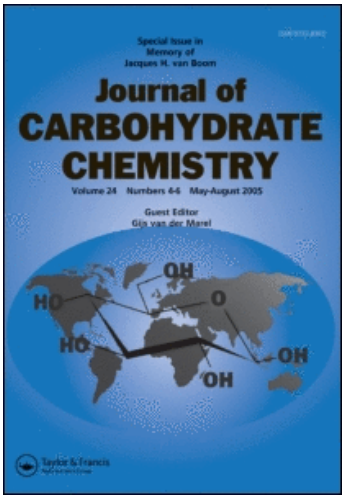

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

π-Facial Selectivity in the Cycloaddition of Nitrile Oxides to 5,6-Dideoxy-5-Enofuranoses

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To cite this Article Blake, Alexander J. , Kirkpatrick, Graeme , McGhie, Karen E. , Paton, R. Michael and Penman, Kenneth J.(1994) 'π-Facial Selectivity in the Cycloaddition of Nitrile Oxides to 5,6-Dideoxy-5-Enofuranoses', Journal of Carbohydrate Chemistry, 13: 3, 409 — 419
To link to this Article: DOI: 10.1080/07328309408009202
URL: http://dx.doi.org/10.1080/07328309408009202

J. CARBOHYDRATE CHEMISTRY, 13(3), 409-419 (1994)

π-FACIAL SELECTIVITY IN THE CYCLOADDITION OF NITRILE OXIDES TO 5,6-DIDEOXY-5-ENOFURANOSES

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Received August 13, 1993 - Final Form December 28, 1993

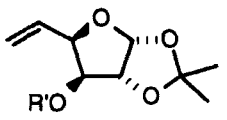
ABSTRACT

Benzonitrile oxide and ethoxycarbonylformonitrile oxide cycloadd regiospecifically and diastereoselectively to α-methyl 5,6-dideoxy-2,3-*O*-isopropylidene-D-*lyxo*-hex-5-enofuranoside **7** to afford isoxazolines **10** and **11**. The π-facial selectivity (*ca.* 7:1) is comparable with that observed for *xylo*-alkene **1**, and much greater than that for its *ribo*-isomer **4**. The structure of isoxazoline **10a** was determined by X-ray crystallography.

INTRODUCTION

5,6-Dideoxyhex-5-enofuranosides provide readily accessible starting materials for the synthesis of higher monosaccharides using nitrile oxide/isoxazoline methodology.[1,2] Of particular significance for the effective use of such compounds is an understanding of the factors controlling π-facial selectivity in their cycloaddition reactions with nitrile oxides ($RC{=}N^{+}{-}O^{-}$). We[1-3] and others[4-6] have reported that various nitrile oxides react with D-*xylo*-hex-5-enofuranoses **1** with high levels of diastereoselectivity (73-93% d.e.) in favour of adducts **2** with *erythro* stereochemistry at C(4)-C(5) over *threo*-isomers **3**. In contrast, for the corresponding D-*ribo* analogue **4**, which is epimeric with **1** at the homoallylic position C(3), *erythro* and *threo* adducts **5** and **6** are formed in approximately equal

amounts.[3] In order to probe the influence of substituents at C(2) we have examined the selectivity of nitrile oxide cycloaddition reactions of D-mannose-derived D-*lyxo*-hex-5-enofuranose analogue **7** using benzonitrile oxide and ethoxycarbonylformonitrile oxide as representative examples.



