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THE TAUTOMERISM OF HETEROAROMATIC COMPOUNDS WITH 5-MEMBERED RINGS—XI[1]

4-HYDROXYISOXAZOLES-4-ISOXAZOLINONES

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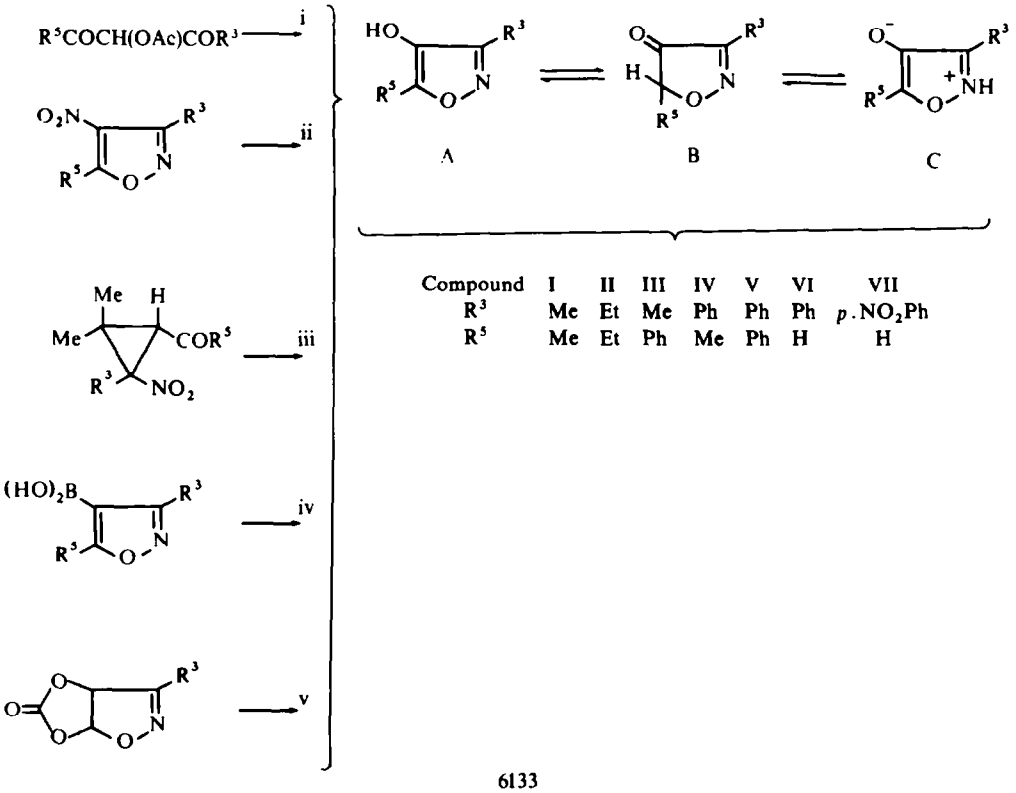
Abstract—Four 4-hydroxyisoxazoles together with model compounds have been investigated by UV. IR and NMR spectroscopy and by pK_a measurements, 4-Hydroxyisoxazoles exist predominantly in the hydroxy-form in a wide range of media.

PREVIOUS papers in this series have concerned the tautomeric behaviour of 3-hydroxy-[2] and 5-hydroxy-isoxazoles.[3,4] Attention is now turned to the corresponding 4-hydroxy compounds, for which there are three possible tautomeric forms: we shall refer to these as the *hydroxy*-(**A**), *oxo*-(**B**), and *betaine* (**C**) forms (Formulae Scheme).

FORMULAE SCHEME



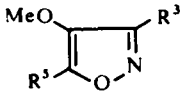
Compound	I	II	III	IV	V	VI	VII
R^3	Me	Et	Me	Ph	Ph	Ph	*p*.NO_2Ph
R^5	Me	Et	Ph	Me	Ph	H	H

4-Hydroxyisoxazoles have previously been prepared[5–12] (Formulae Scheme) by five routes: (i) from 2-acetoxy-1,3-diketones with hydroxylamine; (ii) by reduction and diazotisation of 4-nitroisoxazoles; (iii) by a complex base catalysed rearrangement of nitrocyclopropanes; (iv) by hydrogen peroxide oxidation of isoxazole-4-boronic acids; and (v) by hydrolytic cleavage of 2-oxo-4-aryl-3a, 3b-dihydro[1.3]dioxolo-[4.5-b]isoxazoles. Previous preparative work is summarized in Table 1. together with the previous conclusions concerning the tautomeric structure of these compounds.

