Reaction of Isoxazoles and Isoxazolium Salts with Organometallic Reagents. Synthesis of Dihydroisoxazoles

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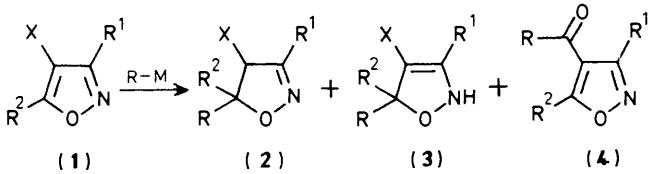
2,3- 2,5-, and 4,5-Dihydroisoxazoles have been selectively synthesized by reaction of isoxazoles with organo-lithium, -magnesium, and -aluminium reagents. Moreover, the reaction of benzoisoxazolium salts with highly basic organolithium compounds leads to phenylaziridines resulting from an unusual ring cleavage-closure process. A mechanism which accounts for all the experimental results is also given.

We reported earlier[1-4] that the reduction of activated isoxazoles by complex metal hydrides provides a good method for the regioselective synthesis of 2,3-, 2,5-, and 4,5-dihydroisoxazoles. The dihydroisoxazole obtained in each reaction depends on the kind of activation experienced by the isoxazole nucleus. Thus, 3,5-dialkylisoxazoles, with electron-withdrawing groups at C-4, on reduction with complex metal hydrides are reduced to 4,5-dihydroisoxazoles regiospecifically, whereas isoxazolium salts react with the same hydrides to give 2,3-dihydroisoxazoles as the sole products. On the other hand, double activation of the isoxazole nucleus by quaternization of the nitrogen and introduction of an electron-withdrawing group into the 4-position gives rise to 2,5-dihydroisoxazoles as the major products. Recently, we found[5] that *N*-alkylisoxazolium salts undergo ring cleavage when treated with lithium dialkylcuprates to give β-enamino ketones in high yields.

In the course of our investigations, it became of interest to devise new methods for the selective synthesis of dihydroisoxazoles as the result of the potential interest that some of our reported dihydroisoxazoles have generated as derivatives with insecticidal activity.†

We now report the reaction of isoxazoles bearing functional groups at C-4 and isoxazolium salts with organo-lithium, -magnesium, and -aluminium compounds. The addition of the organometallic compounds to the isoxazole derivative is remarkably selective affording 2,3-, 2,5-, and 4,5-dihydroisoxazoles as the only products.

4-Nitroisoxazoles (**1a,b**) (Table 1) react easily with Grignard reagents (methyl- and ethyl-magnesium halides) and methyl-lithium at 0 °C giving 4-nitro-4,5-dihydroisoxazoles (**2a—d**) on quenching with aqueous ammonium chloride (Scheme 1). It

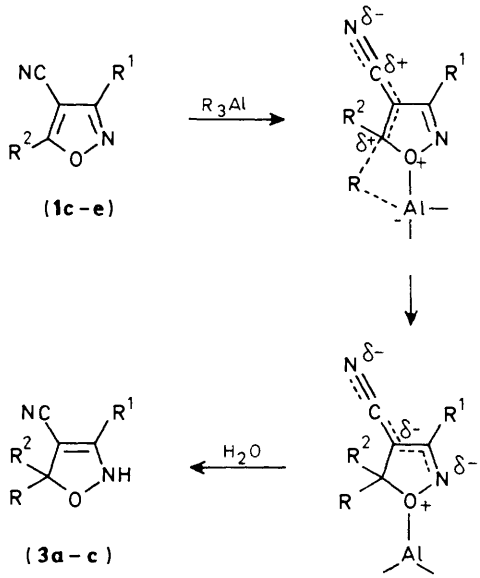


(1) (2) (3) (4)

Scheme 1.

should be noted that the nitro group remains unchanged. The reactivity of (**1b**) towards triethylaluminium (TEA) in benzene at room temperature is low, giving poor yields of (**2d**) along with unchanged (**1b**).