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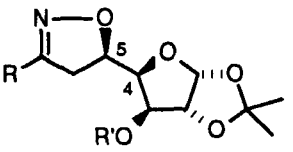

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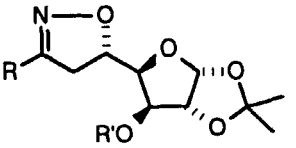

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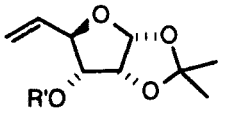

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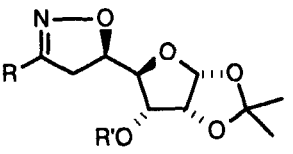

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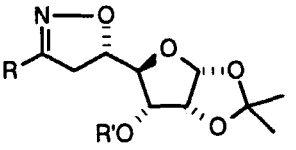

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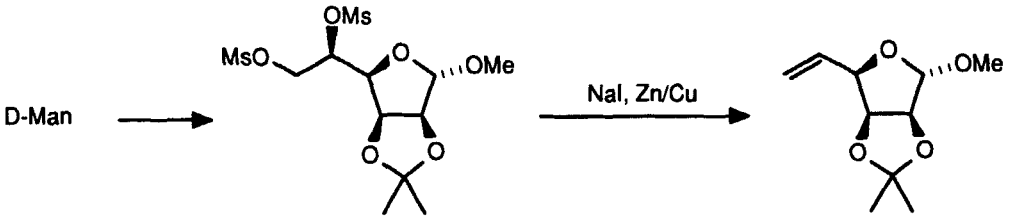
RESULTS AND DISCUSSION

D-*lyxo*-Hex-5-enofuranoside **7** was prepared from D-mannose by a modification of the literature[7] route (Scheme 1). Conversion of D-mannose to methyl 2,3-*O*-isopropylidene-α-D-*lyxo*-furanoside,[8] followed by reaction with methanesulphonyl chloride yielded dimesylate **8**[8] as a shelf-stable crystalline solid. Subsequent treatment of **8** with sodium iodide and a zinc/copper couple afforded alkene **7** in 89% yield. The overall yield from D-mannose was 61%.

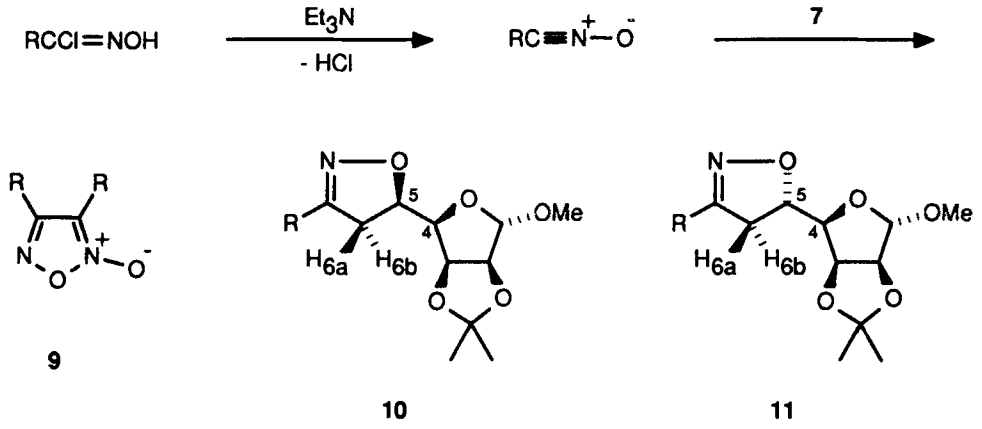


8 **7**

Scheme 1

Cycloaddition reactions– The first nitrile oxide to be examined was benzonitrile oxide (PhCNO), which was generated *in situ* by dehydrochlorination of the corresponding hydroximoyl chloride.[9] The competing dimerisation to 3,4-diphenylfurazan *N*-oxide **9a**[10]

was minimised by slow addition (over 36 hours) of triethylamine to a solution of benzohydroximoyl chloride and a slight excess of alkene **7** (1:1.5) in diethyl ether at 0 °C. From the reaction mixture were isolated by chromatography unreacted **7** (27%), furazan *N*-oxide **9a** (16%) and a mixture of two isoxazoline cycloadducts **10a** and **11a** in a combined yield of 82% (Scheme 2).



