The Stereoselectivity of Addition of *N*-Benzyl-*C*-alkylnitrones to Methyl Crotonate. *X*-Ray Crystal Structure of (3*RS*,4*SR*,5*RS*)-2-Benzyl-4-methoxycarbonyl-5-methyl-3-[(4*RS*)-2,2,5,5-tetramethyl-1,3-dioxolan-4-yl]isoxazolidine

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The addition of *N*-benzyl-*C*-alkyl- and *N*-benzyl-*C*-β-alkoxyalkyl-nitrones (**1a**—**d**) to methyl crotonate gave predominantly the 3,5-*trans*-substituted isoxazolidines (**2a**—**d**), selectivity *ca.* 3:1, whereas *N*-benzyl-*C*-α-alkoxyalkylnitrones (**1e, f**) gave more of the 3,5-*cis*-substituted isoxazolidines (**3e, f**) with selectivities of *ca.* 1:4.

The chiral dimethyldioxolanyl nitrone (**4**) showed only modest diastereoface selectivity in its addition to methyl crotonate. However the more hindered tetramethyldioxolanyl nitrone (**13**) was more stereoselective, providing adduct (**14**) as the only significant product. The structure of this adduct was established by *X*-ray diffraction.

Nitrones are widely used as synthetic intermediates.[1] However, the stereoselectivity of the intermolecular cycloaddition of an acyclic nitrone to an open-chain alkene is difficult to predict, and would appear to be susceptible to minor structural changes in either component.[2] Here, we report on the stereoselectivity of addition of a series of closely related *C*-alkyl- and *C*-alkoxyalkyl-nitrones to methyl crotonate.

Results and Discussion

A series of *N*-benzyl nitrones was prepared, isolated, and treated with an excess of methyl crotonate either at room temperature, or at 70—100 °C. The nitrones used, together with details of the products isolated, are given in Table 1.

It was found that *N*-benzyl-*C*-ethyl-, *N*-benzyl-*C*-isopropyl-, and the *N*-benzyl-*C*-β-alkoxyalkyl-nitrones (**1a**—**d**), reacted with methyl crotonate to give predominantly the 3,5-*trans*-substituted isoxazolidines (**2**) with stereoselectivities of *ca.* 3—4:1 at 20 °C. In contrast, the *N*-benzyl-*C*-α-alkoxyalkyl nitrones (**1e, f**) gave predominantly the 3,5-*cis*-substituted isoxazolidines (**3**), selectivities *ca.* 1:4. It would appear that the site of introduction of an alkoxy group into a *C*-alkyl nitrone can significantly influence its stereochemical behaviour.

Stereochemical assignments were made to the isoxazolidines on the basis of spectroscopic data and chemical correlation. The isoxazolidines were grouped into two sets using ^{1}H n.m.r. spectroscopy, in particular using the $J_{3,4}$ coupling constant, and the chemical shift of 5-H as the criteria, see Table 2. The set with the smaller coupling constant, $J_{3,4} \leqslant 5$ Hz, in which 5-H was always slightly downfield, was assigned structure (**3**), with the *cis*-3,5-configuration, by analogy with the literature.[3,4] This was later confirmed by chemical correlation between the α-alkoxyalkyl adducts (**3e, f**) and alcohol (**18**), and by the *X*-ray structure determination for the isoxazolidine (**14**), see below.

Next, the addition of chiral dioxolanyl nitrones to methyl crotonate was investigated to see whether they exhibited useful diastereoface selectivity.[5] The 2,2-dimethyl-1,3-dioxolan-4-yl nitrone (**4**), obtained from the corresponding aldehyde and benzylhydroxylamine, was found to show only modest stereoselectivity when treated with an excess of methyl crotonate. Three adducts were isolated in a ratio 53:21:26, and identified as the two 3,5-*cis*-substituted isoxazolidines (**5**) and (**6**), together with the 3,5-*trans*-substituted isoxazolidine (**7**). Only traces of the fourth possible adduct (**8**) were found. In contrast the more bulky 2,2,5,5-tetramethyl-1,3-dioxolan-4-yl nitrone (**13**) was more stereoselective. One major adduct was isolated, and identified as the 3,5-*cis*-substituted isoxazolidine (**14**) (55%), together with three minor products (**15**)—(**17**) (combined yield < 10%).

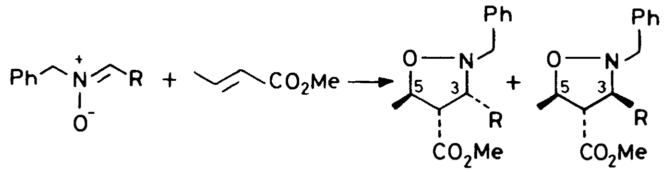
Spectroscopic data and chemical behaviour supported the structural assignments made to adducts (**5**)—(**8**). Two of the isolated adducts were assigned 3,5-*cis*-stereochemistry on the basis of their $J_{3,4}$ values (5.5 and 3.5 Hz), whereas the third isolated adduct showed $J_{3,4} = 10$ Hz, which is in the range expected of a 3,5-*trans*-substituted isoxazolidine. Acid catalysed hydrolysis of the 3,5-*cis*-adducts (**5**) and (**6**) gave the diols (**9**) and (**10**), whereas the 3,5-*trans*-adduct (**7**) gave a mixture of lactones (**11**) and (**12**). Since lactonization should be easier when the carboxy and alcohol functions are *cis*-disposed about the isoxazolidine ring, the formation of these lactones from the isoxazolidine (**7**) but not from the isoxazolidines (**5**) and (**6**), is consistent with these stereochemical proposals. Moreover, ^{1}H n.m.r. data for the lactones (**11**) and (**12**) enable complete configurational assignments to be made, *e.g.* for the lactone (**11**) irradiation of 1-H caused n.O.e.'s for both 5-H (6.3%) and 8-H (6.5%) which suggested that these three protons were all on the same side of the lactone ring. For the lactone (**12**) coupling constant data were interpreted using the conformation shown in Figure 1. The long-range coupling of 1 Hz observed between 4β-H and 6-H is consistent with this conformation, and the couplings observed for 5-H suggest that the 5-OH is axial as shown. The stereochemistry of the 3,5-*trans*-substituted isoxazolidine (**7**) follows from the structures of lactones (**11**) and (**12**).

It was not possible from the spectroscopic data available to decide which of the 3,5-*cis*-substituted isoxazolidines obtained from the nitrone (**4**) and methyl crotonate corresponded to isomer (**5**) and which to isomer (**6**). However, the combined 3,5-*cis*:3,5-*trans* ratio (**5**) + (**6**):(**7**) = 74:26, and this is given in Table 1.

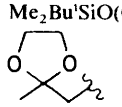
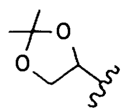
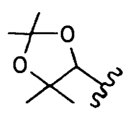
The structure of the major product from the tetramethyldioxolanyl nitrone (**13**) and methyl crotonate was established by *X*-ray diffraction. Figure 2 shows a projection of the molecule which demonstrates that the relative configurations of the four chiral centres are as shown in formula (**14**). One of the minor products was believed to be the other 3,5-*cis*-substituted isoxazolidine (**15**) from its $J_{3,4}$ value, and the other minor products were tentatively identified as a 3,5-*trans*-substituted isoxazolidine (**16**) and a regioisomeric adduct (**17**), the only regioisomeric adduct detected in our work. The combined yield of all these minor products amounted to less than 10%, *cf.* the isolated yield of adduct (**14**) (55%).

Finally, periodate cleavage followed by sodium borohydride

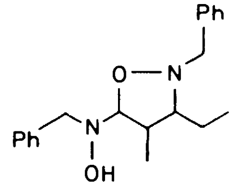
Table 1.



(1) (2) (3)

R	Nitrone[a]	Reaction Temp. (°C)	Reaction time (h)	% Yield[b]	Isoxazolidine (Ratio)
Et	(**1a**)[c]	20	131	57[e]	(**2a**):(**3a**) (77:23)
Et		100	9.5	84	(**2a**):(**3a**) (67:33)
Pr^i	(**1b**)[c]	20	135	75	(**2b**):(**3b**) (74:26)
Pr^i		100	9.5	70	(**2b**):(**3b**) (61:39)
$Me_2Bu^tSiO(CH_2)_2$	(**1c**)[d]	80	6	44	(**2c**):(**3c**) (75:25)
	(**1d**)[c]	20	83	72	(**2d**):(**3d**) (81:19)
		80	6	68	(**2d**):(**3d**) (69:31)
$MeOCH_2$	(**1e**)[d]	20	87	88	(**2e**):(**3e**) (24:76)
$Me_2Bu^tSiOCH_2$	(**1f**)[d]	20	73	76	(**2f**):(**2f**) (15:85)
		70	13	35[f]	(**2f**):(**3f**) (21:79)
	(**4**)[d]	20	158	96	(**7**):(**5**) + (**6**) (26:74)
		70	19	64	(**7**):(**5**) + (**6**) (28:72)
	(**13**)[d]	20	333	59	(**16**):(**14**) + (**15**) (10:90)

[a] The nitrones were prepared from the corresponding aldehydes and benzylhydroxylamine in diethyl ether, 20 °C, 1 h. [b] Yields are of chromatographed products. [c] Nitrones isolated and examined by ^{1}H n.m.r. but used without further purification. [d] Nitrones purified by flash chromatography before use. [e] In addition to isoxazolidines (**2a**) and (**3a**), small amounts of the nitrone dimers (**20**), two isomers, were isolated. [f] Yield based on nitrone precursor.