The behaviour of 4-cyanoisoxazoles (**1c—e**) is perceptibly different from that of the analogous 4-nitro derivatives. Thus, the reaction of (**1c—e**) with TEA leads to 4-cyano-2,5-dihydroisoxazoles (**3a—c**) with very acceptable yields whereas the same substrate (**1c**) undergoes addition to the cyano group by attack of organo-lithium and -magnesium reagents giving 4-acylisoxazoles (**4a,b**) (Schemes 1 and 2). The results are summarized in Table 1.



Scheme 2.

Although formation of 2,5- and 4,5-dihydroisoxazoles clearly involves 1,4-addition of the organometallic reagent to the isoxazole ring, more work needs to be done before the mechanism of the reaction is well understood. The formation of 4-cyano-2,5-dihydroisoxazoles (**3a—c**) rather than 4-cyano-4,5-dihydroisoxazoles could obviously be due to their higher stability. Not so clear, however, is why the 4-nitro derivatives yield 4,5-dihydroisoxazoles (**2a—d**), without contamination of 4-nitro-2,5-dihydroisoxazole. Moreover, 4,5-dihydroisoxazoles (**2a—d**) do not tautomerize to the corresponding 2,5-dihydroisoxazoles. Basic treatment of 4,5-dihydroisoxazoles (**2a—d**) followed by neutralization results in recovery of unchanged 4-nitro-4,5-dihydroisoxazoles. It may be that the steric hindrance of the nitro group is responsible for the above results. In previous papers we have reported similar steric effects for a 4-nitro group of the isoxazole nucleus.[6] Alternatively, the different reactivity of 4-cyanoisoxazoles with organo-lithium, -magnesium, and -aluminium compounds could be explained if we examine the results from the HSAB principle viewpoint. From an analysis based on the reasonable assumption that in the conjugated 4-cyanoisoxazole system the nitrile carbon is harder than C-5 and

† Screening experiments to evaluate activity are being carried out at present.

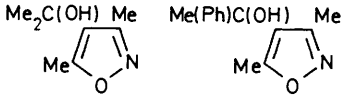
Table 1. Reactions of isoxazoles with organometallic reagents.

Compd.	R^1	R^2	R^3	X	RM	Temp. (°C)	Time (h)	Product	%[a]
(1a)	H	Me	—	NO_2	MeMgI	0	4	**(2a)**	73
(1a)	H	Me	—	NO_2	MeLi	0	3	**(2a)**	55
(1a)	H	Me	—	NO_2	EtMgBr	0	4	**(2b)**[b]	54
(1b)	Me	Me	—	NO_2	MeMgI	20	4	**(2c)**	39
(1b)	Me	Me	—	NO_2	MeLi	0	3	**(2c)**	45
(1b)	Me	Me	—	NO_2	EtMgBr	0	2	**(2d)**[b]	59
(1b)	Me	Me	—	NO_2	TEA[d]	20	4	**(2d)**[b,c]	21
(1c)	Me	Me	—	CN	TEA[d]	80	6	**(3a)**	83
(1d)	Ph	Me	—	CN	TEA[d]	80	6	**(3b)**	45
(1e)	Ph	Ph	—	CN	TEA[d]	80	20	**(3c)**	61
(1c)	Me	Me	—	CN	MeMgI	35	4	**(4a)**	75
(1c)	Me	Me	—	CN	MeLi	35	2	**(4a)**	83
(1c)	Me	Me	—	CN	EtMgBr	0	4	**(4b)**	71
(1f)	Me	Me	—	Ac	MeLi	0	4	**(5a)**	89
(1g)	Me	Me	—	Bz	MeMgI	35	2	**(5b)**	82
(1g)	Me	Me	—	Bz	TMA[d]	80	4	**(5b)**	76
(6a)	Me	Me	Et	Cl	MeMgI	0	15 min	**(7a)**	71
(6a)	Me	Me	Et	Cl	MeLi	0	15 min	**(7a)**	79
(6b)	Me	Me	Et	Br	MeMgI	0	15 min	**(7b)**	78
(6c)	Me	Me	Me	Bz	MeMgI	0	15 min	**(8a)**	72
(6c)	Me	Me	Me	Bz	MeLi	−20	15 min	**(8a)**	50
(6d)	Me	Me	Et	CO_2Et	MeMgI	0	15 min	**(8b)**	76
(6d)	Me	Me	Et	CO_2Et	MeLi	−20	15 min	**(8b)**	25