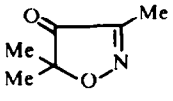
TABLE 1. LITERATURE DATA ON 4-HYDROXYISOXAZOLES

Ref.	Cpd.	M.p.	Route	Conclusions on tautomerism	Derivs.
5	V	123°, 151°	i	OH, chemical evidence-acidic	OMe: OAc
10	IV	115–119	ii	OH, chemical evidence-acidic	OCOPh
6	IV	—	ii	OH + some oxo, IR (solid)	—
	III	77–80	iii	OH + little oxo, IR (solid)	OCOPh
7	I	81–82	iii	—	—
8	I	92–94	i	—	OMe
	II	oil	i	—	OMe
	IV	118–119	i	—	OMe
	V	105, 125	i	—	OTs
9	I	79	iv	—	—
	III	96	iv	—	—
11	V	—	i	OH, polarographic	OCOPh
12	VI	124	v	OH, IR (solid)	OMe: OAc
	VII	171–172	v	OH, IR (solid)	—

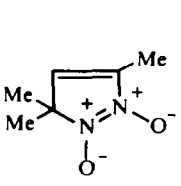
Preparation of compounds. Four 4-hydroxyisoxazoles (I, III, IV, V) were prepared by route (i). From 2-acetoxy-1-phenylbutane-1,3-dione the hydroxyisoxazole IV was obtained as previously[8] described; but reaction with hydroxylamine in acid pH gave, without isolation of any intermediate, the isomer III, previously prepared[9] by route (iv). The m.p.s of some of these compounds vary considerably with the rate of heating, which explains certain discrepancies in Table 1. Three 4-methoxyisoxazoles (VIII–X) were prepared from the corresponding hydroxy-compounds with diazomethane[8] (VIII, IX) or dimethyl sulphate[5] (X).



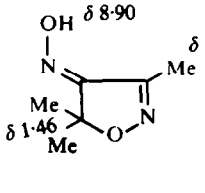
Compound	VIII	IX	X
R^3	Me	Me	Ph
R^5	Me	Ph	Ph



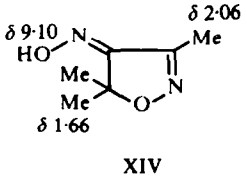
XI



XII

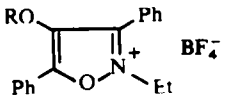


XIII

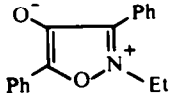


XIV

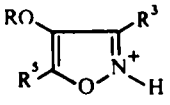
3.5.5-Trimethylisoxazolin-4-one (XI) was previously prepared[13] from its oxime obtained by thermal isomerisation of the 3H-pyrazole-1,2-dioxide (XII). We repeated this preparation successfully but obtained *two* oximes in the ratio 1:9 (by NMR) which we assign to the *syn-anti* isomers (XIII) (oxime, m.p. 114–116°) and (XIV) (oxime, m.p. 156–157°), based on the NMR chemical shifts (for $CDCl_3$ solution) shown in the formulae. Previously only oxime XIV had been isolated.



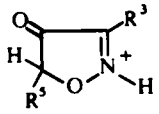
XV R = Ac
XVI R = Me



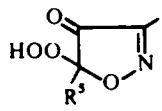
XVII



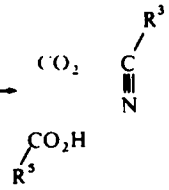
XVIII



XIX



XX



XXI

4-Acetoxy- and 4-methoxy-3,5-diphenylisoxazole were converted into the corresponding 2-ethylisoxazolium fluoroborates (XV, XVI) by triethyloxonium fluoroborate. However, all attempts to convert either of these to the betaine (XVII) to provide a model for tautomer (C) failed, as did attempted preparation of XVII direct from V.

4-Hydroxyisoxazoles are unstable, particularly in dilute solution in non-polar solvents where their rapid decomposition can be followed in the UV spectrum. Benzoic acid was isolated from 4-hydroxy-3-methyl-5-phenylisoxazole: this decomposition could occur by formation of a hydroperoxide of type XX followed by decomposition XX → XXI.