Scheme 2 (**a**, R = Ph; **b**, R = CO_2Et)

The individual adducts were separated by chromatography and purified by crystallisation. They are readily distinguished by their NMR spectra (Table 1). In each case the isoxazoline ring protons give rise to a characteristic ABX system with H(5), which is adjacent to the ring oxygen, at highest chemical shift. The ^3J values of 10-12 Hz and 8-9 Hz for H(5)–H(6a,b), and the geminal coupling of 16-18 Hz for H(6a)–H(6b) are also typical of carbohydrate isoxazolines.[3-6] The isomer ratio (82:18) was measured from the NMR spectrum of the product mixture by comparison of the glycosidic methyl proton signals, which are well separated ($\Delta\delta_H$ = 0.05 ppm) despite their remoteness from the centre of asymmetry.

The structure of the major adduct was determined by X-ray crystallography (Figure 1) which established that it is compound **10a** with *R*-configuration at C(5), the new chiral centre. The minor product is therefore 5-*S* isomer **11a**. Neither of the other two possible cycloadducts in which the oxygen of the nitrile oxide is attached to C(6), rather than C(5), of the dipolarophile were formed; the reaction is therefore regiospecific and diastereoselective (64% d.e.) in favour of the product with D-*manno* configuration, *i.e.* with *erythro* stereochemistry for C(5)-C(6).

Ethoxycarbonylformonitrile oxide (EtO_2CCNO) reacted similarly affording 3,4-di-ethoxycarbonylfurazan *N*-oxide (**9b**, 24%) and a mixture of two isoxazolines **10b** and **11b** in a combined yield of 76%. The isomer ratio (82:18) was determined from the ^1H NMR

TABLE 1. Selected ^1H NMR Data[a] for Isoxazolines **10** and **11**

		10a	**11a**	**10b**	**11b**			**10a**	**11a**	**10b**	**11b**
δ_H/ppm	H(1)	4.91	4.99	4.86	4.96	*J*/Hz	1,2	<1	<1	<1	<1
	H(2)	4.58	4.57	4.52	4.54		2,3	5.9	5.9	6.0	6.0
	H(3)	4.81	4.75	4.71	4.69		3,4	3.6	3.8	3.7	3.8
	H(4)	4.08	4.07	4.06	4.01		4,5	6.3	8.5	5.3	8.5
	H(5)	5.05	4.94	5.03	4.97		5,6a	8.6	10.6	8.3	11.2
	H(6a)	3.45	3.12	3.32	3.40		5,6b	9.7	8.7	11.2	9.1
	H(6b)	3.45	3.57	3.20	2.99		6a,6b	-	16.9	18.1	18.0
	OCH_3	3.30	3.35	3.26	3.32						

a. Recorded in $CDCl_3$ at 200 or 360 MHz

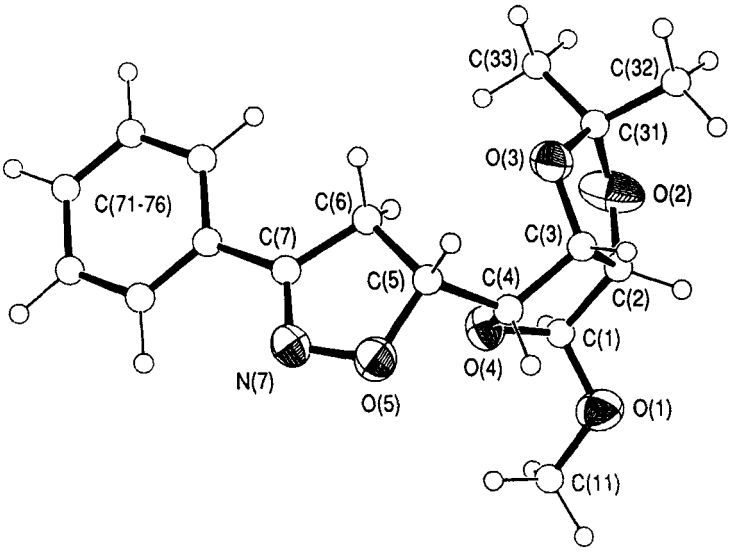


Figure 1 Crystal structure of isoxazoline **10a**

spectrum of the reaction mixture and the individual products were separated by chromatography. The NMR data for the furanose and isoxazoline portions of these adducts are very similar to those for their phenyl analogues **10a** and **11a** (see Table 1). In particular, for the major adduct proton H(1) absorbs at lower frequency ($\Delta\delta_H$ -0.10 ppm) and H(5) at higher frequency ($\Delta\delta_H$ +0.06 ppm) than the corresponding peaks for the