(20)

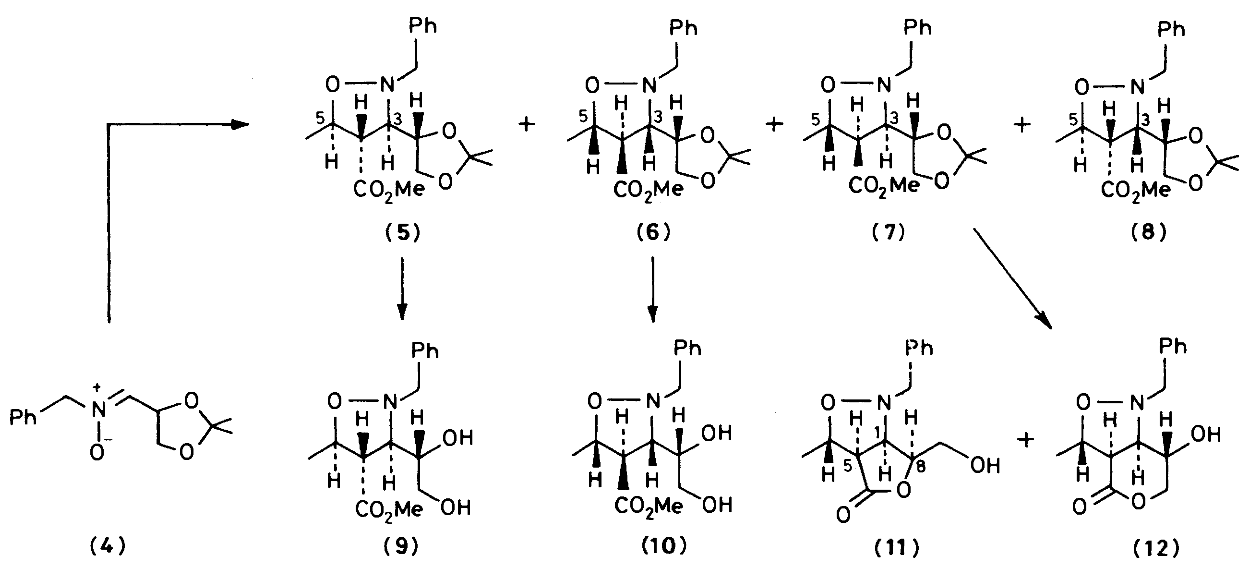
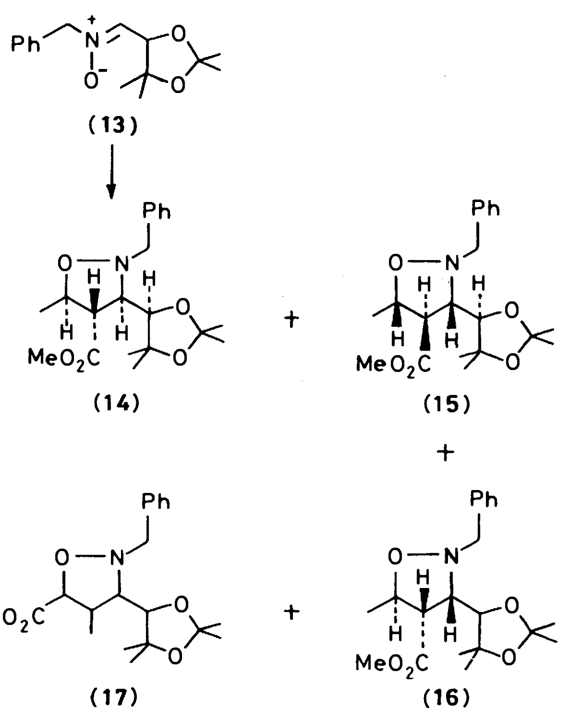


Table 2. Selected chemical shift and coupling constant data for isoxazolidines.

Isoxazolidine	3,5-Relative configuration	5-H p.p.m.	$J_{3,4}$ (Hz)	$J_{4,5}$ (Hz)
(2a)	*trans*	4.5	8.5	8.5
(3a)	*cis*	4.61	5	8
(2b)	*trans*	4.47	8	8
(3b)	*cis*	4.63	5	8
(2c)	*trans*	4.43	8.5	8.5
(3c)	*cis*	4.6	5	8
(2d)	*trans*	4.25	8.5	8.5
(3d)	*cis*	4.45	5.5	7.5
(2e)	*trans*	4.38	8.5	8.5
(3e)	*cis*	4.59	5	8
(2f)	*trans*	4.35	9	9
(3f)	*cis*	4.59	4.5	8
(5)	*cis*	4.60	5.5	8
(6)	*cis*	4.65	3.5	8
(7)	*trans*	4.40	10	8
(9)	*cis*	4.64	4	8
(10)	*cis*	4.71	4	8.5
(14)	*cis*	4.60	2.5	8
(18)	*cis*	4.67	4.5	8
(19)	*cis*	4.68	5	8



reduction of the diols **(9)** and **(10)** gave the alcohol **(18)**.* This alcohol was also obtained by desilylation of the major α-dimethyl-t-butylsilyloxy adduct **(3f)**, and on methylation gave the major *C*-methoxymethyl nitrone adduct **(3e)**. These conversions confirmed the 3,5-*cis*-stereochemistry assigned to adducts **(3e)** and **(3f)**. The alcohol **(18)** was formally characterized as its benzoate **(19)**.

* If the nitrone (4) had been optically pure, then cleavage of diols **(9)** and **(10)** would lead to the different enantiomers of hydroxymethylisoxazolidine **(18)**. Optically pure reagents were not used in our work which was mainly concerned with diastereoface selectivity. If optically pure nitrones had been used however, the use of the more selective nitrone **(13)** would provide an efficient route to the homo-chiral alcohol **(18)**.

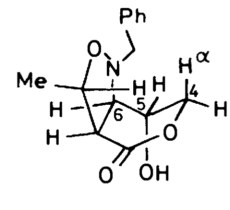


Figure 1.

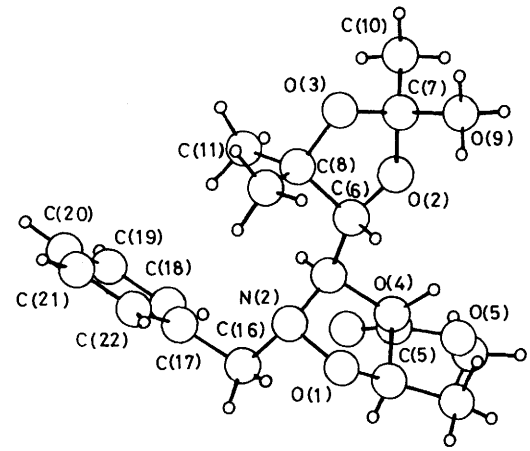
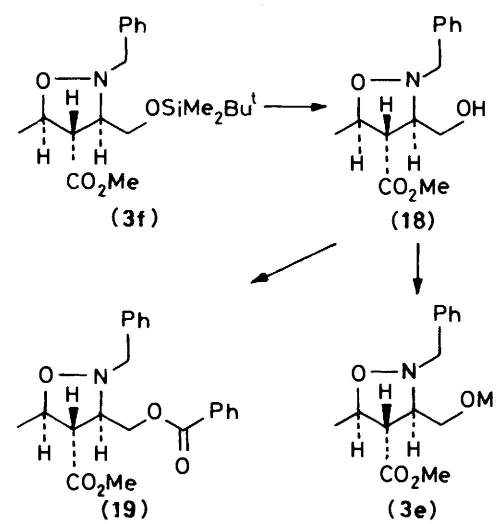
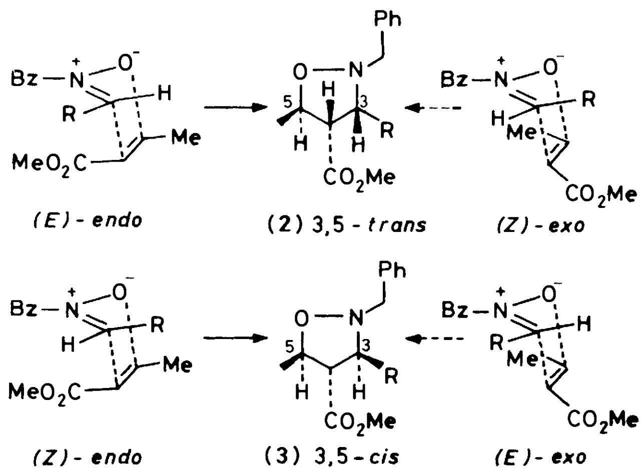


Figure 2. Ball and stick representation of the isoxazolidine **(14)** showing the crystallographic numbering scheme used. Drawn using SNOOPI (E. K. Davies, SNOOPI User Guide, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1982).



Thus the addition of the *N*-benzyl-*C*-alkyl nitrones to methyl crotonate would appear to proceed with useful stereoselectivity, but the nature of the stereoselectivity is dependent upon the precise functionality present in the nitrone. Similar stereochemical complexities have been observed before, during the intermolecular addition of acyclic nitrones to open-chain alkenes, and both 3,5-*cis*- and 3,5-*trans*-substituted isoxazolidines have been the major products from methyl crotonate and different nitrones.[2–4] However, the present work shows just how small a structural change in the nitrone needs to be, to effect a significant change in the stereoselectivity of cycloaddition. The *C*-α-silyloxyethyl nitrone **(1c)** gave predominantly the 3,5-*trans*-adduct (**2c**), whereas the *C*-α-silyloxymethyl nitrone (**1f**) gave predominantly the 3,5-*cis*-adduct (**3f**), and this switch in stereoselectivity was followed by all the other α- and β-alkoxyalkyl nitrones studied.

