Structure of Alcohols obtained by Reaction of Aldehydes and Ketones with *ortho*-Lithiated Oxazolines†

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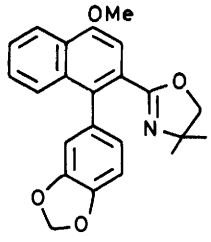
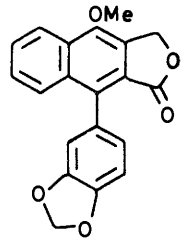
The reaction of aldehydes with *ortho*-lithiated oxazolines typically gives secondary alcohols. Exceptionally, a case is described of the formation of a primary alcohol by the opening of the oxazoline ring. The reaction of ketones with *ortho*-lithiated oxazolines, in contrast to reports in the literature, typically gives primary alcohols, by opening of the oxazoline ring, and not the reported tertiary alcohols. The proposed structures are substantiated by the preparation of derivatives and, particularly, by consideration of the ^{13}C n.m.r. spectra.

The *ortho*-lithiation of oxazolines has become an important method for the development of complex aromatic structures. The synthetic potential indicated by the earlier work of Meyers[1] and Gschwend[2] has recently been exploited[3] in the synthesis of a variety of compounds of biological interest, and also in the synthesis of key precursors[4,5] to compounds of biological importance. Of the methods available of carbon–carbon bond formation *via ortho*-lithiated oxazolines, a favoured approach has been the reaction with aldehydes and ketones. Thus, in the synthesis of lignan lactone derivatives, the reaction of the oxazoline (**1**), first with n-butyl-lithium, and then with paraformaldehyde, is reported[5] to give an intermediate hydroxymethyl derivative which, on hydrolysis under acidic conditions, gives the lactone (**2**). Similarly, the reaction[6] of the Grignard reagent derived from compound (**3**) with *p*-methoxybenzaldehyde, followed by acid hydrolysis of the intermediate, afforded the lactone (**4**). Reactions with ketones have also been reported. Thus, the Grignard reagent derived from (**3**) gives an intermediate on reaction with cycloheptanone[6] which affords compound (**5**) on acid hydrolysis. In these earlier studies, the structures of the intermediate alcohols are not described; however, in a later study Meyers and Gabel[7] report more fully studies with pyridyloxazolines. Lithiation of compounds (**6**) and (**7**) followed by treatment with benzaldehyde is reported to afford isomers (**8**) and (**9**) respectively. Similarly, pentan-3-one is reported to give compound (**10**) from lithiated (**6**), and the isomer (**11**) from lithiated (**7**). Other recent reports have extended the use of oxazolines to the synthesis of a variety of heterocyclic systems. The *ortho*-lithiation of the thiophene derivative (**13**) and the furan derivative (**14**), and subsequent reaction with benzaldehyde,[8] is reported to give the secondary alcohols (**15**) and (**16**), respectively. Similarly, the reaction of an *ortho*-metallated phenyloxazoline with the benzothiophene (**17**) is reported,[9] but the product is only described as an 'unisolated intermediate.'

From the above studies, the utility of *ortho*-lithiation procedures in the synthesis of lactones from oxazolines is well established. The nature of the alcohol intermediates, the precursors to the lactone products, is, however, much less clear. We have recently studied[10] a number of additions of *ortho*-lithiated oxazolines to both aldehydes and ketones. In the following paper[11] we describe aspects of the chemistry of the alcohol products, but in this paper we show that two types of product may be obtained. Lithiation of (**18**) and reaction with *p*-anisaldehyde gives compound (**21**) without opening of the oxazoline ring, but reaction of lithiated (**18**) with cyclohexanone gives the primary alcohol (**27**) with ring-opening. Based on a general survey of the addition to aldehydes and ketones and a comparison of the spectroscopic data for our compounds with literature data we are able to clarify the outcome of this much used procedure and to correct certain literature structural assignments.



(**1**)



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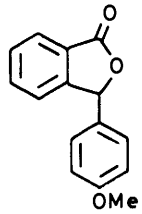

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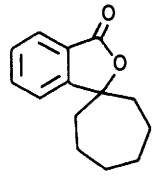

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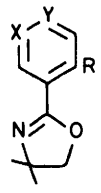


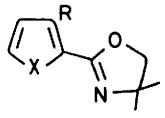
(**3**) X = Y = CH, R = Br
(**6**) X = CH, Y = N, R = H
(**7**) X = N, Y = CH, R = H
(**8**) X = CH, Y = N, R = PhCHOH
(**9**) X = N, Y = CH, R = PhCHOH
(**10**) X = CH, Y = N, R = Et_2COH
(**11**) X = N, Y = CH, R = Et_2COH
(**12**) X = Y = CH, R = $PhCH_2CHOH$

† The use of oxazoline, which refers to dihydro-1,3-oxazole, is not recommended by I.U.P.A.C., but is retained here for ease of comparison with the literature.

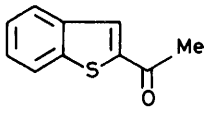
Table. Spectroscopic data for the oxazoline (**18**) and the alcohols (**21**) and (**27**) and their derivatives[a]

Compound	$\nu_{max.}$(cm^{-1})	δ_H/p.p.m.			δ_C/p.p.m.				
	C=N	NC*Me*$_2$	CH_2X[b]	ArC*H*O	C=N	CH_2X[b]	NCMe_2	NC*Me*$_2$	ArCHO
(**18**)	1 640	1.36	4.02		161.97	79.01	67.53	28.38	
(**21**)	1 640	1.00 and 1.27	3.84 and 3.95	5.90	162.52	78.63	67.74	27.76 and 28.22	74.20
(**22**)	1 650	1.24 and 1.28	3.94	7.84	162.26	78.90	67.71	28.08	73.18
(**23**)	1 650	1.30 and 1.32	4.0	8.24		78.64	68.20	28.24 and 28.34	75.88
(**27**)	1 690	1.40	3.46		157.61	73.01	56.85	23.06 and 22.75	
(**28**)	1 690	1.46	4.26		157.4	73.32	55.71	24.25	
(**29**)	1 690	1.58	4.60		157.30	74.85	55.83	24.24	

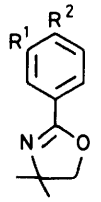
[a] See Experimental section for full details. [b] In compounds (**18**), (**21**), (**22**), and (**23**), X = O; in (**27**), X = OH; in (**28**), X = OAc; in (**29**), X = 3,5-dinitrobenzoyl.