RESULTS AND DISCUSSION

pK_a Values (Table 2) *and UV spectra in aqueous solution* (Table 3). The 4-hydroxyisoxazoles are weak bases, with pK_a values which are each 0·11 to 0·58 H_0 units less negative than the corresponding methoxy compounds. As the potentially tautomeric compounds are slightly *stronger* bases than the models, and as any large proportion of the forms **B** and **C** (of Formulae Scheme) would tend to *reduce* their basicity. this indicates a preponderance of the hydroxy-form **A**. This conclusion depends on the cations formed from the hydroxy and the methoxy compounds being of similar structure: this similar structure is indeed confirmed by the ultraviolet spectra of the cations. The cations must all have structures of type XVIII; the unlikely alternative XIX is ruled out by comparison of the cation spectra of I with VIII and of III with IX: the introduction of a phenyl group in the 5-position clearly causes increased conjugation. Further evidence for the cation structure XVIII is provided by the spectra of the fixed cations XV and XVI.

TABLE 2. pK_a VALUES AT 20°C FOR SUBSTITUTED ISOXAZOLES

Cpd. no.	Isoxazole ring subst.			Proton addition				Proton loss		
	3	4	5	pK_a[a]	λ(nm)	conc (10^4M)	n[b]	pK_a	λ(nm)	conc (10^4M)
I	Me	OH	Me	−1·71 ± 0·07	250	1·48	1·12	8·65 ± 0·05 8·40 ± 0·05[c]	270	0·65
III	Me	OH	C_6H_5	−2·75 ± 0·08	310	0·55	0·90	7·55 ± 0·05	322	0·55
V	C_6H_5	OH	C_6H_5	−3·25 ± 0·08	325	0·43	0·92	7·21 ± 0·05 8·99 ± 0·02[d]	340	0·57
VIII	Me	OMe	Me	−2·27 ± 0·04	250	1·45	1·00	—	—	—
IX	Me	OMe	C_6H_5	−3·03 ± 0·06	300	0·55	0·90	—	—	—
X	C_6H_5	OMe	C_6H_5	−3·36 ± 0·04	312	0·40	0·93	—	—	—

[a] Mean of 7–8 values; standard deviation is given

[b] n is the slope of $\log_{10}[(\varepsilon - \varepsilon_B)/(\varepsilon_{BH^+} - \varepsilon)]$ plotted against H_0

[c] Potentiometric titration

[d] Potentiometric titration in H_2O:EtOH 1:1

TABLE 3. UV SPECTRAL MAXIMA (λ IN NM) AND EXTINCTION COEFFICIENTS ($\varepsilon \times 10^{-3}$) FOR AQUEOUS SOLUTIONS OF IONIC AND NEUTRAL SPECIES

Cpd no.	Isoxazole ring substituents			Cation in 20N H_2SO_4 $\lambda_{max}(\varepsilon \times 10^{-3})$	Neutral species in buffer (pH = 3) $\lambda_{max}(\varepsilon \times 10^{-3})$	Anion in 0·1N NaOH $\lambda_{max}(\varepsilon \times 10^{-3})$
	3	4	5			
I	Me	OH	Me	253 (5·7)	236 (4·2)	270 (4·4)
III	Me	OH	Ph	220 (5·8); 300 (14·0)	217*; 277 (17·9)	230 (8·0); 322 (13·5)
IV	Ph	OH	Me	216*, 245*; 282 (12·8)	239 (7·7); 267*	233 (8·0); 310 (5·2)
V	Ph	OH	Ph	225 (11·7); 322 (22·2)	218*, 241*; 283 (15·9); 289 (16·2)	225 (18·2); 343 (14·9)
VIII	Me	OMe	Me	248 (4·5)	230 (3·9)	—
IX	Me	OMe	Ph	217*, 294 (16·2)	215*; 272 (15·7)	—
X	Ph	OMe	Ph	223 (12·6); 314 (19·9)	221*; 237 (14·0); 276 (18·2); 281*[c]	—
XI	Me	:O	Me_2	269 (4·4)	269 (4·4)	—
XV	Ph	OAc	Ph[a]	226 (10·6); 307 (24·0)[b]	—	—
XVI	Ph	OMe	PH[a]	226 (9·9); 316 (23·1)[b]	—	—

* Indicates prominent shoulders

[a] N^+—Et groups also

[b] Spectrum obtained in EtOH 95%

[c] 50% EtOH : H_2O (vol/vol)

TABLE 4. UV SPECTRA OF 4-HYDROXY (I, III, IV, V) AND 4-METHOXYISOXAZOLES (VIII, IX, X) AS NEUTRAL SPECIES IN VARIOUS SOLVENTS