TABLE 2. π-Facial Selectivity for Cycloaddition of Nitrile Oxides to Alkenes **1**, **4** and **7**

Alkene	Nitrile oxide	Isoxazolines(%) *erythro*	*threo*	Reference
7	PhCNO	82	18	*a*
7	EtO_2CCNO	82	18	*a*
1[b]	PhCNO	84	16	5
		86	14	3
1[b]	EtO_2CCNO	94	6	5
		90	10	3
4[b]	EtO_2CCNO	51	49	3
4[b]	PhCNO	42	58	3

a. present work; *b.* R' = Bn for **1** and **4**

minor product. On this basis the major adduct was assigned structure **10b** which, like **10a**, has the *R*-configuration at the newly-created asymmetric centre C(5) and an *erythro* relationship for C(4)-C(5). The minor isomer therefore has structure **11b**.

π-Facial selectivity– The ratios of products resulting from the cycloaddition of benzonitrile oxide and ethoxycarbonylformonitrile oxide to D-*lyxo*-hex-5-enofuranose **7** are compared in Table 2 with those reported[3-6] for the corresponding reactions with *xylo*-hex-5-enofuranoses **1** and the *ribo* analogue **4**. The degree of selectivity observed in the present work on *lyxo*-alkene **7** in favour of *erythro* adducts is similar to that reported for the same nitrile oxides with *xylo*-alkene **1**, and in marked contrast to the results for *ribo* isomer **4**. In the latter case cycloaddition with ethoxycarbonylformonitrile oxide gave two adducts in approximately equal amounts, and there was a slight preference for *threo* adduct formation in the reaction with benzonitrile oxide.[3] The predominance of *erythro* adducts with dipolarophiles **1** and **7** can be rationalised in terms of the "inside alkoxy effect" proposed by Houk *et al*[11] to account for nitrile oxide cycloadditions to chiral allyl ethers; the preferred transition state has the largest substituent *anti*, the smallest (H) "outside", and the alkoxy in the "inside" position. For 5,6-dideoxy-5-enofuranoses the *anti* substituent is linked *via* the furanose ring to the inside alkoxy as illustrated in Figure 2. Alkenes **1** and **7**, which show similar selectivity towards nitrile oxides, have the same *threo* relationship for the substituents at the allylic and homoallylic positions (Figure 3). In contrast, for the less selective alkene **4** these groups are *erythro* (Figure 4). These

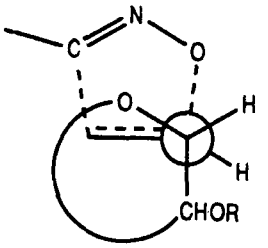


Figure 2

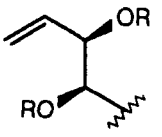


Figure 3

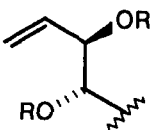


Figure 4

TABLE 3. Cremer and Pople Puckering Parameters[12] for Isoxazoline **10a**

	Isoxazoline O(5)-N(7)-C(7)-C(6)-C(5)	Furanose C(1)-C(2)-C(3)-C(4)-O(4)	Dioxolane C(2)-O(2)-C(31)-O(3)-C(3)
Q/Å	0.030	0.352	0.265
θ/degrees	130.1	136.8	263.0

results highlight the key role played by homoallylic substituents in determining the stereochemical outcome of nitrile oxide cycloadditions to hex-5-enofuranoses. Whereas the homoallylic group at C(3) can either reinforce or oppose the effect of the allylic group, reversal of configuration at the next-removed positon C(2) has little effect.