(**13**) X = S, R = H
(**14**) X = O, R = H
(**15**) X = S, R = PhCHOH
(**16**) X = O, R = PhCHOH

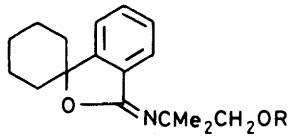


(**17**)



(**18**) $R^1 = R^2 = H$
(**19**) $R^1 = H$, $R^2 = OMe$
(**20**) $R^1 = OMe$, $R^2 = H$

(**21**) $R^1 = OMe$, $R^2 = R^3 = H$, $R^4 = OH$
(**22**) $R^1 = OMe$, $R^2 = R^3 = H$, $R^4 = OAc$
(**23**) $R^1 = OMe$, $R^2 = R^3 = H$, $R^4 = 3,5-dinitrobenzoyloxy$
(**24**) $R^1 = R^2 = R^3 = H$, $R^4 = OH$
(**25**) $R^1 = R^2 = H$, $R^3 = OMe$, $R^4 = OH$
(**26**) $R^1 = R^3 = H$, $R^2 = OMe$, $R^4 = OH$



(**27**) R = H
(**28**) R = Ac
(**29**) R = 3,5—dinitrobenzoyloxy

In the case of the reaction of a typical aldehyde, the lithiation of phenyloxazoline (**18**) using n-butyl-lithium in dry tetrahydrofuran followed by the addition of *p*-anisaldehyde afforded the secondary alcohol (**21**) as an oil. This alcohol was characterised as an acetate (**22**) and a 3,5-dinitrobenzoate (**23**). In a similar manner with a typical ketone, the lithiation of the phenyloxazoline (**18**) followed by the addition of cyclohexanone afforded the primary alcohol (**27**). This alcohol was further characterised as the acetate (**28**) and the 3,5-dinitrobenzoate (**29**).

In the Table are gathered the important spectroscopic data which support the proposed assignment. By analysis of the spectra of the simple oxazoline (**18**), the secondary alcohol (**21**) and its acetate (**22**) and 3,5-dinitrobenzoate (**23**), and the primary alcohol (**27**) and its acetate (**28**) and 3,5-dinitrobenzoate (**29**), a distinction between compounds having an intact oxazoline ring and those with an opened oxazoline ring may be made. This distinction can be seen in features of their i.r., ^{1}H n.m.r., ^{13}C n.m.r., and mass spectra.

(*a*) *I.R. Spectra.*—The $\nu_{max.}$(C=N) band associated with the intact oxazoline ring is observed at *ca.* 1 640 cm^{-1}. In the imino ethers resulting from the opening of the oxazoline ring, the $\nu_{max.}$(C=N) is observed at *ca.* 1 690 cm^{-1}. Imino ethers of closely related structure are known[12] to absorb in the region 1 680—1 700 cm^{-1}. The position of the $\nu_{max.}$(C=N) band in oxazolines is partly determined[13] by the degree of conjugation. Thus, in phenyloxazoline ($\nu_{max.}$ 1 650 cm^{-1}), conjugation decreases the stretching energy relative to that in methyloxazoline ($\nu_{max.}$ 1 670 cm^{-1}). Hence, in the possible products from the lithiation of compound (**18**) and related compounds, the location of the $\nu_{max.}$(C=N) band at 1 690 cm^{-1} might be explained either by the formation of an imino ether such as (**27**), or by the formation of a hindered oxazoline. In the latter case, steric inhibition of resonance might shift the $\nu_{max.}$(C=N) band to higher energy. Below we indicate further evidence that clearly proves the formation of the imino ether (**27**) and related compounds. Hence, in the series of compounds studied, steric factors are not substantially influencing the position of the $\nu_{max.}$(C=N) band in oxazolines and, therefore, the position of this band is an accurate guide to the structure of the products.

(*b*) ^{1}H *N.M.R. Spectra.*—The formation of the esters (**22**) and (**23**) from the secondary alcohol (**21**) leads to little shift in the position of the signal associated with the methylene group. In each of the compounds this resonance occurs in an unexceptional position for an oxazoline [see (**18**)]. In contrast, in the primary alcohol (**27**) and the related esters (**28**) and (**29**), large

differences in chemical shift are observed for the methylene group relative to that of an oxazoline. The data show that the esters (**28**) and (**29**) are derived from the primary alcohol (**27**). Similarly, the formation of the esters (**22**) and (**23**) of the secondary alcohol (**21**) can be seen by the substantial deshielding of the methine resonance (ArC*H*O) in their spectra, relative to that of the alcohol (**21**). Hence, by characterisation of the alcohols (**21**) and (**27**) as their esters, ^{1}H n.m.r. spectroscopy clearly and unequivocally permits the above structural assignments. Without exception we find that secondary alcohols retaining an oxazoline moiety are characterised by the resonance of the methylene group of the oxazoline at *ca.* 3.9 p.p.m. and that primary alcohols formed by cleavage of the oxazoline ring are characterised by a resonance of the methylene group (CH_2OH) at *ca.* 3.45 p.p.m.

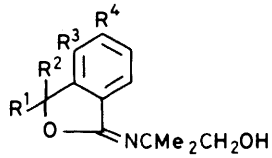
(*c*) ^{13}C *N.M.R. Spectra.*—Structural assignments follow more readily from analysis of the ^{1}H n.m.r. spectra than of the ^{13}C n.m.r. spectra. The imine resonance (Ar*C*=N) is sometimes difficult to recognise because the signal is often weak and because of the proximity of other resonances. The position of the resonance associated with the methylene group of the oxazoline moiety of the secondary alcohols is different from that of the methylene group of the primary alcohols (CH_2OH), but the chemical shift differences are less marked than in the ^{1}H n.m.r. spectra. However, without exception the secondary alcohols are characterised by a methylene resonance at *ca.* 79 p.p.m., whereas the primary alcohols are characterised by a methylene resonance at *ca.* 73 p.p.m.