Solvent	I $\lambda_{max}(\varepsilon \times 10^{-3})$	VIII $\lambda_{max}(\varepsilon \times 10^{-3})$	III $\lambda_{max}(\varepsilon \times 10^{-3})$	IX $\lambda_{max}(\varepsilon \times 10^{-3})$	IV $\lambda_{max}(\varepsilon \times 10^{-3})$	V $\lambda_{max}(\varepsilon \times 10^{-3})$	X $\lambda_{max}(\varepsilon \times 10^{-3})$
Cyclohexane	234[a] (3·9)	227 (3·0)	278[a] (16·0)	217*	238[a] (5·7)	243[a] (12·4)	216* 221* 242 (14·9)
				271[a] (13·5)	267*	283 (16·8), 288 (16·6)	276 (19·2) 281*
Ethylacetate	*b*	*b*	279 (13·0)	273 (14·9)	267*	283 (15·2)	276 (20·1) 280 (20·1)
						288 (15·1)	288* 295*
Ethanol	238 (4·1)	230 (3·6)	217 (9·5)	215*	240 (9·1)	218* 241* 284 (15·6)	222 (12·9) 238 (13·8)
			281 (17·9)	273 (15·5)	267*	290 (16·2) 297*	276 (18·1) 281 (18·2) 288*
$HCOOH—NEt_3$ (20:1 vol/vol)	*b*	*b*	280 (15·5)	274 (13·9)	267*	283* 290 (16·4)	276* 282 (18·4)
						297*	287*
Dimethylsulphoxide	*b*	*b*	284 (16·0)	275 (13·3)	267*	285* 292 (15·6)	278* 283 (16·9)
						298*	288*
Hexamethyl-phosphoramide	*b*	*b*	287 (13·5)	275 (14·4)	267*	285* 293 (15·0)	276* 282 (18·2)
						299 (14·5)	288*

[a] Compounds were dissolved in ethylacetate and then diluted with 99 parts of cyclohexane. Spectra were recorded within 2–3 minutes

[b] End absorption only due to solvent cut-out

* Indicates prominent shoulders

Confirmation of the predominance of the hydroxy structure in aqueous solution is afforded by the UV spectra of the neutral species: again, each hydroxy compound resembles the methoxy analogue and the hypsochromic shift of 6–8 nm caused by the introduction of the O—Me group can be attributed to steric hindrance to conjugation. The similar effect of the introduction of a 5-phenyl group in the two series of neutral species spectra is further evidence of similar structure.

All the compounds are Hammett bases within experimental error ($n = 1{\cdot}0 \pm 0{\cdot}1$).[14] The spectrum of the 5.5-dimethyl model compound XI is the same in 20N. sulphuric acid as in water: it is either a very weak base, or cation and neutral species have the same absorption.

The 4-hydroxyisoxazoles are weak acids of pK_a 7·2–8·6 (in water). The UV spectra are both bathochromically shifted by 35–55 nm on anion formation. but the extinction coefficients are little altered: the bathochromic shift is considerably greater than that encountered for most phenols.[15]

TABLE 5. IR SPECTRAL MAXIMA (CM^{-1}) AND APPARENT EXTINCTION COEFFICIENTS (ε_A) OF 4-HYDROXYISOXAZOLES

Cpd. no.	Substituent 3	4	5	Phase	ν OH free cm^{-1}	ε_A	ν OH bonded cm^{-1}	ε_A	ν Ring cm^{-1}	ε_A
I	CH_3	OH	CH_3	$CHCl_3$ (0·2 mol)	3580	51	3140	69	1660	59
				$CHCl_3$ (0·03 mol)	3580	131	—		(—)	
				KBr	—		3100	(s)	1660	(s)
III	CH_3	OH	C_6H_5	$CHCl_3$ (0·2 mol)	3580	22	3220	97	1600	20
				KBr	—		3100	(s)	1640	(m)
IV	C_6H_5	OH	CH_3	$CHCl_3$ (0·2 mol)	3570	32	3220	98	1640	110
				KBr	—		3050	(s)	1635	(s)
V	C_6H_5	OH	C_6H_5	$CHCl_3$ (0·08 mol)	3560	39	3200	75	1600	33
				KBr	—		3100	(s)	1625	(s)
X	C_6H_5	OCH_3	C_6H_5	$CHCl_3$ (0·2 mol)	—		—		1620	58
				KBr	—		—		1620	(m)

— Indicates no absorption found; (—) indicates region obscured by solvent; m = medium; s = strong

Spectra in non-aqueous media. The UV spectra of the potentially tautomeric compounds (I, III, IV, V) and of the methoxy model compounds (VIII–X) are recorded in Table 4 for a number of solvents of widely varying polarity from cyclohexane to hexamethylphosphoramide. Without exception, wavelength maxima and extinction coefficients are all similar to the values found for aqueous solution. which is good evidence for the predominance of the same tautomeric form over the whole range of solvent polarities.