[a] Yields refer to chromatographed products. Purity higher than 96% (g.l.c. analysis conditions: 3% Dexil 300 on Chromosorb Q, 4 m × 3 mm, 140 °C). [b] Analysis by g.l.c. shows one pure compound, however it has not been possible to prove the actual *Z* or *E* stereochemistry of these compounds. [c] Starting material (60%) was also obtained. [d] Benzene as solvent.

that methyl-lithium and ethylmagnesium iodide are harder than TEA, a unified picture emerges. In the light of this, methyl-lithium adds to the cyano group to give 4-acylisoxazoles selectively whereas the softness of TEA and its affinity to co-ordinate to the oxygen atom of the isoxazole ring seem to be responsible for the formation of 2,5-dihydroisoxazoles as is shown in Scheme 2.

Functional groups other than nitro or cyano do not satisfactorily activate the isoxazole ring. Thus, 4-acetyl- (**1f**) and 4-benzoyl-3,5-dimethylisoxazole (**1g**), on reaction with methylmagnesium iodide, methyl-lithium, or trimethylaluminium

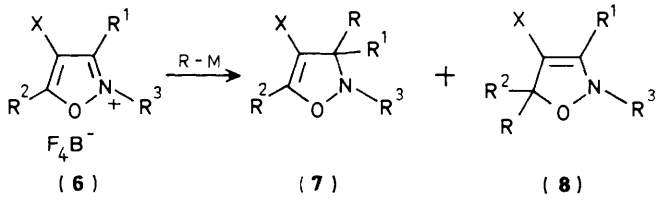


(**5a**) (**5b**)

(TMA) gave the corresponding tertiary alcohols 4-(1-hydroxy-1-methyl)ethyl-3,5-dimethylisoxazole (**5a**) and 4-(1-hydroxy-1-phenyl)ethyl-3,5-dimethylisoxazole (**5b**) respectively (Table 1). Physical constants and spectral and analytical data for compounds (**2a—d**) and (**3a—c**) are given in Table 2.

Isoxazolium salts bearing electron-withdrawing groups at C-4 are extremely susceptible towards nucleophilic attack. The reaction of (**6a—d**) with organo-lithium and -magnesium compounds proceeds readily under mild conditions giving 2,3-dihydroisoxazoles (**7a,b**) or 2,5-dihydroisoxazoles (**8a,b**) (Scheme 3). Under the same conditions TEA was proven to be inactive towards (**6a—d**). The results are listed in Table 1.

With the short reaction times and mild conditions used, the 4-ethoxycarbonyl and 4-benzoyl groups do not undergo attack by the organometallic reagent. This chemoselectivity should be noted (Table 1). The selective formation of 2,3- or 2,5-dihydroisoxazoles seems to be strongly dependent on resonance effects of the substituents at C-4. Thus, conjugation of benzoyl



(**6**) (**7**) (**8**)

Scheme 3.

and ethoxycarbonyl groups with the isoxazole nucleus enhances the electrophilicity of C-5 and consequently compounds (**6c,d**) undergo attack of the organometallic reagents at that position to give 2,5-dihydroisoxazoles (**8a,b**). In contrast, chloro and bromo derivatives which exhibit resonance effects +M undergo nucleophilic attack at C-3 giving 2,3-dihydroisoxazoles (**7a,b**). Physical constants and analytical data for compounds (**7a,b**) and (**8a,b**) are summarized in Table 2.

Benzoisoxazolium salts (**9a,b**) behave similarly to isoxazolium salts when treated with organometallic compounds or sodium borohydride leading to dihydrobenzoisoxazoles (**10a—e**) in high yields (Scheme 4) (Table 3 and 4).