(*d*) *Mass Spectra.*—Mass spectroscopy distinguishes between the structures of the possible primary and secondary alcohols. A very strong fragmentation peak at (M − 31) [*i.e.* (M − CH_2OH)] is associated with the spectra of all the primary alcohols. In contrast, in the spectra of the secondary alcohols retaining the oxazoline moiety, the (M − 31) peak is relatively feeble in comparison to the molecular ion M^+. For example, for the secondary alcohol (**21**) we find M^+ (70%) and M − 31 (67%), and for the primary alcohol (**27**) we find M^+ (<1%) and M − 31 (100%).

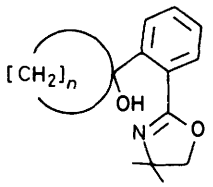
The reactions of lithiated oxazolines with a number of aldehydes and ketones have been investigated and in each case the structures were assigned using the spectroscopic features described in (*a*—*d*) above. Thus, reaction of phenyloxazoline (**18**) with benzaldehyde afforded the secondary alcohol (**24**), and the reaction of the lithiated oxazolines (**19**) and (**20**) afforded (**25**) and a mixture of compounds (**26**) and (**30**), respectively; similarly, phenylacetaldehyde afforded the secondary alcohol (**12**). Under the reaction conditions which lead from cyclohexanone to the primary alcohol (**27**), we find that from lithiated (**18**) the following primary alcohols are obtained: (**31**) from cycloheptanone, (**32**) from acetone, (**33**) from acetophenone, and (**34**) from benzophenone. Similarly, *via* lithiation, the aryloxazoline (**19**) affords compound (**35**) from cyclohexanone, (**36**) from cyclopentanone, and (**37**) from di-isopropyl ketone.

With the exception of the reaction of benzaldehyde, which affords a mixture of products (**26**) and (**30**) from the substituted oxazoline (**20**), the above results fall into a clear pattern; that aldehydes react with lithiated oxazolines to give secondary alcohols, but ketones react to give primary alcohols with opening of the oxazoline ring.

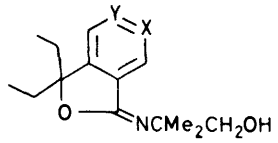
The explanation of this difference probably lies in the greater ease of opening of the oxazoline ring in the tertiary alcohols [*e.g.* (**38**)] relative to the secondary alcohols [*e.g.* (**21**)]. In compound (**38**) and other tertiary alcohols the preferred conformation about the newly formed carbon–carbon bond is likely to place the smallest substituent (in all cases the hydroxy group) close to the oxazoline ring; this will facilitate ring opening. In contrast, in compound (**21**) and related secondary alcohols the hydrogen rather than the hydroxy group is likely to be placed preferentially close to the oxazoline ring. In support of this view, the only case of the formation of a primary alcohol by reaction of a lithiated oxazoline with an aldehyde occurs on reaction of benzaldehyde with lithiated compound (**20**). Although the secondary alcohol (**26**) is observed in solution, equilibration readily affords the fused product (**30**), which may be isolated as a crystalline solid. This exception is explained by the additional steric interactions introduced by the methoxy substituent; these increase the probability of the hydroxy group in (**26**) being placed close to the oxazoline ring. The formation of primary alcohols from a variety of saturated and unsaturated ketones supports this conformational explanation.



(**30**) R^1 = Ph, R^2 = R^4 = H, R^3 = OMe
(**31**) R^1R^2 = $[CH_2]_6$, R^3 = R^4 = H
(**32**) R^1 = R^2 = Me, R^3 = R^4 = H
(**33**) R^1 = Ph, R^2 = Me, R^3 = R^4 = H
(**34**) R^1 = R^2 = Ph, R^3 = R^4 = H
(**35**) R^1 = R^2 = $[CH_2]_5$, R^3 = H, R^4 = OMe
(**36**) R^1 = R^2 = $[CH_2]_4$, R^3 = H, R^4 = OMe
(**37**) R^1 = R^2 = Pr^i, R^3 = H, R^4 = OMe



(**38**) n = 5
(**39**) n = 6



(**40**) X = CH, Y = N
(**41**) X = N, Y = CH

Inspection of the spectra data[5–8] of the cited literature examples of the reaction of lithiated oxazolines with aldehydes requires no correction of the assigned structures. In contrast, comparison of the data for published examples of the reaction of lithiated oxazolines with ketones with the spectral data given here necessitates some revision of the reported assignments. The reaction[6] of the Grignard reagent derived from compound (**3**) with cycloheptanone gives an intermediate which affords the product (**5**) on hydrolysis. The reported spectral data for the intermediate [$\nu_{max.}$ 1 670 cm^{-1}; δ 3.50 (2 H, s)] suggest structure (**31**) rather than the alternative tertiary alcohol (**39**) as assigned previously.[6] The reported data[7] for the products of the reaction of lithiated compounds (**6**) and (**7**) with pentan-3-one do not accord with the assigned structures (**10**) and (**11**). The products from compound (**6**), characterised by $\nu_{max.}$ 1 690 cm^{-1} and δ 3.32 (2 H, s), and (**7**), characterised by $\nu_{max.}$ 1 690 cm^{-1} and δ 3.32 (2 H, s), must have the structures (**40**) and (**41**), respectively. Both the ^{1}H n.m.r. and the i.r. data accord with the results reported here for the primary alcohols obtained by opening of the oxazoline ring, but not with the data for those alcohols which retain the oxazoline ring. Similarly, the 'unisolated intermediate' obtained[9] by the reaction of compound (**17**) with the lithiated compound (**18**) is probably a primary alcohol rather than the

possible tertiary alcohol, and the established procedure of lactone formation by acid hydrolysis of the products from the reaction of metallated oxazolines with aldehydes or ketones probably proceeds from primary alcohol intermediates in the case of ketones. Syntheses of benzanthracenes[14] *via* the reaction of metallated oxazolines with ketones illustrate such procedures.

Further support for these assignments comes from the very recent study of Meyers *et al.*[15] In demonstrating the great potential of chiral phthalides they have isolated the alcohol obtained from the reaction of a chiral oxazoline with *p*-bromoacetophenone. The structure determination by *X*-ray analysis shows that a primary alcohol is formed (by opening of the oxazoline ring) rather than a tertiary alcohol. This opening of the oxazoline is analogous to the examples reported in this work.