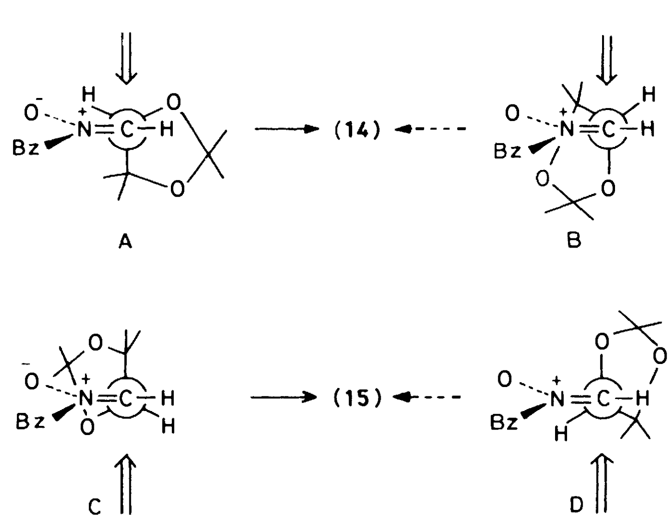
All the nitrones used in this work were isolated before cycloaddition, and were shown by ^{1}H n.m.r. n.O.e. data to be the expected *Z*-isomers implicit in formulae (**1**), (**4**), and (**13**). The isomeric *E*-nitrones could not be detected, but as it has been postulated that isomerization of *Z*-nitrones to the more reactive *E*-nitrones can precede cycloaddition,[3,6] it is possible that either or both *Z*- and *E*-nitrones are involved in our reactions. The 3,5-*cis*-products (**3**) could be formed by the *Z*-nitrone reacting in an *endo*-mode, or the *E*-nitrone in an *exo*-mode. Conversely the 3,5-*trans*-products (**2**) could be formed by the *Z*-nitrone reacting in the *exo*-mode or the *E*-nitrone in an *endo*-mode (see Scheme 1).



Scheme 1.

Perhaps the change in stereoselectivity observed in this work is due to changes in the relative rates of nitrone cycloaddition and isomerization. The α-alkoxyalkyl nitrones are probably the more reactive and could be reacting directly as their *Z*-isomers in the *endo*-mode, to give 3,5-*cis*-substituted isoxazolidines (**3**) as the major products. In contrast, the less reactive β-alkoxyalkyl or unsubstituted *C*-alkyl nitrones isomerize before cycloaddition. The *E*-nitrones so generated now react, again *via* an *endo* transition state, to provide predominantly the 3,5-*trans*-substituted isoxazolidines (**2**).

Of the two chiral nitrones used in this work, the less substituted dimethyldioxolanyl nitrone (**4**) showed little diastereoface selectivity, whereas the tetramethyldioxolanyl nitrone (**13**) was much more selective. These observations parallel those of DeShong who has also studied the stereoselectivity of addition of (**4**) and related nitrones to alkenes, and exploited them in elegant syntheses of amino sugars.[5] Addition to the diastereotopic faces of a π-system is usually explained in terms of the Felkin-Anh model in which attack takes place *anti*-periplanar to the largest allylic substituent in order to minimize unfavourable secondary orbital overlap.[7] For the reactions of the chiral nitrone (**13**) four possible conformations need to be considered depending on whether the oxygen or *gem*-dimethyl substituent is considered to be the 'largest'—see Scheme 2. Molecular models suggest that attack *via* mode A is the least sterically demanding, and may explain the selective formation of the isoxazolidine (**14**). For conformations B and D, in which the alkoxy group is in the orthogonal position, severe steric interactions are generated between the incoming alkene and the



Scheme 2.

gem-dimethyl group, and for conformation C unfavourable interactions between the nitrone oxygen and the dioxolane ring are present. The diastereoface selectivity exhibited by nitrone (**13**) would suggest that this nitrone may be useful in organic synthesis, especially if prepared from an optically active aldehyde.* In contrast, the major 3,5-*trans* adduct (**7**) from the nitrone (**4**) would appear to have been formed *via* a transition state analogous to D.

Experimental

I.r. spectra were measured on Perkin-Elmer 257 and 297 spectrophotometers, and ^{1}H n.m.r. spectra on a Bruker WH-300 spectrometer. M.p.s were determined on a Buchi 510 apparatus, and are uncorrected. Mass spectra were measured on V.G. Micromass 16F and ZAB-IF spectrometers. T.l.c. was carried out using aluminium foil backed, pre-coated plates (Merck Kieselgel 60), flash chromatography using Merck Silica 60, and short column chromatography using Merck Kieselgel 60H.

All solvents were dried and distilled before use. Ether refers to diethyl ether throughout; light petroleum to the fraction b.p. 40—60 °C. *N*-Benzylhydroxylamine was obtained from the reduction of benzaldoxime by sodium cyanoborohydride in methanol, m.p. 57 °C (from light petroleum) (lit.,[8] 58—59 °C). Methoxyacetaldehyde was generated by oxidation of 2-methoxyethanol using chromic acid, and distilled out of the mixture as its aqueous azeotrope.[9]

4-Methoxycarbonyl-2,2,5,5-tetramethyl-1,3-dioxolane was prepared from 3-methylbut-2-enoic acid by oxidation with potassium permanganate, esterification using diazomethane, and protection using 2,2-dimethoxypropane. Distillation gave an oil, b.p. 84—86 °C at 16 mmHg (lit.,[10] 51.5 °C at 1.75 mmHg), which was reduced by lithium aluminium hydride to give 4-hydroxymethyl-2,2,5,5-tetramethyl-1,3-dioxolane.[10]

Preparation of Nitrones.—(Z)-N-*Propylidenebenzylamine* N-*oxide* (**1a**). A mixture of propanal (0.36 ml, 5 mmol) and *N*-benzylhydroxylamine (0.615 g, 5 mmol) in ether (10 ml) was stirred at 20 °C for 1 h. Concentration under reduced pressure gave the nitrone (**1a**) (0.779 g, 96%), m.p. 105—106 °C (from ethyl acetate) (lit.,[11] 105—106 °C) (Found: C, 73.75; H, 7.95; N, 8.6. $C_{10}H_{13}NO$ requires C, 73.6; H, 8.05; N, 8.6%).

(Z)-N-(2-*Methylpropylidene*)*benzylamine* N-*oxide* (**1b**). As above, 2-methylpropanal (0.453 ml, 5 mmol) and *N*-benzyl-

* See footnote on p. 2755.

hydroxylamine (0.615 g, 5 mmol) in ether (10 ml) gave the *title compound* (**1b**) (0.874 g, 99%), m.p. 69.5—70 °C (from ether–light petroleum) (Found: C, 74.65; H, 8.6; N, 7.95. $C_{11}H_{15}NO$ requires C, 74.55; H, 8.55; N, 7.90%); $\nu_{max.}$($CHCl_3$) 3 065 and 1 597 cm^{-1}; δ_H($CDCl_3$) 1.08 (6 H, d, *J* 7 Hz, $CHMe_2$), 2.18 (1 H, m, *J* 7 Hz, $CHMe_2$), 4.86 (2 H, s, CH_2), 6.48 (1 H, d, *J* 7 Hz, vinylic H), and 7.4 (5 H, m, Ar H); *m/z* (d.c.i.) 178 (M^+ + H).

(Z)-N-(3-*Dimethyl-t-butylsilyloxypropylidene*)*benzylamine* N-*oxide* (**1c**). 3-Dimethyl-t-butylsilyloxypropanal (0.885 g, 4.71 mmol) (from the ozonolysis of 4-dimethyl-t-butylsilyloxybut-1-ene) and benzylhydroxylamine (0.55 g, 4.47 mmol) in ether (10 ml) were stirred for 1 h at 20 °C. Concentration under reduced pressure, and flash chromatography using ethyl acetate as the eluant, gave the N-*oxide* (**1c**), as an oil; $\nu_{max.}$(film) 1 595 cm^{-1}; δ_H($CDCl_3$) −0.01 (6 H, s, Me_2Si), 0.83 (9 H, s, Bu^t), 2.68 (2 H, q, *J* 6 Hz, CH_2CH_2O), 3.75 (2 H, t, *J* 6 Hz, CH_2CH_2O), 4.88 (2 H, s, $PhCH_2$), 6.75 (1 H, t, *J* 6 Hz, vinylic H), and 7.38 (5 H, m, ArH), δ_C($CDCl_3$) −5.6 (q, Me_2Si), 18.0 (s, Me_3C), 25.7 (q, Me_3C), 30.3 (t, CH_2CH_2O), 58.9 (t, CH_2CH_2O), 69.1 (t, CH_2N), 128.0, 128.8, and 129.3 (each d, ArC), 132.6 (s, ArC), and 137.1 (d, C=N); *m/z* (i.b.e.i.) 294 (M^+ + H).

(Z)-N-(3,3-*Ethylenedioxybutylidene*)*benzylamine* N-*oxide* (**1d**).—Ethyl 3,3-ethylenedioxybutanoate (5.22 g, 30 mmol)[12] was reduced using di-isobutylaluminium hydride (1M in hexane; 60 ml, 60 mmol) under argon at −80 °C. After 1 h, methanol (12 ml) was added, and the mixture was allowed to warm to 20 °C before being poured into a mixture of ether (600 ml) and aqueous potassium sodium tartrate (300 ml). The mixture was stirred for 5 min, filtered through Celite, and the aqueous layer was separated, and extracted with ether. The combined ethereal solutions were dried ($MgSO_4$), and concentrated under reduced pressure to give 3,3-*ethylenedioxybutanal* (3.1 g), an oil, b.p. 110 °C at 16 mmHg; $\nu_{max.}$(film) 1 727 cm^{-1}; δ_H($CDCl_3$) 1.43 (3 H, s, Me), 2.72 (2 H, d, *J* 3 Hz, CH_2CHO), 4.02 (4 H, s, OCH_2CH_2O), and 9.8 (1 H, t, *J* 3 Hz, CHO). This aldehyde (3.1 g) and *N*-benzylhydroxylamine (2.59 g, 21 mmol) in ether (25 ml) was stirred at 20 °C for 1 h. On cooling to 0 °C, a crystalline product separated out, and was filtered off to give the *title* N-*oxide* (**1d**) (2.2 g, 32%), m.p. 89—90 °C (from ethyl acetate) (Found: C, 66.5; H, 7.25; N, 6.0. $C_{13}H_{17}NO$ requires C, 66.35; H, 7.3; N, 5.95%); $\nu_{max.}$($CHCl_3$) 3 090, 3 070, and 1 600 cm^{-1}; δ_H($CDCl_3$) 1.36 (3 H, s, Me), 2.91 (2 H, d, *J* 5.5 Hz, CH_2CH), 3.92 (4 H, m, OCH_2CH_2O), 4.90 (2 H, s, CH_2Ph), 6.72 (1 H, t, *J* 5.5 Hz, vinylic H), and 7.4 (5 H, m, ArH); *m/z* (e.i.) 236 (M^+ + H).