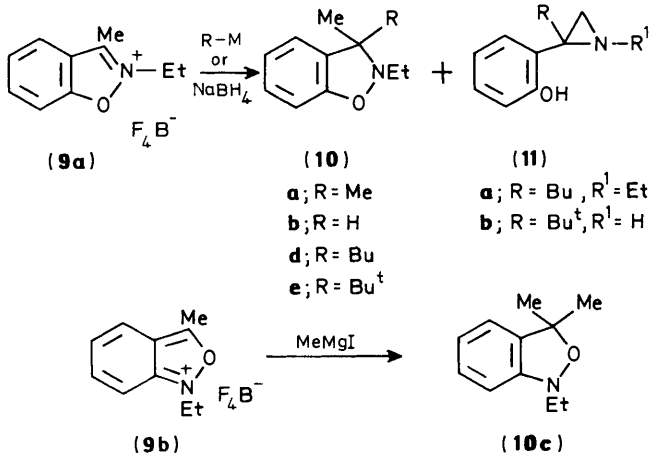
The reaction of (**9a**) with butyl- and t-butyl-lithium gives, surprisingly, not only the expected dihydrobenzoisoxazole (**10d,e**) but also the aziridines (**11a,b**) resulting from an unusual ring cleavage (Scheme 4) (Tables 3 and 4): the ratio of aziridine *vs.* benzoisoxazoline increases when the basicity of the organolithium compound increases. Thus, methyl-lithium reacts with (**9a**) leading to (**10a**) selectively, whereas butyl-lithium affords an equimolar mixture of (**10d**) and (**11a**) and t-butyl-lithium yields preferentially the aziridine (**11b**) (Table 3). The usefulness of this new synthetic route to phenylaziridines is being studied at present.

Although we have not attempted to elucidate the mechanism of the conversion of benzoisoxazolium salts into aziridines a plausible route involving deprotonation followed by lithium

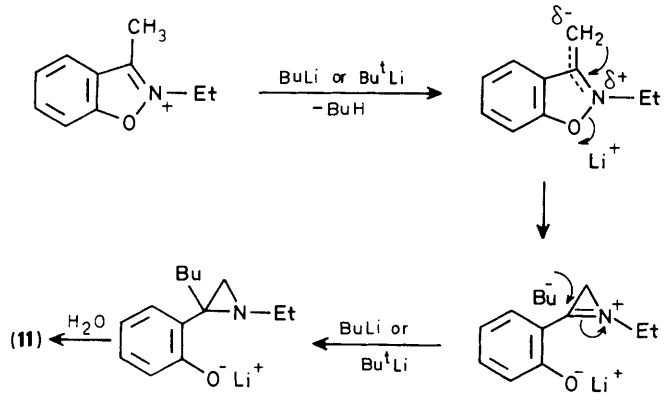
Table 2. Physical data for 2,3-, 2,5-, and 4,5-dihydroisoxazoles