The isolation of products resulting from the opening of the oxazoline ring raises two further general questions: whether the primary alcohols can have a chemistry distinct from that of the tertiary alcohols, which may lead to new synthetic procedures; and whether reaction of metallated oxazolines with electrophiles other than ketones can similarly lead to products from the opening of the oxazoline ring. In the following paper[11] the chemistry of the alcohols is described.

Metallated oxazolines also react[1] with epoxides. The alcohols produced might retain the oxazoline ring, or this could be cleaved. An inspection of the reported spectroscopic data for the alcohols[1] suggests that the oxazoline ring is not cleaved.

Experimental

M.p.s were determined in a capillary tube and are uncorrected. I.r. spectra were obtained using a Perkin-Elmer 157 spectrometer. ^1H and ^{13}C N.m.r. spectra were obtained using a Varian XL100 spectrometer. Mass spectra were obtained at 70 eV using a Kratos MS30 spectrometer. Thin layer chromatography was carried out using Merck Kieselgel 60HF (254 + 366). Flash chromatography was carried out on Macherey Nagel silica gel 60. H.p.l.c. was carried out on Merck Kieselgel 60. Light petroleum refers to the fraction with b.p. 40—60 °C, and ether to diethyl ether.

Preparation of Oxazolines.—The oxazolines were prepared by the method of Meyers *et al.*[6] from the appropriate benzoyl chloride.

The reaction with benzoyl chloride gave 4,4-dimethyl-2-phenyl-2-oxazoline (**18**) (82%), b.p. 80—81 °C (0.35 mmHg) [lit.,[16] b.p. 124 °C (20 mmHg)]; δ 1.36 (6 H, s, CH_3), 4.02 (2 H, s, CH_2O), 7.2—8.1 (5 H, complex, aromatic); δ_C(p.p.m.) 28.38 (CH_3), 67.53 ($NCMe_2$), 79.01 (CH_2O), 128.24 and 131.13 (aromatic CH and C), and 161.97 (Ar*C*=N); $\nu_{max.}$($CHCl_3$) 1 640 cm^{-1}; *m/z* 175 (M^+, 7%) and 160 (M − 15, 100).

The reaction of *p*-anisoyl chloride gave 2-(4-methoxyphenyl)-4,4-dimethyl-2-oxazoline (**19**) (68%), b.p. 144—145 °C (1 mmHg); δ 1.30 (6 H, s, CH_3), 3.75 (3 H, s, OCH_3), 4.02 (2 H, s, CH_2O), and 6.8—8.0 (4 H, complex, aromatic); $\nu_{max.}$($CHCl_3$) 1 650 cm^{-1}.

Reaction of *m*-anisoyl chloride gave 2-(3-methoxyphenyl)-4,4-dimethyl-2-oxazoline (**20**) (74%), b.p. 126—128 °C (0.9 mmHg) [lit.,[17] b.p. 79.0—80.5 °C (0.005 mmHg)]; δ 1.4 (6 H, s, CH_3), 3.90 (3 H, s, OCH_3), 4.10 (2 H, s, CH_2O), and 6.9—7.7 (4 H, complex, aromatic); $\nu_{max.}$($CHCl_3$) 1 640 cm^{-1}; *m/z* 205 (M^+, 27%) and 190 (M − 15, 100).

Reaction of *p*-nitrobenzoyl chloride gave 4,4-*dimethyl*-2-(4-*nitrophenyl*)-2-*oxazoline*, m.p. 87—89 °C (Found: C, 60.1; H, 5.5; N, 12.7. $C_{11}H_{12}N_2O_3$ requires C, 59.9; H, 5.5; N, 12.7%); δ 1.4 (6 H, s, CH_3), 4.10 (2 H, s, CH_2O), and 8.0—8.5 (4 H, complex, aromatic); $\nu_{max.}$($CHCl_3$) 1 650 cm^{-1}; *m/z* 220 (M^+, 2%) and 205 (M − 15, 100).

3-(2-*Hydroxy*-1,1-*dimethylethylimino*)-1,3-*dihydro*-2-*benzofuran*-1-*spirocyclohexane* (**27**).—To a stirred solution of 4,4-dimethyl-2-phenyl-2-oxazoline (**18**) (5.88 g, 33.6 mmol) in anhydrous tetrahydrofuran (100 ml), n-butyl-lithium (26.4 ml; 1.4M-solution in hexane) was added slowly under nitrogen at −78 °C. An orange colour quickly developed and, after being stirred at −78 °C for 1 h, the solution was allowed to warm to −20 °C. Cyclohexanone (3.0 g, 30.6 mmol) in dry tetrahydrofuran (50 ml) was added during 20 min and the orange colour was discharged. The solution was stirred for a further 1 h at −20 °C and then allowed to warm to room temperature. The solvent was removed under reduced pressure and the residue partitioned between ether (100 ml) and water (100 ml) to which saturated aqueous ammonium chloride (20 ml) had been added. Following a second extraction of the aqueous phase with ether (100 ml), the combined ether extracts were washed with water (50 ml), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to afford a yellow oil (7.0 g). Crystallisation from ethyl acetate–light petroleum afforded as a white crystalline solid 3-(2-*hydroxy*-1,1-*dimethylethylimino*)-1,3-*dihydro*-2-*benzofuran*-1-*spirocyclohexane* (**27**) (3.7 g, 44%), m.p. 122—124 °C (Found: C, 74.7; H, 8.4; N, 5.1. $C_{17}H_{23}NO_2$ requires C, 74.7; H, 8.3; N, 5.1%); $\nu_{max.}$($CHCl_3$) 3 400, 2 940, and 1 690 cm^{-1}; *m/z* 273 (M^+, 0.3%), 242 (100); δ 1.40 (6 H, s, CH_3), 1.55—2.0 (10 H, complex, CH_2), 3.25—3.48 (1 H, br, OH), and 3.46 (2 H, s, CH_2O), 7.2—7.9 (4 H, complex, aromatic), δ_C(p.p.m.) 22.76 and 23.06 (CH_2 and CH_3), 25.00 (CH_2), 36.78 (CH_2), 56.86 (Me_2CN), 73.01 (CH_2OH), 88.67 (Ar*C*O), 120.43, 123.76, and 128.43 (aromatic CH), 131.21 (aromatic CH and aromatic C), 150.69 (aromatic C), and 157.60 (C=N).