(Z)-N-(2-*Methoxyethylidene*)*benzylamine* N-*oxide* (**1e**). An excess of aqueous methoxyacetaldehyde (see above) was added to *N*-benzylhydroxylamine (0.5 g, 4.07 mmol) in ether (40 ml), and the mixture stirred at 20 °C for 1 h. The organic layer was separated, dried ($MgSO_4$), and concentrated under reduced pressure to give a residue which was flash chromatographed, using ether–methanol (5:1) as the eluant, to give (Z)-N-(2-*methoxyethylidene*)*benzylamine* N-*oxide* (**1e**) (0.47 g, 63%), m.p. 86—87 °C (from ethyl acetate–light petroleum) (Found: C, 67.25; H, 7.35; N, 7.8. $C_{10}H_{13}NO_2$ requires C, 67.0; H, 7.3; N, 7.8%); $\nu_{max.}$($CHCl_3$) 1 612 cm^{-1}; δ_H($CDCl_3$) 3.37 (3 H, s, MeO), 4.37 (2 H, dt, *J* 4.5, 1 Hz, OCH_2), 4.89 (2 H, br s, CH_2Ph), 6.77 (1 H, t, *J* 4.5 Hz, vinylic H), and 7.4 (5 H, m, ArH); *m/z* (e.i.) 179 (M^+).

(Z)-N-(2-*Dimethyl-t-butylsilyloxyethylidene*)*benzylamine* N-*oxide* (**1f**). Ozonolysis of 3-dimethyl-t-butylsilyloxypropene (5.54 g, 32.2 mmol) in methanol (60 ml) at −78 °C gave, after the addition of dimethyl sulphide (4.72 ml, 64.4 mmol), 20 °C, 2.5 h, and concentration under reduced pressure, an oil, identified as dimethyl-t-butylsilyloxyacetaldehyde. This crude aldehyde and *N*-benzylhydroxylamine (3.15 g, 25.6 mmol) in ether (50 ml) were stirred for 1 h at 20 °C. The mixture was concentrated under reduced pressure, and the residue purified by flash chromatography (eluting with light petroleum–ethyl acetate) to give the *title* N-*oxide* (**1f**) (4.9 g, 69%), an oil; $\nu_{max.}$(film) 3 070, 3 035, and 1 600 cm^{-1}; δ_H($CDCl_3$) 0.06 (6 H, s, Me_2Si), 0.87 (9 H, s, Bu^t), 4.60 (2 H, dt, *J* 4, 1.5 Hz, CH_2O), 4.87 (2 H, s, CH_2Ph), 6.77 (1 H, t, *J* 4 Hz, vinylic H), and 7.4 (5 H, m, ArH); δ_C($CDCl_3$) −5.9 (q, Me_2Si), 17.7 (s, Me_3C) 25.3 (q, Me_3C), 59.4 (t, CH_2O), 68.2 (t, CH_2Ph), 128.3, 128.4, and 128.8 (each d, ArC), 132.1 (s, ArC), and 139.6 (d, C=N); *m/z* (e.i.) 279 (M^+).

(Z)-N-(2,2-*Dimethyl*-1,3-*dioxolan*-4-*yl*)*methylenebenzylamine* N-*oxide* (**4**). A mixture of freshly distilled 4-formyl-2,2-dimethyl-1,3-dioxolane (0.92 g, 3.9 mmol) and *N*-benzylhydroxylamine (0.456 g, 3.71 mmol) in ether (10 ml) was stirred for 1 h at 20 °C. Concentration under reduced pressure and flash chromatography, using ethyl acetate as the eluant, gave the *title* N-*oxide* (**4**) (0.68 g, 78%), m.p. 88—89 °C (Found: C, 66.15; H, 7.15; N, 5.95. $C_{13}H_{17}NO_3$ requires C, 66.35; H, 7.3; N, 5.95%); $\nu_{max.}$($CHCl_3$) 1 598 cm^{-1}; δ_H($CDCl_3$) 1.23 and 1.27 (each 3 H, s, Me), 3.75 (1 H, dd, *J* 6, 8.5 Hz, *H*CHO), 4.26 (1 H, dd, *J* 7, 8.5 Hz, HC*H*O), 4.74 (2 H, s, CH_2Ph), 5.02 (1 H, ddd, *J* 4.5, 6, 7 Hz, CHO), 6.72 (1 H, d, *J* 4.5 Hz, vinylic H), and 7.27 (5 H, m, ArH).

(Z)-N-(2,2,5,5-*Tetramethyl*-1,3-*dioxolan*-4-*yl*)*methylenebenzylamine* N-*oxide* (**13**). 4-Hydroxymethyl-2,2,5,5-tetramethyl-1,3-dioxolane (1.6 g, 10 mmol) in CH_2Cl_2 was added to a mixture of dimethyl sulphoxide (1.7 ml, 22 mmol) and oxalyl chloride (1.0 ml, 11 mmol) in CH_2Cl_2 (30 ml) at −65 °C. After 15 min, triethylamine (7.0 ml, 50 mmol) was added, and after a further 5 min, the mixture was allowed to warm to 20 °C. Water (10 ml) was added, and the mixture extracted into CH_2Cl_2. The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. Bulb-to-bulb distillation (oven temp. 85 °C at 2 mmHg) gave 4-*formyl*-2,2,5,5-*tetramethyl*-1,3-*dioxolane* (284 mg, 18%), as an oil; $\nu_{max.}$(film) 1 735 cm^{-1}; δ_H($CDCl_3$) 1.19, 1.38, 1.41, and 1.51 (each 3 H, s), 4.08 (1 H, d, *J* 1.5 Hz, *CH*CHO), and 9.65 (1 H, d, *J* 1.5 Hz, CHO); *m/z* 143 (M^+ − Me).

Freshly distilled 4-formyl-2,2,5,5-tetramethyl-1,3-dioxolane (284 mg, 1.8 mmol) and *N*-benzylhydroxylamine (225 mg, 1.83 mmol) in ether (6 ml) for 1 h at 20 °C gave, after concentration under reduced pressure and flash chromatography using ether–light petroleum as the eluant, (Z)-N-(2,2,5,5-*tetramethyl*-1,3-*dioxolan*-4-*yl*)*methylenebenzylamine* N-*oxide* (**13**) (372 mg, 79%), as an oil; $\nu_{max.}$(film) 3 065, 3 035, and 1 600 cm^{-1}; δ_H($CDCl_3$) 1.12, 1.39, 1.42, and 1.54 (each 3 H, s, Me), 4.90 (2 H, s, CH_2Ph), 5.08 (1 H, d, *J* 5.5 Hz, CHO), 6.75 (1 H, d, *J* 5.5 Hz, vinylic H), and 7.42 (5 H, m. ArH); δ_C($CDCl_3$) 24.4, 26.7, 27.9, and 28.2 (each q, Me), 69.60 (t, CH_2Ph), 79.1 (d, CHO), 82.3 (s, $OCMe_2$), 108.7 (s, $OCMe_2O$), 128.9, 129.1, and 129.2 (each d, ArC), 132.2 (s, ArC), and 136.0 (d, C=N); *m/z* (e.i.) 264 (M^+ + H).

Preparation of Isoxazolidines.—2-*Benzyl*-3-*ethyl*-4-*methoxycarbonyl*-5-*methylisoxazolidines* (**2a**) *and* (**3a**). (*Z*)-*N*-Propylidenebenzylamine *N*-oxide (**1a**) (241 mg, 1.48 mmol) and methyl crotonate (1.5 ml) were stirred together at 20 °C for 131 h. Concentration under reduced pressure and flash chromatography, using light petroleum–ethyl acetate as the eluant, gave three fractions. The first fraction was a mixture of isoxazolidines (**2a**) and (**3a**) (220 mg, 57%), ratio 77:23 (^{1}H n.m.r.). Repeated chromatography separated the isoxazolidines to give (3RS,4RS,5SR)-2-*benzyl*-3-*ethyl*-4-*methoxycarbonyl*-5-*methylisoxazolidine* (**3a**), as an oil; $\nu_{max.}$($CHCl_3$) 3 025 and 1 730 cm^{-1}; δ_H($CDCl_3$) 0.83 (3 H, t, *J* 7.5 Hz, CH_2Me), 1.38 (3 H, d, *J* 6 Hz, 5-Me), 1.49 and 1.65 (each 1 H, m, CH_2Me), 2.69 (1 H, dd, *J* 5, 8 Hz, 4-H), 3.30 (1 H, dt, *J* 5, 7.5 Hz, 3-H), 3.78 (3 H, s, CO_2Me), 3.99 and 4.15 (each 1 H, d, *J* 12.5 Hz, CH_2Ph), 4.61 (1 H, dq, *J* 8, 6 Hz, 5-H), and 7.35 (5 H, m, ArH); *m/z* (e.i.) 263