Compd.[a]	B.p. (°C)/Torr [M.p.]	^{1}H N.m.r. ($CDCl_3$, TMS)[b] (mult., *J*/Hz) R	R^1	R^2	4-H	Molecular formula	Found (%) (Required) C	H	N
(**2a**)	Oil[c]	1.30 (s, 3 H)	7.05 (d, 2, 1 H)	1.40 (s, 3 H)	5.25 (d, 2)	$C_5H_8N_2O_3$	42.0 (41.67)	5.5 (5.59)	19.2 (19.44)
(**2b**)	Oil[c]	1.80 (q, 8, 2 H) 1.10 (t, 8, 3 H)	7.25 (d, 2, 1 H)	1.40 (s, 3 H)	5.50 (d, 2)	$C_6H_{10}N_2O_3$	45.9 (45.57)	6.2 (6.37)	17.7 (17.71)
(**2c**)	Oil[c]	1.25 (s, 3 H)	1.90 (s, 3 H)	1.30 (s, 3 H)	5.10 (s)	$C_6H_{10}N_2O_3$	45.3 (45.57)	6.2 (6.37)	17.5 (17.71)
(**2d**)	Oil[c]	1.70 (m, 2 H) 0.95 (m, 3 H)	2.10 (s, 3 H)	1.30 (s, 3 H)	5.40 (s)	$C_7H_{12}N_2O_3$	48.6 (48.83)	7.1 (7.02)	16.4 (16.27)
(**3a**)	[69—70][d]	3.10 (q, 8, 2 H) 1.25 (t, 8, 3 H)	2.15 (s, 3 H)	2.10 (s, 3 H)		$C_8H_{12}N_2O$	63.3 (63.13)	8.0 (7.95)	18.6 (18.41)
(**3b**)	[92—93][d]	3.15 (q, 7, 2 H) 1.15 (t, 7, 3 H)	7.3—7.8 (m, 5 H)	2.35 (s, 3 H)		$C_{13}H_{14}N_2O$	73.0 (72.87)	6.5 (6.59)	13.0 (13.07)
(**3c**)	[115—117][d]	3.15 (q, 8, 2 H) 1.15 (t, 8, 3 H)	7.5—8.2 (m, 5 H)	7.60 (m, 5 H)		$C_{18}H_{16}N_2O$	78.6 (78.24)	5.6 (5.84)	9.9 (10.14)
(**7a**)	Oil[c]	1.20 (s, 3 H)	1.20 (s, 3 H)	1.80 (s, 3 H)		$C_8H_{14}ClNO$	54.5 (54.70)	7.9 (8.03)	7.8 (7.97)
(**7b**)	Oil[c]	1.25 (s, 3 H)	1.25 (s, 3 H)	1.85 (s, 3 H)		$C_8H_{14}BrNO$	43.9 (43.65)	6.5 (6.41)	6.6 (6.36)
(**8a**)	39—41/2	1.50 (s, 3 H)	1.65 (s, 3 H)	1.50 (s, 3 H)		$C_{14}H_{17}NO_2$	72.4 (72.70)	7.3 (7.41)	5.9 (6.06)
(**8b**)	30—33/2	1.30 (s, 3 H)	2.05 (s, 3 H)	1.30 (s, 3 H)		$C_{11}H_{19}NO_3$	62.3 (61.95)	9.1 (8.98)	6.6 (6.57)

[a] (C=C) Stretching bands for the dihydroisoxazoles appear near 1 620—1 700 cm^{-1}. [b] N-CH_2 CH_3 resonances for (**7a,b**) and (**8b**) are found at *ca.* 1.3 and 3.5. N-CH_3 resonance for (**8a**) is found at 3.0. [c] Unstable oily compound. It decomposes during distillation. [d] From hexane.



Scheme 4.



Scheme 5.

Table 3. Reactions of benzoisoxazolium salts with organometallic reagents.

Compd.	RM	Temp. (°C)	Time (min)	Products (%)[a]
(**9a**)	MeLi	0	15	(**10a**) 88
(**9a**)	MeMgI	0	15	(**10a**) 82
(**9a**)	$NaBH_4$[b]	0	15	(**10b**) 91
(**9b**)	MeMgI	0	15	(**10c**) 93
(**9a**)	BuLi	0	15	(**10d**) 41 + (**11a**) 41
(**9a**)	^{t}BuLi	0	15	(**10e**) 9 + (**11b**) 82

[a] Yields refer to chromatographed products. [b] In EtOH.

salt-catalyzed ring cleavage, is consistent with all the observations (see Scheme 5).

Since the first step of the reaction seems to involve deprotonation of the methyl group attached at C-5, the strength of the organometallic base could govern the proportion of the aziridine observed. The loss of the ethyl group in one of the stages of the reaction to give (**11b**) may occur, as is known to proceed in the classical Hofmann degradation.