The IR spectra (Table 5) demonstrate that the hydroxy form is the preferred tautomer for both chloroform solutions and the crystalline state of each of the compounds (I. III. IV. V). 0·2 Molar solutions in chloroform show bands near 3580 cm^{-1} for free ν O—H (*cf* free ν O—H for 3-hydroxy-4,5-dimethylisoxazole at 3550 cm^{-1} in $CHCl_3$[2] and also bands at 3100–3200 cm^{-1} for associated ν O—H. The dimethyl

TABLE 6. PROTON RESONANCE CHEMICAL SHIFTS (PPM ON δ SCALE) AT 60 MHz

Cpd. no.	Solvent	3-Position		4-Position		5-Position	
I	$CDCl_3$	CH_3	2·30	OH	7·32	CH_3	2·20
IV	$CDCl_3$	C_6H_5	7·2–7·9	OH	6·53	CH_3	2·24
III	$CDCl_3$	CH_3	2·27	OH	6·13	C_6H_5	7·3–8
X	$CDCl_3$	C_6H_5	7·4–8·1	OCH_3	3·70	C_6H_5	7·4–8·1
IX	CCl_4	CH_3	2·24	OCH_3	3·73	C_6H_5	7·1–7·9
VIII	CCl_4	CH_3	2·33	OCH_3	3·72	CH_3	2·15
XI	CCl_4	CH_3	2·07	C=O	—	$(CH_3)_2$	1·30
a	$CDCl_3$	C_6H_5	7·4–7·9	$OCOCH_3$	2·30	C_6H_5	7·4–7·9
XV[b]	$CO(CD_3)_2$	C_6H_5	7·7–8·3	$OCOCH_3$	2·35	C_6H_5	7·7–8·3
XVI[c]	$CO(CD_3)_2$	C_6H_5	7·6–8·3	OCH_3	3·78	C_6H_5	7·6–8·3

[a] 3,5-Diphenyl-4-acetoxyisoxazole
[b] The 2-ethyl group shows at 1·76t and 4·88q (J = 7·3 Hz)
[c] The 2-ethyl group shows at 1·70t and 4·78q (J = 6·9 Hz)

compound was also examined in 0·03M solution: only the higher frequency band is found. In the solid state, only bonded ν O—H was found for each compound.

NMR spectra (Table 6) provide further confirmation for the hydroxy structure. and in particular exclude any large proportion of the 5(H)-form (B). The 5-position Me groups in compounds I and IV give rise to singlets at a similar chemical shift to that for the 5-Me group in the methoxy-compound VIII, and distinct from that for the 5,5-dimethyl compound XI.

CONCLUSIONS

All the physical evidence is in agreement with the predominance of the 4-hydroxy-tautomeric forms for all four compounds investigated, over a wide range of media of varying polarity.

EXPERIMENTAL

M.p.'s are uncorrected, IR and UV spectral data were obtained on a Perkin Elmer 125 and a Unicam SP 800A spectrophotometer respectively; pK_a values were measured spectrophotometrically using a Unicam SP 500. NMR spectra (sols in $CDCl_3$) were obtained at 35° with a Perkin Elmer R12 spectrometer at 60 MHz.

4-Hydroxy-5-methyl-3-phenylisoxazole, m.p. 118–120° (lit.[8] 118–119°); 4-acetoxy-3,5-diphenylisoxazole, m.p. 101–102° (lit.[5] 103°) and 4-methoxy-3,5-diphenylisoxazole, m.p. 68–69° (lit.[5] 69–70°) were prepared by the literature methods.[5,8]

4-Hydroxy-3,5-dimethylisoxazole. 3-Acetoxyacetylacetone (5·2 g) and hydroxylamine hydrochloride (5·0 g) in 1:4 EtOH aq were heated under reflux for 3 hr. The solvent was evaporated and the residue recrystallized from water to give 4-hydroxy-3,5-dimethylisoxazole (2·0 g, 50%) m.p. 77–84°, raised by sublimation at 72°/0·05 mm to 87–89° (dec) (lit. 81–82°;[7] 92–94°;[8] 79°[9]).