(M^+); followed by (3RS,4SR,5RS)-2-*benzyl*-3-*ethyl*-4-*methoxycarbonyl*-5-*methylisoxazolidine* (**2a**), also an oil; $\nu_{max.}$(film) 3 030 and 1 735 cm^{-1}; δ_H($CDCl_3$) 0.86 (3 H, t, *J* 7.5 Hz, CH_2Me), 1.36 (3 H, d, *J* 6 Hz, 5-Me), 1.47 (2 H, m, CH_2Me), 3.13 (1 H, t, *J* 8.5 Hz, 4-H), 3.17 (1 H, m, 3-H), 3.73 (3 H, s, CO_2Me), 3.95 and 4.04 (each 1 H, d, *J* 13.5 Hz, CH_2Ph), 4.45 (1 H, m, 5-H), and 7.34 (5 H, m, ArH). The second fraction was identified as a *nitrone dimer* (**20a**) (45 mg, 19%), m.p. 99.5—100 °C (from ether–light petroleum) (Found: C, 73.4; H, 8.0; N, 8.45. $C_{20}H_{26}N_2O_2$ requires C, 73.05; H, 7.95; N, 8.35%); $\nu_{max.}$($CHCl_3$) 3 575 cm^{-1}; δ_H($CDCl_3$) 0.92 (3 H, t, *J* 7.5 Hz, CH_2Me), 1.11 (3 H, d, *J* 7 Hz, 4-Me), 1.45 (2 H, m, CH_2Me), 2.95 (2 H, m, 3-H and 4-H), 3.79, 4.07, 4.10, and 4.14 (each 1 H, d, *J* 13.5 Hz, *H*CHPh), 4.38 (1 H, d, *J* 3 Hz, 5-H), 4.56 (1 H, br s, OH), and 7.34 (10 H, m, ArH); *m/z* (i.b.e.i.) 326 (M^+). The third fraction was also identified as a *nitrone dimer* (**20b**) (8 mg, 3%), an oil; $\nu_{max.}$($CHCl_3$) 3 560, 3 250, and 3 005 cm^{-1}; δ_H($CDCl_3$) 1.04 (3 H, t, *J* 7.5 Hz, CH_2Me), 1.20 (3 H, d, *J* Hz, 4-Me), 1.68 (2 H, m, CH_2Me), 2.40 (1 H, m, 4-H), 2.91 (1 H, dt, *J* 3.5, 7.5 Hz, 3-H), 3.69 (1 H, d, *J* 13 Hz, HC*H*Ph), 3.78 and 3.95 (each 1 H, d, *J* 14 Hz, *H*CHPh), 4.14 (1 H, d, *J* 13 Hz, HC*H*Ph), 4.28 (1 H, d, *J* 3.5 Hz, 5-H), 6.37 (1 H, br s, OH), and 7.35 (10 H, m, ArH); *m/z* (d.c.i.) 327 (M^+ + H).

2-*Benzyl*-4-*methoxycarbonyl*-5-*methyl*-3-(1-*methylethyl*)-*isoxazolidines* (**2b**) *and* (**3b**). (*Z*)-*N*-(2-Methylpropylidene)-benzylamine *N*-oxide (**1b**) (409 mg, 2.31 mmol) and methyl crotonate (1.2 ml) were stirred together at 20 °C for 135 h. Concentration under reduced pressure, and flash chromatography using light petroleum–ethyl acetate as the eluant, gave a mixture of the isoxazolidines (**2b**) and (**3b**) (493 mg, 77%) in the ratio 74:26 (^{1}H n.m.r.). Short column chromatography using benzene–ether (20:1) as the eluant, gave firstly (3RS,4RS,5SR)-2-*benzyl*-4-*methoxycarbonyl*-5-*methyl*-3-(1-*methylethyl*)*isoxazolidine* (**3b**), as an oil; $\nu_{max.}$($CHCl_3$) 1 729 cm^{-1}; δ_H($CDCl_3$) 0.83 and 0.87 (each 3 H, d, *J* 7 Hz, $CHMe_2$), 1.38 (3 H, d, *J* 6 Hz, 5-Me), 1.70 (1 H, m, $CHMe_2$), 2.80 (1 H, dd, *J* 5, 8 Hz, 4-H), 3.18 (1 H, dd, *J* 5, 7.5 Hz, 3-H), 3.78 (3 H, s, CO_2Me), 3.97 and 4.22 (each 1 H, d, *J* 13 Hz, CH_2Ph), 4.63 (1 H, dq, *J* 8, 6 Hz, 5-H), and 7.35 (5 H, m, ArH). Secondly (3RS,4SR,5RS)-2-*benzyl*-4-*methoxycarbonyl*-5-*methyl*-3-(1-*methylethyl*)*isoxazolidine* (**2b**), also an oil, was eluted; $\nu_{max.}$($CHCl_3$) 1 732 cm^{-1}; δ_H($CDCl_3$) 0.77 and 0.94 (each 3 H, d, *J* 7 Hz, $CHMe_2$), 1.32 (3 H, d, *J* 6 Hz, 5-Me), 1.80 (1 H, m, $CHMe_2$), 3.11 (1 H, br t, *J* 8 Hz, 4-H), 3.20 (1 H, m, 3-H), 3.68 (3 H, s, CO_2Me), 3.87—4.03 (2 H, br AB q, *J* 13 Hz, CH_2Ph), 4.47 (1 H, m, 5-H), and 7.31 (5 H, m, ArH).

2-*Benzyl*-3-(2-*dimethyl*-t-*butylsilyloxyethyl*)-4-*methoxycarbonyl*-5-*methylisoxazolidines* (**2c**) *and* (**3c**). (*Z*)-*N*-(3-Dimethyl-t-butylsilyloxypropylidene)benzylamine *N*-oxide (**1c**), from 3-dimethyl-t-butylsilyloxypropanal (303 mg, 1.6 mmol) and *N*-benzylhydroxylamine (198 mg, 1.61 mmol) and methyl crotonate (0.85 ml) in benzene (4 ml), were heated under reflux for 6 h. Concentration under reduced pressure and flash chromatography using light petroleum–ether (5:1) as the eluant gave isoxazolidines (**2c**) and (**3c**) (304 mg, 44%), ratio 75:25 (^{1}H n.m.r.). The faster moving adduct was identified as (3RS,4RS,5SR)-2-*benzyl*-3-(2-*dimethyl*-t-*butylsilyloxyethyl*)-4-*methoxycarbonyl*-5-*methylisoxazolidine* (**3c**), an oil; $\nu_{max.}$($CHCl_3$) 1 732 and 1 595 cm^{-1}; δ_H($CDCl_3$) −0.03 and 0.00 (each 3 H, s, MeSi), 0.84 (9 H, s, Bu^t), 1.37 (3 H, d, *J* 6 Hz, 5-Me), 1.68 and 1.85 (each 1 H, m, *H*CHCH$_2$O), 2.77 (1 H, dd, *J* 5, 8 Hz, 4-H), 3.58 (3 H, m, CH_2O and 3-H), 3.77 (3 H, s, CO_2Me), 3.97 and 4.15 (each 1 H, d, *J* 13 Hz, HC*H*Ph), 4.60 (1 H, dq, *J* 8, 6 Hz, 5-H), and 7.33 (5 H, m, ArH); *m/z* (c.i.) 394 (M^+ + H). The slower moving adduct was identified as (3RS,4SR,5RS)-2-*benzyl*-3-(2-*dimethyl*-t-*butylsilyloxyethyl*)-4-*methoxycarbonyl*-5-*methylisoxazolidine* (**2c**), an oil; $\nu_{max.}$($CHCl_3$) 1 734 and 1 594 cm^{-1}; δ_H($CDCl_3$) −0.01 and 0.01 (each 3 H, s, MeSi), 0.86 (9 H, s, Bu^t), 1.36 (3 H, d, *J* 6 Hz, 5-Me), 1.63 and 1.72 (each 1 H, m, CH_2CH_2O), 3.17 (1 H, t, *J* 8.5 Hz, 4-H), 3.58 (3 H, m, CH_2CH_2O and 3-H), 3.73 (3 H, s, CO_2Me), 3.95 and 4.01 (each 1 H, d, *J* 13.5 Hz, HC*H*Ph), 4.43 (1 H, m, 5-H), and 7.33 (5 H, m, ArH); *m/z* (c.i.) 394 (M^+ + H).

2-*Benzyl*-3-(2,2-*ethylenedioxypropyl*)-4-*methoxycarbonyl*-5-*methylisoxazolidines* (**2d**) *and* (**3d**). (*Z*)-*N*-(3,3-Ethylenedioxybutylidene)benzylamine *N*-oxide (**1d**) (2.03 g, 8.62 mmol) and methyl crotonate (4.6 ml) were stirred together for 83 h at 20 °C. Concentration under reduced pressure and flash chromatography using ether–light petroleum (1:1) as the eluant gave the isoxazolidines (**2d**) and (**3d**) (2.08 g, 72%), ratio 81:19 (^{1}H n.m.r.). Recrystallization from ether–light petroleum gave (3RS,4SR,5RS)-2-*benzyl*-3-(2,2-*ethylenedioxypropyl*)-4-*methoxycarbonyl*-5-*methylisoxazolidine* (**2d**), m.p. 69.5—70 °C (Found: C, 64.7; H, 7.55; N, 4.25. $C_{18}H_{25}NO_5$ requires C, 64.45; N, 7.5; N, 4.2%); $\nu_{max.}$($CHCl_3$) 1 733 cm^{-1}; δ_H($CDCl_3$) 1.29 (3 H, s, Me), 1.33 (3 H, d, *J* 6 Hz, 5-Me), 1.89 (1 H, dd, *J* 2, 15 Hz, HC*H*), 2.23 (1 H, dd, *J* 7.5, 15 Hz, *H*CH), 3.05 (1 H, t, *J* 8.5 Hz, 4-H), 3.33 (1 H, m, 3-H), 3.72 (3 H, s, CO_2Me), 3.81—3.94 (4 H, m, OCH_2CH_2O and 1 H, d, *H*CHPh), 4.09 (1 H, d, *J* 14 Hz, HC*H*Ph), 4.25 (1 H, m, 5-H), and 7.34 (5 H, m, ArH); *m/z* (e.i.) 335 (M^+). The minor *isoxazolidine* (**3d**) was characterized by ^{1}H n.m.r. spectroscopy; δ_H($CDCl_3$) 1.28 (3 H, s, Me), 1.38 (3 H, d, *J* 6 Hz, 5-Me), 1.98 (1 H, dd, *J* 9, 15 Hz, *H*CH), 2.10 (1 H, dd, *J* 4, 15 Hz, HC*H*), 2.93 (1 H, dd, *J* 5.5, 7.5 Hz, 4-H), 3.60 (1 H, m, 3-H), 3.77 (3 H, s, CO_2Me), 3.81—3.94 (4 H, m, OCH_2CH_2O), 4.00 and 4.10 (each 1 H, d, *J* 14 Hz, HC*H*Ph), 4.45 (1 H, dq, *J* 7.5 and 6 Hz, 5-H), and 7.34 (5 H, m, ArH).