Structure of isoxazoline **10a**– The Cremer and Pople puckering parameters[12] for the isoxazoline, furanose and 1,3-dioxolane rings are given in Table 3. The isoxazoline is nearly planar with the torsion angles involving the ring atoms ranging from 0.9 to 2.9 Å, and all atoms lying within 0.05 Å of the best plane through them. The ϕ value of 130.1° indicates that the ring is in a near twist conformation (ϕ = 126°). For the furanose ϕ = 136.8° indicating that it is intermediate between twist (ϕ = 126°) and envelope (°*E*, ϕ = 144°); O(4) lies 0.52 Å above the best plane through C(1)–C(2)–C(3)–C(4). Likewise the conformation of the 1,3-dioxolane (ϕ = 263.0°) is also between envelope (ϕ = 252°) and twist (ϕ = 270°). The phenyl substituent at C(7) is twisted by *ca.* 9° out of the plane of the isoxazoline.

Selected H–C–C–H torsion angles from the X-ray data are compared with the corresponding observed and calculated[13] proton-proton couplings in Table 4. A noteworthy feature of the crystal structure is the 77.3° torsion angle for H(4)–C(4)–C(5)–

TABLE 4. Selected Torsion Angles Involving Hydrogen [H(X)–C(X)–C(Y)–H(Y)] for Isoxazoline **10a** with Observed and Calculated[a] Coupling Constants.

	H_X,H_Y					
	1,2	2,3	3,4	4,5	5,6a	5,6b
Angle/degrees	94.5	4.6	27.3	77.3	3.0	119.8
J_{calc}/Hz	1.5	8.0	6.5	1.5	8.0	3.9
J_{obs}/Hz	<1	5.9	3.6	6.3	9.7	8.6

a. $7.76\cos^2\theta - 1.1\cos\theta + 1.4$ (ref. 13)

H(5) involving the protons attached to the carbon atoms linking the furanose and newly formed isoxazoline ring. In solution the corresponding ^1H–^1H coupling is 6.3 Hz, which is much greater than the calculated value (1.5 Hz). This suggests that the preferred conformation in solution differs markedly from that found in the crystal. In contrast, other reported isoxazolines show a generally good correlation between the two values. For example, for isoxazoline **2** (R=Ph, R'=Bn)[3] the coupling of 8.2 Hz is consistent with the antiperiplanar arrangement found in the crystal (torsion angle 179.5°). In the crystal of isomer **5** (R= Ph, R'=Bn)[3] the C–H bonds are near orthogonal (torsion angle 77.3°) and this is reflected in the coupling of 2.1 Hz. Isoxazolines **10a**, **10b**, **11a** and **11b** all have comparable couplings between H(4) and H(5), suggesting that they adopt similar conformations in solution.

In conclusion, cycloaddition of nitrile oxides to D-mannose-derived dipolarophile **7** occurs regiospecifically and diastereoselectively with the major adduct having D-*manno* configuration, *i.e.* corresponding to an *erythro* relationship between C(4) and the new asymmetric centre at C(5). This alkene therefore provides a readily accessible starting material for the synthesis of novel carbohydrate derivatives using nitrile oxide/isoxazoline methodology.

EXPERIMENTAL

General Procedures. Melting points were determined in a metal block and are uncorrected. TLC was carried out on Silica Gel F_{254} (Merck) with detection by UV

absorbance or staining with $KMnO_4$. Silica Gel 60 (Merck) was used for dry flash-column chromatography. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. FAB mass spectra were recorded on a Kratos MS50TC instrument. Brucker WH360 and WP200Y spectrometers were used to obtain NMR spectra.

