Me	3·80	H	*ca.* 7·50[b]	7·35–7·62 (8H); 7·98–8·14 (2H)
	CD_3COCD_3	Me	3·73	H	*ca.* 7·45[b]	7·30–7·60 (8H); 8·03–8·20 (2H)
IVe	$CDCl_3$	Me	3·83	Me	3·55	7·33–7·68 (8H); 8·02–8·18 (2H)
IVf	$CDCl_3$	Me	8·38	COMe	2·13	7·30–7·55 (6H); 7·75–7·92 (4H)
VIII	$CDCl_3$	Me	3·78[c]	--	--	7·30–7·53 (6H); 7·67–7·83 (4H)
Va	CD_3COCD_3	--	--	H	*ca.* 7·62[b]	7·50–7·84 (6H); 8·05–8·22 (4H)
Vb	$CDCl_3$	--	--	Me	3·78	7·47–7·72 (6H); 8·03–8·21 (4H)
Vc	$CDCl_3$	--	—	COMe	2·32	7·43–7·68 (6H); 7·77–7·93 (4H)

br Broad

[a] Ppm values relative to TMS internal standard were recorded on a Varian A60A spectrometer.

[b] The OH signal appears in the aromatic absorption region. The value indicated gives the mean value of that particular aromatic multiplet.

[c] Singlet for N-1 and N-2 methyls

dependent as usual for pyrazoles.† Surprisingly the chemical shifts of the O- and N-Me protons could not be used to distinguish them, since the peaks appeared close together and were unpredictable. Particularly unexpected was the finding that the N-Me peaks of both the neutral compound IVe and its zwitterionic isomer VIII had very similar chemical shifts (3·83 and 3·78 ppm respectively), in spite of there being a difference in formal electronic charge on the nitrogen.

CONCLUSIONS

In conclusion, IR, UV and PMR spectra of 4-hydroxy-3,5-diphenylpyrazole (IVa), 4-hydroxy-1-methyl-3,5-diphenylpyrazole (IVd) and 4-hydroxy-3,5-diphenylisoxazole (Va) provide strong evidence for their existence as enolic forms both in solution and the solid state. An overall picture of the keto-enol tautomerism of hydroxylated five-membered heteroaromatic systems is slowly emerging. For the case where the keto form is a lactone or lactam, it is generally the more stable tautomer, whereas in the less usual case, studied in this work, where the keto form is a ketone, the enol is the more stable. It is seen that there is a delicate balance between the stabilizing effects present in the acyclic conjugation of the keto tautomer on the one hand, against the aromatic-type stabilizing effects in the enol on the other hand. The observed reversal of the equilibrium with structural change can be crudely rationalized as arising from the inherently high stabilities of esters and amides, and hence lactones and lactams. Looking to the future, it is hoped that numerical values for keto-enol equilibria of representative heterocycles will be determined, and that they will be correlated with theoretical or semi-empirical energy calculations.

EXPERIMENTAL

M.ps were determined on a Meltemp apparatus and are uncorrected. IR spectra were obtained on a Beckman IR 5A spectrophotometer, or on a Beckman IR 12 spectrophotometer when marked with an asterisk (*).

4-Hydroxy-3,5-diphenylpyrazole (IVa)[10]: m.p. 235–237°, IR (0·03 M dioxan) OH and NH ν_{max} 3285, 3115 cm^{-1}.

4-Methoxy-3,5-diphenylpyrazole (IVb). A solution of 1·18 g (5 mmoles) of IIIa in 60 ml of 10% NaOH (heated to 60° to dissolve, and diluted to a volume of 90 ml with water) was shaken vigorously with 2·5 ml of dimethyl sulfate. The solids that separated were filtered. The filtrate was again treated with 2·5 ml of dimethyl sulfate and a second crop of solid isolated. The combined crude products were washed well with H_2O and dried: m.p. 136–150°, 1·03 g. Recrystallization from C_6H_6-petroleum ether (60–80°) mixture gave crystals: m.p. 160·5–162·5°; 0·76 g (60·8%). IR (nujol): ν_{max} 3206, 1601, 1268, 1144, 985, 956, 727, 689 cm^{-1}; (0·03 M $CHCl_3$)* OH ν_{max} 3456, *ca.* 3232 cm^{-1}. (Calc. for $C_{16}H_{14}N_2O$: C, 76·78; H, 5·64; N, 11·19. Found: C, 77·05; H, 5·48; N, 11·10%).