The alcohol (**27**) was further characterised by acetylation with acetic anhydride in pyridine to give the acetate (**28**); $\nu_{max.}$($CHCl_3$) 1 730 and 1 690 cm^{-1}; δ 1.46 (6 H, s, CH_3), 1.55—2.0 (10 H, complex, CH_2), 2.00 (3 H, s, $COCH_3$), 4.26 (2 H, s, CH_2O), and 7.15—7.90 (4 H, complex, aromatic); δ_C(p.p.m.) 20.97 (COMe), 22.76 (CH_2), 24.25 (CH_3), 24.92 (CH_2), 33.68 (CH_2), 55.71 (Me_2CN), 72.32 (CH_2O), 89.01 (Ar*C*O), 120.43, 124.03, 128.48, 130.87, and 131.33 (aromatic CH and aromatic C), 150.75 (aromatic C), 157.4 (C=N), and 171.13 (CO).

The alcohol (**27**) was also characterised as the 3,5-dinitrobenzoate (**29**), m.p. 175—177 °C; $\nu_{max.}$($CHCl_3$) 1 730 and 1 690 cm^{-1}; δ 1.58 (6 H, s, CH_3), 1.64—2.10 (10 H, complex, CH_2), 4.60 (2 H, s, CH_2O), 7.15—7.80 (4 H, complex, aromatic), and 9.20 (3 H, s, aromatic); δ_C(p.p.m.) 22.87 (CH_2), 24.24 (CH_3), 25.05 (CH_2), 36.82 (CH_2), 55.83 ($NCMe_2$), 74.85 (CH_2O), 89.06 (Ar*C*O), 120.43, 122.21, 123.97, 128.58, 129.52, 131.11, and 131.33 (aromatic CH and aromatic C), 134.65, 148.77, and 150.79 (aromatic C), 157.30 (Ar*C*=N), and 162.72 (CO).

2-[2-*Hydroxy*(4-*methoxyphenyl*)*methylphenyl*]-4,4-*dimethyl*-2-*oxazoline* (**21**).—Following the above procedure, the reaction of 4,4-dimethyl-2-phenyl-2-oxazoline (**18**) (1.9 g, 12.1 mmol) in tetrahydrofuran (50 ml) with n-butyl-lithium (9.5 ml; 1.4M-solution in hexane) with the subsequent addition of *p*-anisaldehyde (1.5 g, 11 mmol) and work-up as described above afforded a crude yellow oil (2.5 g). This oil was purified by h.p.l.c. [hexane–ethyl acetate (19:1)] to give unchanged (**18**) (0.7 g) and, as a yellow oil, 2-[2-*hydroxy*-(4-*methoxyphenyl*)-*methylphenyl*]-4,4-*dimethyl*-2-*oxazoline* (**21**) (1.3 g, 45%) (Found: M^+, 311.1484. $C_{19}H_{21}NO_3$ requires *M*, 311.1522); $\nu_{max.}$($CHCl_3$) 3 360 and 1 640 cm^{-1}; *m/z* 311 (M^+, 71%); δ 1.00 (3 H, s, CH_3), 1.27 (3 H, s, CH_3), 3.68 (3 H, s, OCH_3), 3.84 (1 H, d, *J* 10 Hz), 3.95 (1 H, d, *J* 10 Hz), 5.90 (1 H, s, CH), and 6.7—7.9 (8 H, complex, aromatic). The OH resonance was not observed; δ_C(p.p.m.) 27.76 (CH_3), 28.22 (CH_3), 55.01 (OCH_3), 67.74

($NCMe_2$), 74.20 (Ar*C*OH), 78.63 (CH_2O), 113.19, 126.73, 127.38, 127.78, 130.11, 130.55, and 131.31 (aromatic CH and C), 135.59 (aromatic C), 145.12 (aromatic C), 158.50 (aromatic C), and 162.52 (Ar*C*=N).

The alcohol (**21**) was further characterised by acetylation with acetic anhydride in pyridine to give the acetate (**22**); $\nu_{max.}$($CHCl_3$) 1 730 and 1 650 cm^{-1}; δ 1.24 (3 H, s, CH_3), 1.28 (3 H, s, CH_3), 1.92 (3 H, s, $COCH_3$), 3.64 (3 H, s, OCH_3), 3.94 (2 H, s, CH_2O), 6.70—7.90 (8 H, complex, aromatic), and 7.84 (1 H, s, ArC*H*O); δ_C(p.p.m.) 21.09 (CH_3), 28.08 ($NCMe_2$), 55.04 (OCH_3), 67.71 ($NCMe_2$), 73.18 (Ar*C*HO), 78.90 (CH_2O), 113.64, 126.72, 127.17, 127.56, 129.30, 130.22, 130.88, and 132.29 (aromatic CH and aromatic C), 140.23 and 159.23 (aromatic C), 162.26 (ArC=N), and 169.74 (CO).

The alcohol (**21**) was also characterised as the 3,5-dinitrobenzoate (**23**), $\nu_{max.}$($CHCl_3$) 1 735 and 1 650 cm^{-1}; δ 1.30 (3 H, s, CH_3), 1.32 (3 H, s, CH_3), 3.70 (3 H, s, OCH_3), 4.00 (2 H, s, CH_2O), 6.70—7.90 (8 H, complex, aromatic), 8.24 (1 H, s, ArC*H*O), and 9.0—9.2 (3 H, complex, aromatic); δ_C(p.p.m.) 28.24 (CH_3), 28.34 (CH_3), 55.19 (OCH_3), 68.20 ($NCMe_2$), 75.88 (ArC*H*O), and 78.64 (CH_2O). At lower field the following resonances are observed, but are difficult to assign: δ_C 113.75, 122.33, 126.80, 127.21, 128.05, 129.44, 130.30, 131.07, 134.11, 139.22, 148.58, 159.50, 161.04, and 161.64 p.p.m.