4-Hydroxy-3-methyl-5-phenylisoxazole. 2-Acetoxy-1-phenylbutane-1,3-dione (9·0 g) and hydroxylamine hydrochloride (4·5 g) were converted, as above, into 4-hydroxy-3-methyl-5-phenylisoxazole (6 g, 83%), needles (from benzene), m.p. 96–99° (dec) (lit. 96°;[3] 77–80°[6]) identical with and undepressed on admixture with an authentic sample obtained by oxidation of the corresponding 4-boronic acid derivative.[9]

Acetoxydibenzoylmethane monoxime. Hydroxylamine hydrochloride (5 g) in water (10 ml) and acetoxydibenzoylmethane (10 g) in EtOH (80 ml) were mixed and kept at 20° overnight. The *monoxime* (6·2 g,

58%) separated; it crystallised from EtOH as needles, m.p. 178°. (Found: C, 68·7; H, 5·2; N, 4·4. $C_{17}H_{15}NO_4$ requires: C, 68·7; H, 5·1; N, 4·7%).

4-Hydroxy-3,5-diphenylisoxazole. Acetoxydibenzoylmethane monoxime (5 g), EtOH (95%, 50 ml), and H_2SO_4 (2·5 ml) were heated under reflux for 3 hr. The cold solution was poured onto ice to precipitate 4-hydroxy-3,5-diphenylisoxazole (4·2 g, 100%) which, after recrystallisation from benzene, gave needles, m.p. 122–125° (decomp.) (lit. m.p. 123°;[5] 105, 125°[8]).

4-Methoxy-3,5-dimethylisoxazole. 4-Hydroxy-3,5-dimethylisoxazole (1·8 g) in ether (20 ml) was treated gradually with ethereal diazomethane until evolution of nitrogen ceased. After 2 hr the solvent was evaporated off and the 4-methoxy-3,5-dimethylisoxazole (1·6 g, 74%) distilled at 110–115°/1 mm (oil bath temp) (lit.[8] 95–100°/12 mm).

4-Methoxy-3-methyl-5-phenylisoxazole. 4-Hydroxy-3-methyl-5-phenylisoxazole (0·5 g) and diazomethane as above gave the *methoxy-isoxazole* (0·35 g, 67%) as an oil, b.p. 130–140°/0·2 mm. (Found: C, 69·5; H, 6·1; N, 7·1. $C_{11}H_{11}NO_2$ requires: C, 69·8; H, 5·8; N, 7·4%).

3,5,5-Trimethyl-4-isoxazolinone. 3,3,5-Trimethyl-3*H*-pyrazole 1,2-dioxide was converted into 3,5,5-trimethyl-4-isoxazolinone by the literature route.[13] The 3,5,5-trimethyl-4-isoxazolinone oxime intermediate was separated by filtration and afforded oxime XIV by crystallisation from chloroform, m.p. 156–157° (lit. m.p. 156[13a,b] 156–157[13c]). Ether extraction of the aqueous mother liquors afforded *oxime* XIII, as needles, m.p. 114–116° from chloroform. (Found: C, 50·5; H, 7·0; N, 19·4. $C_6H_{10}N_2O_2$ requires: C, 50·7; H, 7·1; N, 19·7%); NMR: ($CDCl_3$), oxime XIV δ 1·66 (s, 6H), 2·06 (s, 3H), 9·10 (s, 1H); oxime XIII δ 1·46 (s, 6H), 2·44 (s, 3H), 8·90 (s, 1H).

4-Acetoxy-2-ethyl-3,5-diphenylisoxazolium fluoroborate. Triethyloxonium fluoroborate (1·89 g) and 4-acetoxy-3,5-diphenylisoxazole (2·5 g) in dichloromethane (30 ml) were kept at 20° for 15 hr. The solvent was evaporated and the residue dissolved in warm acetone. Ether precipitated the *fluoroborate* (2·6 g, 78%) as prisms, m.p. 158–159°. (Found: C, 57·2; H, 4·9; N, 3·7. $C_{19}H_{18}BF_4NO_3$ requires: C, 57·7; H, 4·6; N, 3·6%).

2-Ethyl-4-methoxy-3,5-diphenylisoxazolium fluoroborate. 4-Methoxy-3,5-diphenylisoxazole (0·5 g) was converted as above into the *fluoroborate* (0·58 g, 74%) which crystallised from acetone–ether as colourless needles m.p. 176–177°. (Found: C, 59·1; H, 4·9; N, 3·8. $C_{18}H_{18}BF_4NO_2$ requires: C, 58·9; H, 4·9; N, 3·8%).

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