We conclude that 4-functionalized isoxazoles as well as isoxazolium salts are a reliable source of 2,3-, 2,5-, and 4,5-dihydroisoxazoles with a wide variety of substitution patterns. We note in these reactions that the regioselectivity of the addition compounds is clean in the sense that a dihydroisoxazole is formed. The degree of regioselectivity of every kind seen in this work is remarkable in view of the opportunity the reaction presents for the formation of mixtures.

Experimental

All m.p.s are uncorrected. Ether was freshly distilled from phosphorus pentaoxide and stored over sodium. 3,5-Dimethyl-4-nitroisoxazole,[7] 5-methyl-4-nitroisoxazole,[8] 4-cyano-3,5-dimethylisoxazole,[9] 4-cyano-5-methyl-3-phenylisoxazole,[10] 4-cyano-3,5-diphenylisoxazole,[11] 4-benzoyl-3,5-dimethylisoxazole,[12] 4-acetyl-3,5-dimethylisoxazole,[13] 4-bromo-3,5-di-

Table 4. Physical data of benzoisoxazolines

Compd.[a]	B.p. (°C)/Torr	^{1}H N.m.r. ($CDCl_3$, TMS)[b] (mult., *J*/Hz)	Molecular formula	Elemental analysis: found (calc.) C	H	N
(**10a**)	48—50/2	1.80 (s, 6 H, 3-Me)	$C_{11}H_{15}NO$	74.8 (74.54)	8.7 (8.53)	8.0 (7.90)
(**10b**)	34—37/2.5	1.70 (d, 7, 3 H, 3-Me), 4.65 (q, 7, 1 H, 3-H)	$C_{10}H_{13}NO$	73.2 (73.59)	7.8 (8.03)	8.5 (8.58)
(**10c**)	33—35/2	1.55 (s, 6 H, 3-Me)	$C_{11}H_{15}NO$	74.7 (74.54)	8.4 (8.53)	7.7 (7.90)
(**10d**)[d]	Oil[c]	0.90—1.80 (m, 9 H, Bu), 1.40 (s, 3 H, 3-Me)	$C_{14}H_{21}NO$	76.2 (76.67)	9.5 (9.65)	6.3 (6.39)
(**10e**)	Oil[c]	0.90 (s, 9 H, Bu^t), 1.50 (s, 3 H, 3-Me)	$C_{14}H_{21}NO$	76.3 (76.67)	9.9 (9.65)	6.2 (6.39)

[a] I.r. spectra show a strong absorption at around 1 620 cm^{-1}. [b] N–CH_2 CH_3 resonances are found at *ca.* 1.80—1.90 and 2.9—3.0 and ArH at 6.80—7.20. [c] Unstable oily compound. It decomposes during distillation. [d] ^{13}C N.m.r. ($CDCl_3$) 13.59, 13.98, 20.84(CH_3 groups), 23.18, 26.45, 39.83, 46.44(CH_2 groups), 69.60(non-Ar quaternary C), 108.15, 120.88, 122.30, 127.99(Ar CH groups), 134.20, and 155.91(Ar quaternary C).

methylisoxazole,[14] 4-chloro-3,5-dimethylisoxazole,[15] 4-ethoxycarbonyl-3,5-dimethylisoxazole,[10] 3-methyl-1,2-benzisoxazole,[16] and 3-methyl-2,1-benzisoxazole[17] were prepared according to literature procedures. Isoxazolium salts were synthesized by conventional methods.[18,19]

I.r. spectra were recorded with a Pye-Unicam SP-1100 spectrometer. ^{1}H N.m.r. and ^{13}C n.m.r. were obtained on either a Varian T-60A or a Bruker WP-200-SY spectrometer. Electron ionization mass spectra were obtained on a Hewlett-Packard 5946-A machine.