2-[2-*Hydroxy*(*phenyl*)*methylphenyl*]-4,4-*dimethyl*-2-*oxazoline* (**24**).—Following the above procedure, the reaction of 4,4-dimethyl-2-phenyl-2-oxazoline (**18**) (4.95 g, 31.1 mmol) in tetrahydrofuran (100 ml) with n-butyl-lithium (34 ml; 1.4M-solution in hexane), with subsequent addition of benzaldehyde (3.0 g, 28.3 mmol) and work-up, afforded a dark oil (7.3 g). Distillation (Kugelrohr) afforded unchanged (**18**) (1.65 g) and then, as a yellow oil, 2-[2-hydroxy(phenyl)methylphenyl]-4,4-dimethyl-2-oxazoline (**24**) (5.65 g, 71%), b.p. 174—178 °C (0.4 mmHg) (Found: M^+, 281.1400. $C_{18}H_{19}NO_2$ requires *M*, 281.1416); $\nu_{max.}$($CHCl_3$) 3 440, 3 200, and 1 640 cm^{-1}; *m*/*z* 281 (M^+, 59%); δ 1.00 (3 H, s, CH_3), 1.34 (3 H, s, CH_3), 3.88 (1 H, d, *J* 10 Hz), 4.02 (1 H, d, *J* 10 Hz), 5.93 (1 H, s, CH), and 7.1—7.95 (9 H, complex, aromatic). The OH resonance was not observed. δ_C(p.p.m.) 27.68 (CH_3), 28.27 (CH_3), 67.79 ($NCMe_2$), 74.89 (Ar*C*OH), 78.72 (CH_2O), 126.63, 126.78, 127.03, 127.53, 127.78, 130.46, 130.61, and 131.41 (aromatic CH and C), 143.53 and 144.68 (aromatic C), and 162.47 (ArC=N).

2-[2-*Hydroxy*(*phenyl*)*methyl*-4-*methoxyphenyl*]-4,4-*dimethyl*-2-*oxazoline* (**25**).—Following the above procedure, the reaction of 2-(4-methoxyphenyl)-4,4-dimethyl-2-oxazoline (**19**) (2.1 g, 10.4 mmol) in tetrahydrofuran (50 ml) with n-butyl-lithium (11.4 ml; 1.4M-solution in hexane), with subsequent addition of benzaldehyde (1.0 g, 9.4 mmol) and work-up, afforded a red oil (3.1 g). The crude oil was purified by flash chromatography [eluant, light petroleum–ether (2:1)] to give, as a pale yellow oil, 2-[2-hydroxy(phenyl)methyl-4-methoxyphenyl]-4,4-dimethyl-2-oxazoline (**25**) (1.5 g, 52%) (Found: M^+, 311.1567. $C_{19}H_{21}NO_3$ requires *M*, 311.1521); $\nu_{max.}$($CHCl_3$) 1 640 cm^{-1}; *m*/*z* 311 (M^+, 61%); δ 1.00 (3 H, s, CH_3), 1.32 (3 H, s, CH_3), 3.92 (1 H, d, *J* 10 Hz), 4.03 (1 H, d, *J* 10 Hz), 3.80 (3 H, s, OCH_3), 5.90 (1 H, s, CH), and 6.6—8.0 (8 H, complex, aromatic). The OH resonance was not observed. δ_C(p.p.m.) 27.78 (CH_3), 28.33 (CH_3), 55.27 (OCH_3), 67.74 ($NCMe_2$), 75.03 (Ar*C*OH), 78.62 (CH_2O), 111.93 (aromatic CH), 116.70 (aromatic CH), 118.99 (aromatic C), 126.69 (aromatic CH), 127.83 (aromatic CH), 132.59 (aromatic CH), and 143.29, 146.92, 161.78, and 162.23 (aromatic C and ArC=N).

1-(2-*Hydroxy*-1,1-*dimethylethylimino*)-4-*methoxy*-3-*phenyl*-1,3-*dihydro*-2-*benzofuran* (**30**).—Following the above procedure, the reaction of 2-(3-methoxyphenyl)-4,4-dimethyl-2-oxazoline (**20**) (6.37 g, 31.1 mmol) in tetrahydrofuran (50 ml) with n-butyl-lithium (24.4 ml; 1.4M-solution in hexane) with subsequent addition of benzaldehyde (3.0 g, 28.2 mmol) and work-up as described above afforded, as a white crystalline solid from ethyl acetate–light petroleum, 1-(2-*hydroxy*-1,1-*dimethylethylimino*)-4-*methoxy*-3-*phenyl*-1,3-*dihydro*-2-*benzofuran* (**30**) (6.9 g, 84%), m.p. 142—144 °C (Found: C, 73.3; H, 6.8; N, 4.4. $C_{19}H_{21}NO_3$ requires C, 73.3; H, 6.8; N, 4.5%); $\nu_{max.}$($CHCl_3$) 3 440 and 1 700 cm^{-1}; *m*/*z* 311 (M^+, 16%), 280 (100); δ (60 MHz) 1.33 (6 H, s, CH_3), 2.9—3.3 (1 H, br, OH), 3.3—3.6 (2 H, m, CH_2), 3.7 (3 H, s, OCH_3), 6.5 (1 H, s, CH), and 6.7—7.6 (8 H, complex, aromatic). After 14 h at *ca.* 30 °C, a solution of (**30**) in $CDCl_3$ showed additional signals at δ 0.74 (3 H, s, CH_3), 1.24 (3 H, s, CH_3), 3.76 (1 H, d, *J* 10 Hz), 3.86 (1 H, d, *J* 10 Hz), 3.84 (3 H, s, OCH_3), and additional aromatic resonances. The following signals in the ^{13}C n.m.r. spectrum were associated with (**30**); 23.15 (CH_3), 56.21 ($NCMe_2$), 72.86 p.p.m. (CH_2OH), and the following signals with the isomer (**26**), 27.34 (CH_3), 27.93 (CH_3), 67.65 ($NCMe_2$), and 78.62 p.p.m. (CH_2O).