Methyl 5,6-Dideoxy-2,3-*O*-isopropylidene-α-D-*lyxo*-hex-5-enofuranoside (7).[7] To a stirred solution of methyl 1,2-*O*-isopropylidene-5,6-dimethanesulphonyl-α-D-*gluco*-furanoside[8] (7.0 g, 17.95 mmol) and dried sodium iodide (13.45 g, 89.7 mmol) in dimethyl formamide (85 mL) and 1,2-dimethoxyethane (14 mL) was added zinc-copper couple (prepared from 5.87 g zinc dust). The mixture was heated under reflux for 70 minutes, allowed to cool and poured into water (230 mL), and the product extracted into toluene (3 x 150 mL). The combined toluene extracts were washed with water, dried ($MgSO_4$) and concentrated *in vacuo* to a syrup. The product was purified by dry flash chromatography on silica to afford an oil (3.20 g, 89%); δ_H (200 MHz, $CDCl_3$) 5.90 (ddd, $J_{5,6a}$ = 17.5, $J_{5,6b}$ = 10.3, $J_{5,4}$ = 7.3 Hz, H-5), 5.32 (ddd, 1H, $J_{6a,6b}$ = 1.8 Hz, H-6a), 5.23 (ddd, 1H, H-6b), 4.82 (s, 1H, H-1), 4.58 (dd, 1H, $J_{3,2}$ = 5.9, $J_{3,4}$ = 3.7 Hz, H-3), 4.49 (d, 1H, H-2), 4.29 (dddd, 1H, $J_{4,6a}$ = 1.0, $J_{4,6b}$ = 0.9 Hz, H-4), 3.25 (s, 3H, OMe), 1.37, 1.22 ppm (s, 2 x 3H, CMe_2); δ_C (50 MHz, $CDCl_3$) 132.2 (C-5), 118.6 (C-6), 112.5 (*C*Me_2), 106.8 (C-1), 85.0 (C-4), 81.3, 80.8 (C-2,3), 54.3 (OMe), 25.7, 24.3 (Me).

Cycloaddition of Benzonitrile Oxide. A solution of triethylamine (390 mg, 3.86 mmol) in diethyl ether (25 mL) was added over 41 h using a motorised syringe pump to a stirred solution of alkene **7** (965 mg, 4.83 mmol) and benzohydroximoyl chloride[9] (500 mg, 3.22 mmol) in diethyl ether (25 mL) at 0 °C. After stirring for a further 6 hours, the precipitated $Et_3N.HCl$ was removed by filtration and the filtrate washed with water (25 mL). The ether layer was dried ($MgSO_4$) and concentrated *in vacuo* to afford a yellow solid. Dry flash chromatography (silica, 15 -> 30% Et_2O in hexane, gradient elution) yielded unreacted **7** (260 mg, 27%) and diphenylfurazan *N*-oxide **9a** (62 mg, 16%) followed by a fraction containing the isoxazoline cycloadducts. 10% of this mixture was retained for isomer ratio determination and the remainder rechromatographed to afford in order of elution 5*R*-5-(2,3-*O*-isopropylidene-1-*O*-methyl-α-D-*lyxo*-tetrofuranos-4-yl)-3-phenyl-2-isoxazoline **10a** (707 mg, 69%) [white needles (from MeOH), mp 123-125 °C; $[\alpha]_D^{22}$ -35.2° (*c* 1.29, $CHCl_3$); δ_C (50 MHz, $CDCl_3$) 156.7 (C-7), 129.9, 128.5, 126.6 (5 x Ph*C*H), 129.4 (Ph*C*), 112.5 (*C*Me_2), 107.1 (C-1), 84.8, 79.4, 79.1, 78.1 (C-2, C-3, C-4, C-5), 54.6 (OMe), 37.3 (C-6), 25.7, 24.2 (Me); *m/z* (FAB, thioglycerol) 320.14979 (*M*+1), $C_{17}H_{22}NO_5$ requires 320.14979] and 5*S*-5-(2,3-*O*-isopropylidene-1-*O*-methyl-α-D-*lyxo*-tetrofuranos-4-yl)-3-phenyl-2-isoxazoline **11a** (133 mg, 13%) [white solid (from MeOH), mp 130-131 °C; $[\alpha]_D^{22}$ 24.8° (*c* 1.17, $CHCl_3$); δ_C (50 MHz, $CDCl_3$) 156.2 (C-8), 130.0, 128.5, 126.5 (5 x Ph*C*H), 129.2 (Ph*C*), 112.8 (*C*Me_2), 107.3 (C-1), 84.7, 81.3,