General Procedure.—The isoxazole (20 mmol) in dry ether (40 ml) was added to a stirred solution of the organometallic reagent (40 mmol) in ether under nitrogen at the temperature shown in Tables 1 or 3. The mixture was stirred at that temperature for an appropriate time (Tables 1 and 3) and then hydrolysed with saturated aqueous ammonium chloride. The ethereal layer was separated, dried ($MgSO_4$), and evaporated to provide a crude residue which was chromatographed on silica gel (Merck 40—63), with dichloromethane as eluant, to give the products (Tables 1 and 3). The reaction of (**9a**) with butyllithium and t-butyl-lithium yielded the mixtures (**10d**) and (**11a**) and (**10e**) and (**11b**) respectively which were separated by elution of the mixtures through a silica gel column using dichloromethane–ether (6:1). The aziridines (**11a**) and (**11b**) were always the 2nd fraction eluted. The characteristics of all the dihydro-isoxazoles and -benzoisoxazoles obtained are summarized in Tables 2 and 4. Physical and spectral data for (**11a,b**) and (**5a,b**) are given below:

1-*Butyl*-2-*ethyl*-1-o-*hydroxyphenylaziridine* (**11a**), colourless liquid, b.p. 116—119 °C at 1 Torr; $\nu_{max.}$(film) 3 350 cm^{-1} (OH); δ_H(200 MHz; $CDCl_3$) 0.88 (3 H, t, *J* 7.5 Hz, *Me*CH_2CH_2), 1.12 (3 H, t, *J* 8.0 Hz, *Me*CH_2N), 1.28 (4 H, m, Me-$CH_2CH_2CH_2$), 1.64 (2 H, t, *J* 7.5 Hz, PrCH_2), 1.88 (2 H, m, aziridine ring CH_2), 2.43 (2 H, q, *J* 8.0 Hz, MeCH_2N), and 6.80—7.25 (4 H, m, ArH); δ_C($CDCl_3$) 13.97, 15.16 (Me groups), 22.60, 25.27, 32.16, 34.08, 35.86 (CH_2 groups), 63.04 (nonaromatic quaternary C), 117.00, 118.29, 127.54, 128.47 (aromatic CH groups), 127.46, and 158.12 (aromatic quaternary C) (Found: C, 76.9; H, 9.7; N, 6.4. $C_{14}H_{21}NO$ requires C, 76.71; H, 9.59; N, 6.39%).

2-o-*Hydroxyphenyl*-2-*t-butylaziridine* (**11b**), colourless viscous oil, R_F (dichloromethane) 0.25; $\nu_{max.}$(film) 3 480 cm^{-1} (OH, NH); δ_H($CDCl_3$) 1.0 (9 H, s, Bu^t), 1.25 (1 H, br s, NH), 1.55 (2 H, m, aziridine ring CH_2), and 6.7—7.2 (4 H, m, ArH) (Found: C, 75.2; H, 9.1; N, 7.5. $C_{12}H_{17}NO$ requires C, 75.39; H, 8.90; N, 7.33%).

4-(1-*Hydroxy*-1-*methylethyl*)-3,5-*dimethylisoxazole* (**5a**), colourless liquid, b.p. 109—113 °C at 1 Torr, $\nu_{max.}$(film) 3 490 cm^{-1} (OH); δ_H($CDCl_3$) 1.45 (6 H, s, CMe_2), 2.1 (3 H, s, 3-Me), 2.3 (3 H, s, 5-Me), and 4.2 (1 H, br s, OH) (Found: C, 62.1; H, 8.4; N, 8.9. $C_8H_{13}NO_2$ requires C, 61.93; H, 8.38; N, 9.03%).

4(1-*Hydroxy*-1-*phenylethyl*)-3,5-*dimethylisoxazole* (**5b**), colourless crystals, m.p. 62—63 °C (from hexane); $\nu_{max.}$(Nujol) 3 450 cm^{-1} (OH); δ_H($CDCl_3$) 1.6 (3 H, s, *Me*COH), 2.05 (3 H, s, 3-Me), 2.3 (3 H, s, 5-Me), 4.55 (1 H, br s, OH), and 7.20—7.35 (5 H, m, ArH) (Found: C, 72.2; H, 7.1; N, 6.6. $C_{13}H_{15}NO_2$ requires C, 71.88; H, 6.91; N, 6.45%).

Acknowledgements

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