2-*Benzyl*-4-*methoxycarbonyl*-3-*methoxymethyl*-5-*methylisoxazolidines* (**2e**) and (**3e**). (*Z*)-*N*-(2-Methoxyethylidene)-benzylamine *N*-oxide (**1e**) (500 mg, 2.79 mmol) and methyl crotonate (3 ml) were stirred together at 20 °C for 87 h. Concentration under reduced pressure, and flash chromatography using light petroleum–ether (2:1) as the eluant, gave an inseparable mixture of 2-*benzyl*-4-*methoxycarbonyl*-3-*methoxymethyl*-5-*methylisoxazolidines* (**2e**) and (**3e**) (0.68 g, 88%), ratio 24:76 (^{1}H n.m.r.), as an oil; $\nu_{max.}$(film) 1 737 cm^{-1}; δ_H($CDCl_3$) for isomer (**2e**) 1.32 (3 H, d, *J* 7 Hz, 5-Me), 2.98 (1 H, t, *J* 8.5 Hz, 4-H), 3.23 (3 H, s, MeO), 3.19—3.52 (3 H, m, CH_2O and 3-H), 3.70 (3 H, s, CO_2Me), 4.05 (2 H, s, CH_2Ph), 4.38 (1 H, dq, *J* 8.5, 7 Hz, 5-H), and 7.31 (5 H, m, ArH); δ_H($CDCl_3$) for isomer (**3e**) 1.38 (3 H, d, *J* 6 Hz, 5-Me), 2.88 (1 H, dd, *J* 5, 8 Hz, 4-H), 3.28 (3 H, s, OMe), 3.19—3.52 (2 H, m, CH_2O), 3.67 (1 H, m, 3-H), 3.77 (3 H, s, CO_2Me), 4.05 and 4.18 (each 1 H, d, *J* 13 Hz, HC*H*Ph), 4.59 (1 H, dq, *J* 8, 6 Hz, 5-H), and 7.31 (5 H, m, ArH); *m/z* (e.i.) 279 (M^+).

2-*Benzyl*-3-*dimethyl*-t-*butylsilyloxymethyl*-4-*methoxycarbonyl*-5-*methylisoxazolidines* (**2f**) *and* (**3f**). (*Z*)-*N*-(2-Dimethyl-t-butylsilyloxyethylidene)benzylamine *N*-oxide (**1f**) (1.71 g, 6.13 mmol) and methyl crotonate (3.25 ml) were stirred together at 20 °C for 73 h. Concentration under reduced pressure, and flash chromatography using light petroleum–ether, (6:1) as the eluant, gave an inseparable mixture of 2-*benzyl*-3-*dimethyl*-t-*butylsilyloxymethyl*-4-*methoxycarbonyl*-5-*methylisoxazolidines* (**2f**) and (**3f**) (1.76 g, 76%), ratio 15:85 (^{1}H n.m.r.), as an oil; $\nu_{max.}$(film) 1 737 cm^{-1}; δ_H($CDCl_3$) for isomer (**2f**) −0.02 and 0.01 (each 3 H, s, MeSi), 0.85 (9 H, s, Bu^t), 1.32 (3 H, d, *J* 6 Hz, 5-Me), 2.98 (1 H, t, *J* 9 Hz, 4-H), 3.47—3.58 (3 H, m, CH_2O and 3-H), 3.70 (3 H, s, CO_2Me), 4.07 (2 H, s, CH_2Ph), 4.35 (1 H, m, 5-H), and 7.34 (5 H, m, ArH); δ_H($CDCl_3$) for isomer (**3f**) −0.02 and 0.01 (each 3 H, s, MeSi), 0.85 (9 H, s, Bu^t), 1.38 (3 H, d, *J* 6 Hz, 5-Me), 2.89 (1 H, dd, *J* 4.5, 8 Hz, 4-H), 3.47—3.58 (2 H, m, CH_2O), 3.64 (1 H, m, 3-H), 3.76 (3 H, s, CO_2Me), 4.07 and 4.20 (each 1 H, d, *J* 13 Hz, CH_2Ph), 4.59 (1 H, dq, *J* 8, 6 Hz, 5-H), and 7.34 (5 H, m, ArH); *m/z* (e.i.) 379 (M^+).

2-*Benzyl*-3-(2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*)-4-*methoxycarbonyl*-5-*methylisoxazolidines* (**5**)—(**8**). (*Z*)-*N*-(2,2-Dimethyl-1,3-dioxolan-4-ylmethylene)benzylamine *N*-oxide (**4**) (243 mg, 1.03

mmol) and methyl crotonate (1 ml) were stirred together for 158 h at 20 °C. Concentration under reduced pressure, and flash chromatography using light petroleum–ether (3:1) as the eluant, gave the isoxazolidines (**5**)—(**8**) (332 mg, 96%), ratio (^{1}H n.m.r.) 53:21:26:trace (see text). Repeated short column chromatography gave the separate isoxazolidines for characterization. The first two eluted isomers were identified as (3SR,4RS,5SR)-2-*benzyl*-3-(2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*)-4-*methoxycarbonyl*-5-*methylisoxazolidines* (**5**) and (**6**), both oils; isomer (**I**), $\nu_{max.}$($CHCl_3$) 1 730 cm^{-1}; δ_H($CDCl_3$) 1.29 and 1.31 (each 3 H, s, MeC*Me*), 1.43 (3 H, d, *J* 6 Hz, 5-Me), 3.11 (1 H, dd, *J* 3.5, 8 Hz, 4-H), 3.35 (1 H, dd, *J* 4, 8.5 Hz, *H*CHO), 3.55 (1 H, dd, *J* 3.5, 7 Hz, 3-H), 3.80 (3 H, s, CO_2Me), 3.96 (2 H, m, HC*H*C*H*O), 3.98 and 4.17 (each 1 H, d, *J* 12 Hz, HCHPh), 4.65 (1 H, dq, *J* 8, 6 Hz, 5-H), and 7.36 (5 H, m, ArH); *m/z* (e.i.) 336 (M^+ + H); isomer (**II**), $\nu_{max.}$($CHCl_3$) 1 733 cm^{-1}; δ_H($CDCl_3$) 1.29 and 1.37 (each 3 H, s, MeC*Me*), 1.42 (3 H, d, *J* 6.5 Hz, 5-Me), 2.89 (1 H, dd, *J* 5.5, 8 Hz, 4-H), 3.72 (1 H, t, *J* 5.5 Hz, 3-H), 3.78 (3 H, s, CO_2Me), 3.89 (1 H, dd, *J* 5.5, 8.5 Hz, HC*H*CHO), 4.04 (2 H, m, *H*CHC*H*O), 4.10 and 4.23 (each 1 H, d, *J* 13 Hz, HCHPh), 4.60 (1 H, dq, *J* 8, 6 Hz, 5-H), and 7.36 (5 H, m, ArH); *m/z* (e.i.) 335 (M^+); the third eluted isomer was (3RS,4RS,5SR)-2-*benzyl*-3-[(4SR)-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]-4-*methoxycarbonyl*-5-*methylisoxazolidine* (**7**), an oil; $\nu_{max.}$($CHCl_3$) 1 737 cm^{-1}; δ_H($CDCl_3$) 1.29 (3 H, d, *J* 6 Hz, 5-Me), 1.33 and 1.42 (each 3 H, s, MeC*Me*), 2.96 (1 H, dd, *J* 8, 10 Hz, 4-H), 3.22 (1 H, dd, *J* 8.5, 10 Hz, 3-H), 3.62 (1 H, dd, *J* 7, 8 Hz, HC*H*CHO), 3.72 (3 H, s, CO_2Me), 3.91 (1 H, dd, *J* 6.5, 8 Hz, *H*CHCHO), 3.92 (1 H, d, *J* 14 Hz, HC*H*Ph), 4.33—4.48 (2 H, m, CHO and 5-H), 4.45 (1 H, d, *J* 14 Hz, *H*CHPh), and 7.35 (5 H, m, ArH); *m/z* (e.i.) 335 (M^+).

2-*Benzyl*-4-*methoxycarbonyl*-5-*methyl*-3-(2,2,5,5-*tetramethyl*-1,3-*dioxolan*-4-*yl*)*isoxazolidines* (**14**)—(**16**). (*Z*)-*N*-(2,2,5,5-Tetramethyl-1,3-dioxolan-4-ylmethylene)benzylamine *N*-oxide (**13**) (0.55 g, 2.08 mmol) and methyl crotonate (10 ml) were stirred together for 333 h and 20 °C. Concentration under reduced pressure, and short column chromatography using light petroleum–ether as the eluant, gave three fractions. The first eluted material was identified as (3RS,4SR,5RS)-2-*benzyl*-4-*methoxycarbonyl*-5-*methyl*-3-[(4RS)-2,2,5,5-*tetramethyl*-1,3-*dioxolan*-4-*yl*]*isoxazolidine* (**14**) (417 mg, 55%), m.p. 73.5—74 °C (from ether–light petroleum) (Found: C, 66.4; H, 8.05; N, 4.0. $C_{20}H_{29}NO_5$ requires C, 66.1; H, 8.05; N, 3.85%); $\nu_{max.}$($CHCl_3$) 1 740 and 1 595 cm^{-1}; δ_H($CDCl_3$) 0.73 and 1.32 (each 3 H, s, Me), 1.34 (6 H, s, 2 × Me), 1.45 (3 H, d, *J* 6 Hz, 5-Me), 3.25 (1 H, dd, *J* 2.5, 8 Hz, 4-H), 3.67 (1 H, d, *J* 10 Hz, CHO), 3.76 (1 H, dd, *J* 2.5, 10 Hz, 3-H), 3.83 (3 H, s, CO_2Me), 3.93 and 4.15 (each 1 H, d, *J* 12.5 Hz, *H*CHPh), 4.60 (1 H, dq, *J* 8, 6 Hz, 5-H), and 7.35 (5 H, m, ArH); *m/z* (d.c.i.) 364 (M^+ + H); the second eluted product was identified as 2-*benzyl*-5-*methoxycarbonyl*-4-*methyl*-3-(2,2,5,5-*tetramethyl*-1,3-*dioxolan*-4-*yl*)-*oxazolidine* (**17**) (23 mg, 3%), m.p. 79—80 °C; $\nu_{max.}$($CHCl_3$) 1 730 and 1 595 cm^{-1}; δ_H($CDCl_3$) 0.87, 1.32, 1.38, and 1.39 (each 3 H, s, Me), 1.51 (3 H, d, *J* 7 Hz, 4-Me), 2.97 (1 H, m, 4-H), 3.01 (1 H, dd, *J* 3.5, 9.5 Hz, 3-H), 3.77 (1 H, d, *J* 9.5 Hz, CHO), 3.78 (3 H, s, CO_2Me), 3.91 and 4.22 (each 1 H, d, *J* 13.5 Hz, *H*CHPh), 4.47 (1 H, d, *J* 8 Hz, 5-H), and 7.32 (5 H, m, ArH); *m/z* (d.c.i.) 364 (M^+ + H). The third fraction (39 mg, 5%) was believed to contain a mixture of isoxazolidines (**15**) and (**16**); $\nu_{max.}$($CHCl_3$) 1 735 cm^{-1}; *m/z* (d.c.i.) 364 (M^+ + H).