A small amount of the N,O-methyl derivative (IVe) was also isolated: m.p. 88·5–89·5° (see below).

4-Acetoxy-3,5-diphenylpyrazole (IVc). A solution of 0·25 g (5 mmoles) of 99–100% hydrazine hydrate in 1 ml of AcOH was added to a solution of 1·13 g (4 mmoles) of 2-acetoxy-1,3-diphenyl-1, 3-propanedione[13] in 6 ml of AcOH under stirring at room temperature. After addition of the hydrazine solution, stirring was continued for 40 min. H_2O (4 ml) was then added resulting in precipitation. The crude product melted at 162–168°: 1·05 g. Recrystallization from benzene-petroleum ether (b.p. 60–80°) mixture afforded 0·94 g

† In the PMR spectra of 3,5-diphenylpyrazole we have observed the NH to appear at 8·65 ppm in $CDCl_3$, and at 12·57 ppm in acetone-d_6. Finar and Mooney[12] discuss the NH peak in the PMR spectra of pyrazoles

(85%) of long needles: m.p. 178–180°. IR (nujol): ν_{max} 3226, 1782 (shoulder), 1762, 1613, 1205 (shoulder), 1195, 1182 (shoulder), 1146, 956, 689 cm^{-1}. (Calc. for $C_{17}H_{14}N_2O_2$: C, 73·36: H, 5·07: N, 10·07. Found: C, 73·17: H, 5·10: N, 10·04%).

4-*Hydroxy*-1-*methyl*-3,5-*diphenylpyrazole* (IVd). The method was according to the preparation of 4-hydroxy-3,5-diphenylpyrazole (IVa)[10] with slight modification.

Methylhydrazine (0·6 ml, *ca.* 10 mmoles) was added dropwise to a warm solution of 2·26 g (8 mmoles) of the 2-acetoxy-1,3-diphenyl-1,3-propanedione in 20 ml of 95% EtOH. The mixture was refluxed for 0·5 hr and then H_2O added to produce a hot saturated solution. On cooling, needles separated: m.p. 175–177°: 1·84 g (92%). The product recrystallized from EtOH gave the same melting range. IR (nujol): ν_{max} 3175 (shoulder), 1604, 1262, 1157, 921, 856, 760, 697 cm^{-1}: (0·03 M $CHCl_3$)* OH ν_{max} 3576 cm^{-1}: (0·03 M dioxane)* OH ν_{max} 3302 cm^{-1}. (Calc. for $C_{16}H_{14}N_2O$: C, 76·78: H, 5·64: N, 11·19. Found: C, 76·80: H, 5·42: N, 11·14%).

4-*Methoxy*-1-*methyl*-3,5-*diphenylpyrazole* (IVe). As for IVb above, treatment of a solution of 1 g (4 mmoles) of IVd in 50 ml of 10% NaOH solution diluted to a volume of 90 ml with H_2O, with 4 ml of dimethyl sulfate yielded the desired product (IVe): m.p. 88·5–89·5° (C_6H_6-petroleum ether, 40–60°); 0·76 g (72%). IR (nujol): ν_{max} 1596, 1310, 1267, 1054, 780, 766, 733, 695 cm^{-1}. (Calc. for $C_{17}H_{16}N_2O$: C, 77·25; H, 6·10; N, 10·60. Found: C, 77·37: H, 6·13: N, 10·76%).

4-*Acetoxy*-1-*methyl*-3,5-*diphenylpyrazole* (IVf). A mixture of 0·5 g (2 mmoles) of IVd and 2·5 ml of Ac_2O was heated in an oil bath (100°) to form a solution and heated for a further 15–20 min. The cooled mixture was then added to 30 ml of ice-cold H_2O. Yield of the dried, crude product, m.p. 101–106°, was almost quantitative. Recrystallization from C_6H_6-petroleum ether (b.p. 60–80°) mixture afforded crystals: m.p. 109–111°: 0·525 g (89·9%). IR (nujol): ν_{max} 1799 (shoulder), 1759, 1604, 1317, 1212, 1169, 1053, 899, 774, 761, 702, 683 cm^{-1}. (Calc. for $C_{18}H_{16}N_2O_2$: C, 73·98, H, 5·52, N, 9·59. Found: C, 74·23: H, 5·61: N, 9·57%).