TABLE 5. Fractional Co-ordinates for Isoxazoline **10a**

	x	y	z	U_{iso}
C(1)	0.5318(4)	0.6264	0.7371(4)	0.0487(21)
O(1)	0.5300(3)	0.5261(4)	0.8252(3)	0.0599(17)
C(11)	0.4812(6)	0.4090(5)	0.7666(5)	0.074(3)
C(2)	0.5647(5)	0.7443(5)	0.8169(4)	0.0516(20)
C(3)	0.3786(4)	0.8040(5)	0.8291(3)	0.0427(17)
O(2)	0.6626(3)	0.8350(4)	0.7477(4)	0.0730(19)
O(3)	0.3872(3)	0.9161(4)	0.75510(25)	0.0514(14)
C(31)	0.5713(5)	0.9501(5)	0.7443(4)	0.0531(21)
C(32)	0.6310(6)	1.0322(6)	0.8575(5)	0.077(3)
C(33)	0.5951(8)	1.0142(8)	0.6148(5)	0.101(4)
C(4)	0.2539(4)	0.7093(5)	0.7643(3)	0.0399(16)
O(4)	0.36386(25)	0.6436(4)	0.67405(20)	0.0440(12)
C(5)	0.0895(4)	0.7600(5)	0.6927(3)	0.0426(17)
C(6)	0.1193(4)	0.8154(5)	0.5576(3)	0.0491(19)
C(7)	0.0006(4)	0.7333(5)	0.4753(3)	0.0393(17)
O(5)	-0.0301(3)	0.6530(4)	0.67105(22)	0.0498(13)
N(7)	-0.0777(3)	0.6458(4)	0.53736(25)	0.0456(16)
C(71)	-0.0236(3)	0.7456(4)	0.33320(14)	0.0421(17)
C(72)	-0.1132(3)	0.6533(4)	0.26072(14)	0.0500(19)
C(73)	-0.1320(3)	0.6657(4)	0.12585(14)	0.0591(23)
C(74)	-0.0612(3)	0.7704(4)	0.06345(14)	0.067(3)
C(75)	0.0285(3)	0.8628(4)	0.13593(14)	0.069(3)
C(76)	0.0473(3)	0.8504(4)	0.27080(14)	0.0531(21)

80.2, 79.6 (C-2, C-3, C-4, C-5), 54.6 (OMe), 37.5 (C-6), 25.8, 24.6 (Me); *m/z* (FAB, thioglycerol) 320.14979 (*M*+1), $C_{17}H_{22}NO_5$ requires 320.14979]. ^1H NMR data for isoxazolines **10a** and **11a** are given in Table 1. The isomer ratio (**10a**:**11a** = 82:18) was measured from the ^1H NMR spectrum of the mixture of adducts by comparison of the OMe peaks at 3.30 and 3.35 ppm.

10a: Anal. Calcd for $C_{17}H_{21}NO_5$: C, 63.9; H, 6.6; N, 4.4. Found: C, 64.0; H, 6.8; N, 4.3.

11a: Anal. Calcd for $C_{17}H_{21}NO_5$: C, 63.9; H, 6.6; N, 4.4. Found: C, 63.8; H, 6.4; N, 4.6.