Hydrolysis of the Isoxazolidines (**5**)—(**7**).—(3*SR*,4*RS*,5*SR*)-2-Benzyl-3-(2,2-dimethyl-1,3-dioxolan-4-yl)-4-methoxycarbonyl-5-methylisoxazolidine (**5**) or (**6**) isomer (**I**) (207 mg, 0.62 mmol) was stirred in methanolic HCl (1M; 3 ml) at 20 °C for 48 h. The mixture was concentrated under reduced pressure, and dilute aqueous ammonia added until basic. Saturated sodium chloride (5 ml) was added, and the mixture extracted into $CHCl_3$. After drying ($MgSO_4$), and concentration under reduced pressure, the residue was chromatographed on silica gel using ethyl acetate–light petroleum (2:1) as the eluant, to give (3RS,4SR,5RS)-2-*benzyl*-3-(1,2-*dihydroxyethyl*)-4-*methoxycarbonyl*-5-*methylisoxazolidine* (**9**) or (**10**), isomer (**I**) (168 mg, 92%), an oil; $\nu_{max.}$($CHCl_3$) 3 500, 3 010, and 1 730 cm^{-1}; δ_H($CDCl_3$) 1.41 (3 H, d, *J* 6 Hz, 5-Me), 2.67 (1 H, br s, OH), 3.15 (1 H, dd, *J* 4, 8 Hz, 4-H), 3.43—3.63 (5 H, m, 3-H and C*H*OHC*H*$_2$OH), 3.79 (3 H, s, CO_2Me), 4.02 and 4.18 (each 1 H, d, *J* 12 Hz, *H*CHPh), 4.64 (1 H, dq, *J* 8.5, 6 Hz, 5-H), and 7.36 (5 H, m, ArH); *m/z* (e.i.) 295 (M^+).

A mixture of isoxazolidines (**5**) or (**6**), isomer (**II**) and (**7**) (168 mg, 0.5 mmol), ratio (**6**):(**7**) = 3:2, was treated with methanolic HCl as above. Column chromatography of the crude product using ethyl acetate–light petroleum as the eluant gave three fractions. The first fraction (29 mg, 17%) was recrystallized from ethyl acetate–light petroleum to give (1RS,5SR,6RS,9SR)-7-*benzyl*-5-*hydroxy*-9-*methyl*-3,8-*dioxa*-7-*azabicyclo*[4.3.0]*nonan*-2-*one* (**12**), m.p. 112—114 °C (Found: C, 64.05; H, 6.35; N, 5.3. $C_{14}H_{17}NO_4$ requires C, 63.85; H, 6.5; N, 5.3%); $\nu_{max.}$($CHCl_3$) 3 600, 3 005, and 1 738 cm^{-1}; δ_H(C_6D_6) 1.22 (3 H, d, *J* 6 Hz, 9-Me), 2.14 (1 H, br s, OH), 2.63 (1 H, dd, *J* 8.5, 10 Hz, 1-H), 2.83 (1 H, ddd, *J* 1, 4, 10 Hz, 6-H), 3.18 (1 H, ddd, *J* 2, 4, 5.5 Hz, 5-H), 3.65 (1 H, ddd, *J* 1, 5.5, 11 Hz, 4β-H), 3.79 and 3.83 (each 1 H, d, *J* 14 Hz, *H*CHPh), 3.99 (1 H, dq, *J* 8.5, 6 Hz, 9-H), 4.10 (1 H, dd, *J* 2, 11 Hz, 4α-H), and 7.19 (5 H, m, ArH); *m/z* (e.i.) 263 (M^+). The second fraction was identified as (1RS,4SR,5RS,8SR)-2-*benzyl*-8-*hydroxymethyl*-4-*methyl*-3,7-*dioxa*-2-*azabicyclo*[3.3.0]*octan*-6-*one* (**11**) (31 mg, 24%), m.p. 122—124 °C (from ethyl acetate); $\nu_{max.}$($CHCl_3$) 3 600, 3 380, 3 010, and 1 770 cm^{-1}; δ_H(C_6D_6) 1.01 (3 H, d, *J* 6 Hz, 4-Me), 2.29 (1 H, dd, *J* 3.5, 8.5 Hz, OH), 2.43 (1 H, dd, *J* 6, 9 Hz, 5-H), 3.01 (1 H, dd, *J* 6, 9 Hz, 1-H), 3.40 (1 H, ddd, *J* 3.5, 5, and 12 Hz, 9-H), 3.59 (1 H, ddd, *J* 3.5, 6.5, and 12 Hz, 9-H), 3.58 and 3.67 (each 1 H, d, *J* 14 Hz, *H*CHPh), 3.73 (1 H, ddd, *J* 5, 6, and 6.5 Hz, 8-H), and 7.10 (5 H, m, ArH); *m/z* (e.i.) 263 (M^+). The third fraction was identified as (3RS,4SR,5RS)-2-*benzyl*-3-(1,2-*dihydroxyethyl*)-4-*methoxycarbonyl*-5-*methylisoxazolidine* (**9**) or (**10**), isomer (**II**) (75 mg, 51%), as an oil; $\nu_{max.}$($CHCl_3$) 3 540, 3 010, and 1 732 cm^{-1}; δ_H($CDCl_3$) 1.43 (3 H, d, *J* 6 Hz, 5-Me), 2.48 (1 H, br s, OH), 2.92 (1 H, d, *J* 6 Hz, OH), 3.02 (1 H, dd, *J* 4, 8.5 Hz, 4-H), 3.38—3.58 (3 H, m, C*H*OHC*H*$_2$OH), 3.65 (1 H, dd, *J* 4, 5.5 Hz, 3-H), 3.81 (3 H, s, CO_2Me), 4.02 and 4.22 (each 1 H, d, *J* 12 Hz, *H*CHPh), 4.71 (1 H, dq, *J* 8.5, 6 Hz, 5-H), and 7.35 (5 H, m, ArH); *m/z* (e.i.) 295 (M^+).

(3RS,4SR,5RS)-2-*Benzyl*-3-*hydroxymethyl*-4-*methoxycarbonyl*-5-*methylisoxazolidine* (**18**). A mixture of the isoxazolidines (**2f**) and (**3f**) (2.2 g, 5.8 mmol), ratio 15:85 (^{1}H n.m.r.) in methanolic HCl (1M; 30 ml) was stirred at 20 °C for 5.5 h. The solution was concentrated under reduced pressure, diluted with brine (30 ml), and made basic by the addition of dilute aqueous ammonia. Extraction into $CHCl_3$, and flash chromatography using ether–light petroleum (2:1) as the eluant gave (3RS,4SR,5RS)-2-*benzyl*-3-*hydroxymethyl*-4-*methoxycarbonyl*-5-*methylisoxazolidine* (**18**) (1.2 g, 78%), as an oil; $\nu_{max.}$($CHCl_3$) 3 550, 3 005, and 1 735 cm^{-1}; δ_H($CDCl_3$) 1.39 (3 H, d, *J* 6 Hz, 5-Me), 2.20 (1 H, t, *J* 6 Hz, OH), 2.76 (1 H, dd, *J* 4.5, 8 Hz, 4-H), 3.49 (2 H, m, CH_2OH), 3.60 (1 H, dt, *J* 4.5, 6 Hz, 3-H), 3.79 (3 H, s, CO_2Me), 4.02 and 4.23 (each 1 H, d, *J* 12 Hz, *H*CHPh), 4.67 (1 H, dq, *J* 8, 6 Hz, 5-H), and 7.35 (5 H, m, ArH); *m/z* (e.i.) 265 (M^+). Benzoyl chloride (0.13 ml, 1.17 mmol) was added to a solution of the hydroxy ester (**18**) (62 mg, 0.23 mmol) and di-isopropylamine (0.2 ml, 1.17 mmol) in CH_2Cl_2 (1 ml) and the mixture stirred for 16 h at 20 °C. Aqueous work-up and extraction into CH_2Cl_2 gave, after flash chromatography using light petroleum–ether (3:1) as the eluant, the *benzoate* (**19**) (67 mg, 78%), m.p. 63 °C (from ether–light petroleum) (Found: C, 68.35; H, 6.25; N, 3.75. $C_{21}H_{23}NO_5$ requires C, 68.1; H, 6.3; N, 3.8%); $\nu_{max.}$($CHCl_3$) 3 005, 1 724, and 1 601 cm^{-1}; δ_H($CDCl_3$) 1.43 (3 H, d, *J* 6 Hz, 5-Me), 2.85 (1 H, dd, *J* 5, 8 Hz, 4-H), 3.76