2-[2-*Hydroxy*(*benzyl*)*methylphenyl*]-4,4-*dimethyl*-2-*oxazoline* (**12**).—Following the same procedure, the reaction of 4,4-dimethyl-2-phenyl-2-oxazoline (**18**) (1.60 g, 9.15 mmol) in anhydrous tetrahydrofuran (50 ml) with n-butyl-lithium (6.3 ml; 1.4M-solution in hexane), with subsequent addition of freshly distilled phenylacetaldehyde (1.0 g, 8.32 mmol) and work-up as described above, afforded a yellow oil (2.95 g). Distillation (Kugelrohr) afforded unchanged (**18**) (0.9 g) and, as an orange oil, 2-[2*hydroxy*(*benzyl*)*methylphenyl*]-4,4-*dimethyl*-2-*oxazoline* (**12**) (1.44 g, 59%); b.p. 90—100 °C (0.9 mmHg) (Found: M^+, 295.1499. $C_{19}H_{21}NO_2$ requires *M*, 295.1426); $\nu_{max.}$($CHCl_3$) 1 640 cm^{-1}; *m*/*z* 295 (M^+, 9%); δ 1.44 (3 H, s, CH_3), 1.46 (3 H, s, CH_3), 3.0—3.4 (2 H, complex, ArCH_2), 4.15 (2 H, s, CH_2O), 4.9—5.16 (1 H, complex, CH), and 7.0—8.0 (9 H, complex, aromatic); δ_C(p.p.m.) 28.33 ($NCMe_2$), 42.98 (ArCH_2), 68.14 ($NCMe_2$), 75.91 (ArCH_2*C*OH), 78.71 (CH_2O), 126.08, 127.98, 128.23, 128.41, 129.07, 129.34, 130.79, and 131.42 (aromatic CH and C), and 139.45 and 144.78 (aromatic C).

3-(2-*Hydroxy*-1,1-*dimethylethylimino*)-1,3-*dihydro*-2-*benzofuran*-1-*spirocycloheptane* (**31**).—Following the above procedure, the reaction of 4,4-dimethyl-2-phenyl-2-oxazoline (**18**) (6.86 g, 39.3 mmol) in tetrahydrofuran (100 ml) with n-butyl-lithium (39.1 ml, 43.0 mmol; 1.1M-solution in hexane), with subsequent addition of cycloheptanone (4.0 g, 35.8 mmol) and work-up as described above afforded, as a white crystalline solid from light petroleum, 3-(2-hydroxy-1,1-dimethylethylimino)-1,3-dihydro-2-benzofuran-1-spirocycloheptane (**31**) (4.5 g, 45%), m.p. 105—107 °C (lit.,[6] m.p. 95—97 °C); $\nu_{max.}$($CHCl_3$) 3 400 and 1 685 cm^{-1}; *m*/*z* 287 (M^+, 1%) and 256 (*M* − 31, 100); δ 1.42 (6 H, s, CH_3), 1.5—2.2 (12 H, complex, CH_2), 3.15 (1 H, br, OH), 3.44 (2 H, s, CH_2O), and 7.2—7.8 (4 H, complex, aromatic).

1-(2-*Hydroxy*-1,1-*dimethylethylimino*)-3,3-*dimethyl*-1,3-*dihydro*-2-*benzofuran* (**32**).—Following the above procedure, the reaction of 4,4-dimethyl-2-phenyl-2-oxazoline (**18**) (3.3 g, 18.9 mmol) in tetrahydrofuran (50 ml) with n-butyl-lithium (14.8 ml; 1.4M-solution in hexane), with subsequent addition of acetone (1.0 g, 17.2 mmol) and work-up as described above, afforded, as a white crystalline solid from ethyl acetate–light petroleum, 1-(2-*hydroxy*-1,1-*dimethylethylimino*)-3,3-*dimethyl*-1,3-*dihydro*-2-*benzofuran* (**32**) (1.85 g, 46%), m.p. 85—87 °C (Found: C, 72.1; H, 8.2; N, 6.0. $C_{14}H_{19}NO_2$ requires C, 72.1; H, 8.2; N, 5.9%); $\nu_{max.}$($CHCl_3$) 3 460 and 1 700 cm^{-1}; *m*/*z* 202 (*M* − 31, 100%); δ 1.33 (6 H, s, CH_3), 1.62 (6 H, s, CH_3), 2.86—3.26 (1 H, br, OH), 3.45 (2 H, s, CH_2O), and 7.3—7.8 (4 H, complex, aromatic).

1-(2-*Hydroxy*-1,1-*dimethylethylimino*)-3-*methyl*-3-*phenyl*-1,3-*dihydro*-2-*benzofuran* (**33**).—Following the above procedure, the reaction of 4,4-dimethyl-2-phenyl-2-oxazoline (**18**) (3.2 g, 18.3 mmol) in tetrahydrofuran (100 ml) with n-butyl-lithium (14.4 ml; 1.4M-solution in hexane), with subsequent addition of acetophenone (2.0 g, 16.6 mmol) and work-up as described above, afforded a crude red oil (5.76 g). This oil was purified by flash chromatography [eluant, light petroleum–ether (1:1)] to give, as a yellow oil, 1-(2-hydroxy-1,1-dimethylethylimino)-3-methyl-3-phenyl-1,3-dihydro-2-benzofuran (**33**) (3.15 g, 64%), $\nu_{max.}$($CHCl_3$) 3.460, 2 960, and 1 700 cm^{-1}; *m/z* 295 (M^+, 6%), 280 (6), and 264 (54); δ (60 MHz), 1.40 (6 H, s, CH_3), 1.95 (3 H, s, CH_3), 2.8—3.3 (1 H, br, OH), 3.45 (2 H, s, CH_2), and 7.1—7.9 (9 H, complex, aromatic).

1-(2-*Hydroxy*-1,1-*dimethylethylimino*)-3,3-*diphenyl*-1,3-*dihydro*-2-*benzofuran* (**34**).—Following the above procedure, the reaction of 4,4-dimethyl-2-phenyl-2-oxazoline (**18**) (2.11 g, 12.1 mmol) in tetrahydrofuran (100 ml) with n-butyl-lithium (9.5 ml; 1.4M-solution in hexane), with subsequent addition of benzophenone (2.0 g, 11.0 mmol) and work-up as described above, afforded an orange oil (5.76 g). This crude oil was purified by flash chromatography [eluant, light petroleum–ether (1:1)] to give, as a yellow oil, 1-(2-hydroxy-1,1-dimethylethylimino)-3,3-diphenyl-1,3-dihydro-2-benzofuran (**34**) (2.45 g, 62%), *m/z* 357 (M^+, 19%), 326 (M − 31, 100); δ (60 MHz), 1.40 (6 H, s, CH_3), 3.75 (2 H, s, CH_2O), and 7.15—7.95 (14 H, complex, aromatic).