Cycloaddition of Ethoxycarbonylformonitrile Oxide. Using the procedure described above ethyl chloro(hydroxyimino)acetate and alkene **7** (1:1.5) afforded diethoxycarbonylfurazan *N*-oxide **9b** (24%), and a mixture of isoxazolines (76%) which were separated by chromatography to yield: 5*R*-3-ethoxycarbonyl-5-(2,3-*O*-isopropylidene-1-*O*-methyl-α-D-*lyxo*-tetrofuranos-4-yl)-2-isoxazoline **10b** [white needles (from EtOH), mp 72-73 °C; $[\alpha]_D^{24}$ -43.8° (*c* 1.025, $CHCl_3$); δ_C (50 MHz, $CDCl_3$) 159.4 (C=O), 150.9 (C-7), 112.1 (CMe_2), 106.6 (C-1), 84.5, 80.7, 78.9, 78.8 (C-2, C-3, C-4, C-5), 62.0 (OCH_2), 54.8 (OMe), 36.0 (C-6), 26.1, 24.7, 14.7 (Me); *m/z* (FAB, thioglycerol) 316.13963 (*M*+1), $C_{14}H_{22}NO_7$ requires 316.13961] and 5*S*-3-ethoxycarbonyl-5-(2,3-*O*-

isopropylidene-1-*O*-methyl-α-D-*lyxo*-tetrofuranos-4-yl)-2-isoxazoline **11b** [oil, $[\alpha]_D^{24}$ 90.0° (*c* 1.64, $CHCl_3$); δ_C (50 MHz, $CDCl_3$) 159.3 (C=O), 150.7 (C-7), 112.4 (CMe_2), 107.0 (C-1), 84.5, 82.6, 80.8, 79.4 (C-2, C-3, C-4, C-5), 62.1 (OCH_2), 55.0 (OMe), 36.7 (C-6), 26.4, 25.2, 14.8 (Me)]; *m/z* (FAB, thioglycerol) 316.13963 (*M*+1), $C_{14}H_{22}NO_7$ requires 316.13961]. ^1H NMR data for isoxazolines **10b** and **11b** are given in Table 1. The isomer ratio (**10b**:**11b** = 82:18) was measured from the ^1H NMR spectrum by comparison of the H(4) peaks at 4.06 and 4.01 ppm.

10b: Anal. Calcd for $C_{14}H_{21}NO_7$: C, 53.3; H, 6.7; N, 4.4. Found: C, 53.4; H, 6.6; N, 4.5.

Crystal Data for Isoxazoline 10a. $C_{17}H_{21}NO_5$, M = 319.33, monoclinic, space group $P2_1$, with a = 7.4987(6), b = 10.6197(8), c = 10.2660(7) Å, β = 91.277(7)°U = 817.4 Å^3, D_{calc} = 1.297 g cm^{-3}, Z = 2, μ = 0.089 mm^{-1}. Bond lengths and angles, torsion angles, atomic co-ordinates involving hydrogen, and thermal parameters are given in Supplementary Tables 6-11, which have been deposited with the Cambridge Crystallographic Data Centre.

Data collection and processing. Stoë Stadi-4 four-circle diffractometer, graphite-monochromated Mo-K_α *X*-radation, T = 295 K, ω/2θ mode, 1138 data collected to $2\theta_{max}$ = 45°, of which 1055 with $F > 4\sigma(F)$ were used in all calculations. No significant crystal decay was apparent.

Structure solution and refinement. Automatic direct methods[14] located all non-hydrogen atoms which were then refined anisotropically; iterative cycles of least-squares refinement and difference Fourier synthesis[15] indicated the positions of hydrogen atoms which were thereafter refined in fixed, calculated positions with a fixed isotropic thermal parameter of 0.08 Å^2. The hand of the structure was identified form the existing known asymmetric centres C(1)-C(4). The phenyl ring was constrained to be a rigid hexagon. All non-hydrogen atoms were allowed anisotropic thermal motion. Final convergence gave R and R_w of 0.0363 and 0.0537, respectively, S = 0.95 for 195 refined parameters. The final difference Fourier synthesis exhibited no feature outwith ±0.18 eÅ^{-3}. Inlaid atomic scattering factors were used.[15] Molecular geometry calculations utilised CALC,[16] and the figures were produced by ORTEP.[17]

ACKNOWLEDGEMENTS

We thank Drs I.H. Sadler and D. Reed for assistance with NMR spectra, and Dr R.O. Gould for performing the puckering parameter calculations. We are grateful to the SERC and DENI for research and maintenance (KJP & KEM) grants.

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