Table 3. Bond lengths with e.s.d.s in parentheses × 10^3

O(1)–N(2)	1.44(6)	C(7)–(10)	1.50(3)
O(1)–C(5)	1.43(4)	O(3)–C(8)	1.45(2)
N(2)–C(3)	1.47(2)	C(8)–C(11)	1.51(7)
N(2)–C(16)	1.48(1)	C(8)–C(12)	1.51(4)
C(3)–C(4)	1.54(7)	C(13)–O(4)	1.19(5)
C(3)–C(6)	1.52(5)	C(13)–O(5)	1.33(2)
C(4)–C(5)	1.54(5)	O(5)–C(14)	1.44(0)
C(4)–C(13)	1.50(5)	C(16)–C(17)	1.50(4)
C(5)–C(15)	1.51(7)	C(17)–C(18)	1.37(0)
C(6)–O(2)	1.42(0)	C(17)–C(22)	1.39(2)
C(6)–C(8)	1.53(5)	C(18)–C(19)	1.39(5)
O(2)–C(7)	1.43(3)	C(19)–C(20)	1.40(5)
C(7)–O(3)	1.43(0)	C(20)–C(21)	1.36(0)
C(7)–C(9)	1.51(3)	C(21)–C(22)	1.37(8)

Table 4. Bond angles with e.s.d.s in parentheses

C(5)–O(1)–N(2)	107.6(1)	C(10)–C(7)–C(9)	112.6(1)
C(3)–N(2)–O(1)	102.8(1)	C(8)–O(3)–C(7)	109.7(1)
C(16)–N(2)–O(1)	108.3(1)	O(3)–C(8)–C(6)	100.0(1)
C(16)–N(2)–C(3)	113.1(1)	C(11)–C(8)–C(6)	113.9(1)
C(4)–C(3)–N(2)	105.9(1)	C(11)–C(8)–O(3)	109.5(1)
C(6)–C(3)–N(2)	108.5(1)	C(12)–C(8)–C(6)	113.7(1)
C(6)–C(3)–C(4)	109.6(1)	C(12)–C(8)–O(3)	106.8(1)
C(5)–C(4)–C(3)	103.4(1)	C(12)–C(8)–C(11)	112.0(1)
C(13)–C(4)–C(3)	115.5(1)	O(4)–C(13)–C(4)	126.5(1)
C(13)–C(4)–C(5)	111.1(1)	O(5)–C(13)–C(4)	109.6(1)
C(4)–C(5)–O(1)	103.8(1)	O(5)–C(13)–O(4)	123.9(1)
C(15)–C(5)–O(1)	108.1(1)	C(14)–O(5)–C(13)	116.7(1)
C(15)–C(5)–C(4)	114.4(1)	C(17)–C(16)–N(2)	109.4(1)
O(2)–C(6)–C(3)	108.0(1)	C(18)–C(17)–C(16)	120.0(2)
C(8)–C(6)–C(3)	119.5(1)	C(22)–C(17)–C(16)	119.8(2)
C(8)–C(6)–O(2)	102.6(1)	C(22)–C(17)–C(18)	120.2(2)
C(7)–O(2)–C(6)	106.7(1)	C(19)–C(18)–C(17)	119.2(3)
O(3)–C(7)–O(2)	105.7(1)	C(20)–C(19)–C(18)	120.3(3)
C(9)–C(7)–O(2)	110.4(1)	C(21)–C(20)–C(19)	119.5(3)
C(9)–C(7)–O(3)	108.8(1)	C(22)–C(21)–C(20)	120.4(3)
C(10)–C(7)–O(2)	108.1(1)	C(21)–C(22)–C(17)	120.4(3)
C(10)–C(7)–O(3)	111.0(1)		

(3 H, s, CO_2Me), 3.89 (1 H, ddd, *J* 5, 6, 7.5 Hz, 3-H), 4.13 (1 H, d, *J* 12.5 Hz, *H*CHPh), 4.21—4.35 (3 H, m, HC*H*Ph and CH_2O), 4.68 (1 H, dq, *J* 8, 6 Hz, 5-H), and 7.28—7.9 (10 H, m, ArH); *m/z* (e.i.) 369 (M^+). Treatment of the diols (**9**) and (**10**) with sodium periodate in methanol–water, followed by reduction of the crude product with sodium borohydride in ethanol, gave in each case, after chromatography on silica gel, the hydroxymethylisoxazolidine (**18**) identical (^{1}H n.m.r., i.r., t.l.c.) with the sample prepared above.

A solution of the hydroxymethylisoxazolidine (**18**) (52 mg, 0.2 mmol) in *N*,*N*-dimethylformamide (0.75 ml) was added to sodium hydride (60% dispersion in oil; 20 mg, 0.5 mmol, washed with light petroleum). After efferverscence had subsided, methyl iodide (0.05 ml, 0.8 mmol) was added, and the mixture stirred at 20 °C for 15 h. Aqueous work-up and flash chromatography gave the methoxymethylisoxazolidine (**3e**) identical with the sample prepared by cycloaddition as described above.

Crystal Data for Isoxazolidine (**14**).—$C_{20}H_{29}NO_5$, M = 363.5, triclinic, space group $P\bar{1}$, a = 11.549(2), b = 6.563(1), c = 14.146(2) Å, α = 101.44(1), β = 90.38(1), γ = 103.89(1), V = 1 019 Å^3, (by least squares refinement on 25 setting angles for 25 automatically centred reflections λ = 1.5418 Å) Z = 2, D_c = 1.18 g cm^{-3}, μ(Cu-K_α) 0.689 mm^{-1}.

Data Collection and Processing.—Intensities of 5 755 reflections were measured in the range (4 ⩾ 2θ ⩾ 15°) ±*h* + *k* ± *l* on an Enraf-Nonius CAD-4F diffractometer using ω/2θ scans. The structure was solved by direct methods MULTAN 80;[13] 3 371 independent reflections uncorrected for absorption [$I > 3\sigma(I)$] were used in the refinement, initially with istropic and finally anisotropic temperature factors. Hydrogen atoms were located in difference Fourier maps and included in the refinement with constraints being applied to the C–H bonds.[14] The refinement was by full matrix least squares to *R* 0.050 (R_ω 0.074).[15]

Empirical weight was calculated for each reflection so as to give no systematic variation of $\omega(|F_o| - |F_c|)$ *vs.* $|F_o|$ or

Table 5. Atomic co-ordinates for isoxazolidine (**14**) × 10^4

Atom	*x/a*	*y/b*	*z/c*
O(1)	1 917(1)	8 117(2)	8 056.2(9)
N(2)	1 210(1)	5 940(2)	7 738.6(9)
C(3)	2 042(1)	4 657(2)	7 917.8(9)
C(4)	2 869(1)	6 014(2)	8 798.7(9)
C(5)	2 562(1)	8 217(2)	8 941(1)
C(6)	2 779(1)	4 333(2)	7 034.6(9)
O(2)	3 671.0(8)	3 314(2)	7 257.3(6)
C(7)	4 126(1)	2 506(2)	6 357(1)
O(3)	3 211.0(9)	2 302(2)	5 634.0(7)
C(8)	2 176(1)	2 867(2)	6 089(1)
C(9)	5 239(1)	4 089(3)	6 160(1)
C(10)	4 345(2)	357(3)	6 397(1)
C(11)	1 288(2)	848(4)	6 229(1)
C(12)	1 657(2)	4 023(4)	5 431(1)
C(13)	2 718(1)	5 141(2)	9 709(1)
O(4)	1 848(1)	3 942(2)	9 913.6(9)
O(5)	3 711(1)	5 937(2)	10 280.9(8)
C(14)	3 700(2)	5 319(4)	11 203(1)
C(15)	3 640(2)	10 118(3)	9 072(2)
C(16)	148(1)	5 635(3)	8 325(1)
C(17)	−736(1)	3 580(3)	7 870(1)
C(18)	−956(2)	1 875(4)	8 323(2)
C(19)	−1 759(3)	−33(5)	7 879(3)
C(20)	−2 331(2)	−188(6)	6 987(3)
C(21)	−2 103(2)	1 513(6)	6 543(2)
C(22)	−1 314(2)	3 404(4)	6 980(2)
H(1)	1 595(13)	3 280(23)	8 028(11)
H(2)	3 697(14)	6 177(26)	8 646(12)
H(3)	2 038(15)	8 321(28)	9 489(12)
H(4)	3 145(13)	5 741(23)	6 898(11)
H(5)	5 106(16)	5 546(29)	6 211(13)
H(6)	5 460(16)	3 660(28)	5 511(13)
H(7)	5 924(16)	4 168(28)	6 622(13)
H(8)	5 015(18)	492(30)	6 916(14)
H(9)	3 631(17)	−604(30)	6 555(14)
H(10)	4 571(18)	−274(29)	5 755(14)
H(11)	543(16)	1 168(27)	6 475(13)
H(12)	1 106(16)	−166(28)	5 615(13)
H(13)	1 616(16)	189(28)	6 691(13)
H(14)	1 365(17)	3 027(30)	4 804(14)
H(15)	963(18)	4 513(31)	5 745(14)
H(16)	2 236(17)	5 282(31)	5 319(14)
H(17)	3 530(21)	3 733(35)	11 135(15)
H(18)	4 498(19)	5 896(36)	11 510(15)
H(19)	3 132(20)	5 838(35)	11 624(15)
H(20)	4 047(19)	10 389(34)	9 716(16)
H(21)	3 370(19)	11 423(34)	9 009(16)
H(22)	4 212(19)	9 814(33)	8 565(16)
H(23)	−249(15)	6 875(28)	8 322(12)
H(24)	351(15)	5 606(28)	9 030(13)
H(25)	−489(24)	1 962(29)	8 939(18)
H(26)	−1 905(24)	−1 239(35)	8 206(16)
H(27)	−2 861(25)	−1 516(36)	6 667(15)
H(28)	−2 542(24)	1 408(29)	5 919(18)
H(29)	−1 116(23)	4 681(35)	6 644(15)

(sinθ)/λ.[16] All calculations were performed on the Chemical Crystallography VAX 11/750 computer.

Bond lengths, bond angles, and fractional atomic co-ordinates for isoxazoline (**14**) are listed in Tables 3—5. Tables of temperature factors are available as a Supplementary Publication [SUP No.56351 (5 pp.)].* The structure factors are available on request from the editorial office.

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* For details of the Supplementary Publications scheme see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1985, Issue 1.

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