Anhydro-4-*hydroxy*-1,2-*dimethyl*-3,5-*diphenylpyrazolium hydroxide* (VIII).

A. A mixture of 1 g (4 mmoles) of 4-hydroxy-1-methyl-3,5-diphenylpyrazole (IVd) and 3·8 ml (40 mmoles) of dimethyl sulfate was heated in an oil-bath (100–130°) until dissolution and then for another 10 min. After cooling, 40 ml of absolute ether was added and the mixture was well stirred to cause crystallization. The crystals were filtered, washed three times with absolute ether: m.p. 212–252° (dec.): 1·48 g. This product was the methosulfate salt of VIII. Recrystallization from acetone-H_2O mixture raised the m.p. to 244–252° (dec.): 1·35 g (90%).

The methosulfate salt (1·35 g) was dissolved in minimum amounts of H_2O and the solution was made alkaline to phenolphthalein with 10% NaOH solution. It was then extracted with 25 portions of 15 ml of $CHCl_3$ and the solvent of the extracts was evaporated to give yellow crystals; m.p. 195–198° (dec.): 0·92 g. Recrystallization from $CHCl_3$-petroleum ether (b.p. 60–80°) mixture gave 0·86 g (90·5%) of the anhydro-4-hydroxypyrazolium hydroxide (VIII): m.p. 201–203° (dec.). The extraction process was more conveniently replaced by anion exchange of the methanolic solution of the methosulfate (over Amberlite IR 45, Fisher Scientific Co.). The product is soluble in H_2O, MeOH, EtOH and $CHCl_3$, but only very slightly soluble in other organic solvents. IR (KBr): ν_{max} 3054, 1598, 1446, 1381, 1353, 1178, 1168, 1154, 1120, 1051, 762, 749, 729, 703 cm^{-1}. (Calc. for $C_{17}H_{16}N_2O$: C, 77·25: H, 6·10: N, 10·60. Found: C, 76·64: H, 5·98: N, 10·74%).

B. A mixture of a solution of 0·564 g (2 mmoles) of 2-acetoxy-1,3-diphenyl-1,3-propanedione[13] in 8 ml of MeOH and a solution of 0·345 g (2·6 mmoles) of $CH_3NHNHCH_3 \cdot 2HCl$ in 2 ml of H_2O was refluxed for 2 hr. The solvent (MeOH) was evaporated at reduced pressure and then 3 ml of H_2O added. The mixture was chilled in an ice-bath and filtered. The aqueous filtrate was made alkaline to phenolphthalein with NaOH solution and worked up as in (A). The product (VIII) was identical with the one obtained in (A): 0·222 g (42%): m.p. 201–203° (dec.).

4-*Hydroxyisoxazoles*. 4-Hydroxy-3,5-diphenylisoxazole (Va), 4-methoxy-3,5-diphenylisoxazole (Vb) and 4-acetoxy-3,5-diphenylisoxazole (Vc) were prepared according to Blatt and Hawkins.[11]

4-*Hydroxy*-3,5-*diphenylisoxazole* (Va): m.p. 120–122° (dec.) (lit. m.p. 122–123°;[11] 105°,[6]) ‡ This compound was found to be unstable towards air and light as reported,[11] but the substance could be stored relatively unchanged over prolonged periods in a vacuum desiccator in a refrigerator. IR (nujol): ν_{max} *ca.*3170 (shoulder), 1620, 1245, 1173, 937, 771, 760, 706, 688 cm^{-1}: (0·03 M $CHCl_3$)* OH ν_{max} 3564 cm^{-1}.

‡ Blatt and Hawkins report[11] two forms of Va, mp's 122–123° and 151°, and Cabiddu *et al.*[6] observe two polymorphs with identical IR spectra, m.p.'s 103° and 125°. In our hands the product obtained was in only one form m.p. 120–122°

4-Methoxy-3,5-diphenylisoxazole (Vb): m.p. 67·5–69·5° (lit. m.p. 69–70°[11]). IR (nujol): ν_{max} 1617, 1212, 981, 927, 782, 731, 690 cm^{-1}.

4-Acetoxy-3,5-diphenylisoxazole (Vc): m.p. 97·5–99·5° (lit. m.p. 103°[11]). IR (nujol): ν_{max} 1768, 1737 (shoulder), 1191, 1170, 1153, 933, 877, 760, 701, 694 cm^{-1}.

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