3-(2-*Hydroxy*-1,1-*dimethylethylimino*)-6-*methoxy*-1,3-*dihydro*-2-*benzofuran*-1-*spirocyclohexane* (**35**).—Following the above procedure, the reaction of 2-(4-methoxyphenyl)-4,4-dimethyl-2-oxazoline (**19**) (6.9 g, 33.6 mmol) in tetrahydrofuran (100 ml) with n-butyl-lithium (26 ml; 1.4M-solution in hexane), with subsequent addition of cyclohexanone (3.0 g, 30.6 mmol) and work-up as described above, afforded, as a white crystalline solid from ethyl acetate–light petroleum, 3-(2-*hydroxy*-1,1-*dimethylethylimino*-6-*methoxy*-1,3-*dihydro*-2-*benzofuran*-1-*spirocyclohexane* (**35**) (4.7 g, 52%), m.p. 115—117 °C (Found: C, 71.2; H, 8.3; N, 4.6. $C_{18}H_{25}NO_3$ requires C, 71.4; H, 8.2; N, 4.6%); $\nu_{max.}$($CHCl_3$) 3 420 and 1 690 cm^{-1}; *m/z* 303 (M^+, 1%), 272 (100); δ 1.44 (6 H, s, CH_3), 1.60—1.96 (10 H, complex, CH_2), 3.2—3.5 (1 H, br, OH), 3.45 (2 H, s, CH_2O), 3.85 (3 H, s, OMe), and 6.68—7.83 (3 H, complex, aromatic); δ_C(p.p.m.) 22.72 (CH_3), 23.15 (CH_2), 25.00 (CH_2), 36.73 (CH_2), 55.62 (OCH_3), 55.66 (Me_2CN), 73.03 (CH_2OH), 88.03 (ArCO), 105.08, 115.16, and 125.01 (aromatic CH), 123.61 (aromatic C), 152.89 (aromatic C), 159.51 (COMe), and 162.60 (C=N).

3-(2-*Hydroxy*-1,1-*dimethylethylimino*)-6-*methoxy*-1,3-*dihydro*-2-*benzofuran*-1-*spirocyclopentane* (**36**).—Following the above procedure, the reaction of 2-(4-methoxyphenyl)-4,4-dimethyl-2-oxazoline (**19**) (5.36 g, 26.1 mmol) in tetrahydrofuran (100 ml) with n-butyl-lithium (20.5 ml; 1.4M-solution in hexane), with subsequent addition of cyclopentanone (2.0 g, 23.8 mmol) and work-up as described above, afforded, as a white crystalline solid from ethyl acetate–light petroleum, 3-(2-*hydroxy*-1,1-*dimethylethylimino*)-6-*methoxy*-1,3-*dihydro*-2-*benzofuran*-1-*spirocyclopentane* (**36**) (2.7 g, 40%), m.p. 106—108 °C (Found: C, 70.8; H, 8.0; N, 4.8. $C_{17}H_{23}NO_3$ requires C, 70.6; H, 8.0; N, 4.8%); $\nu_{max.}$($CHCl_3$) 3 440 and 1 690 cm^{-1}; *m/z* 289 (M^+, 0.5%), 258 (100); δ 1.36 (6 H, s, CH_3), 2.0 (8 H, br s, CH_2), 3.34 (1 H, OH), 3.42 (2 H, s, CH_2O), 3.82 (3 H, s, OCH_3), and 6.6—7.7 (3 H, complex, aromatic); δ_C(p.p.m.) 23.18 (CH_3), 24.96 (CH_2), 40.12 (CH_2), 55.67 (OCH_3), 56.67 ($NCMe_2$), 72.99 (CH_2O), 96.68 (ArCO), 104.88, 115.22, and 124.66 (aromatic CH), 124.36, 150.56, and 157.47 (COMe), and 162.83 (ArC=N).

1-(2-*Hydroxy*-1,1-*dimethylethylimino*)-3,3-*di-isopropyl*-5-*methoxy*-1,3-*dihydro*-2-*benzofuran* (**37**).—Following the above procedure, the reaction of 2-(4-methoxyphenyl)-4,4-dimethyl-2-oxazoline (**19**) (6.0 g, 29.2 mmol) in tetrahydrofuran (100 ml) with n-butyl-lithium (22 ml; 1.4M-solution in hexane), with subsequent addition of di-isopropyl ketone (3.0 g, 26.3 mmol) and work-up as described above, afforded, as a white crystalline solid from light petroleum 1-(2-*hydroxy*-1,1-*dimethylethylimino*)-3,3-*di-isopropyl*-5-*methoxy*-1,3-*dihydro*-2-*benzofuran* (**37**) (6.9 g, 82%), m.p. 96—98 °C (Found: C, 71.6; H, 9.0; N, 4.3. $C_{19}H_{29}NO_3$ requires C, 71.4; H, 9.1; N, 4.3%); $\nu_{max.}$($CHCl_3$) 3 420, 2 960, and 1 685 cm^{-1}; *m/z* 288 (M − 31, 100%); δ 0.8—0.95 (12 H, complex, CH_3), 1.38 (6 H, s, CH_3), 2.2—2.6 (2 H, sept., CH), 3.3—3.55 (3 H, br s, OH and CH_2O), 3.85 (3 H, s, OCH_3), and 6.7—7.8 (3 H, complex, aromatic); δ_C(p.p.m.) 16.79 and 17.03 (CH_3), 23.05 (CH_3), 33.17 (CH), 55.57 (OCH_3), 56.61 ($NCMe_2$), 72.90 (CH_2O), 96.42 (ArCO), 106.56, 114.40, and 124.72 (aromatic CH), 126.15, 148.31, 159.05 (COMe), and 162.23 (ArC=N).

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