Stereocontrol in cyclisation of dioxolanyl radicals

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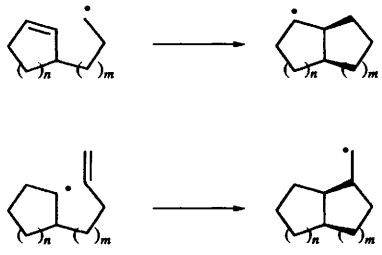
Appropriate nitrate esters are cleaved under photolytic or thermal (tributyltin radical) conditions to yield dioxolanyl radicals which undergo stereoselective cyclisation to heterocyclic products. The X-ray crystallographic structures for compounds **30a** and **35** are reported.

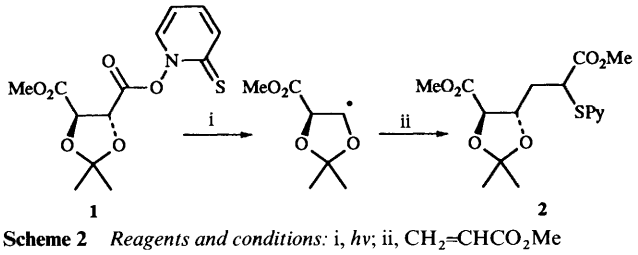
Introduction

Radical cyclisations featuring formation of a ring-junction (Scheme 1) bond proceed stereoselectively to form *cis*-fused [5,5] and [5,6] bicyclic products.[1] The aim of this research is to utilise this stereochemical control in the cyclisation of dioxolanyl radicals.[2,3] The bicyclic dioxolane products (*vide infra*) would be protected *cis*-diols which occur widely in natural metabolites.



Scheme 1

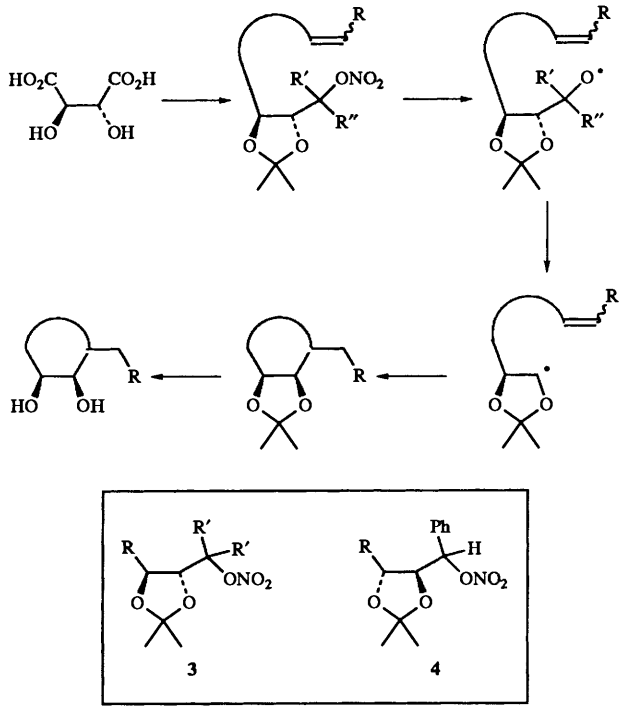
Intermolecular additions of dioxolanyl radicals to alkenes have already been demonstrated by Barton *et al.*[4] to be stereoselective as seen in the conversion **1** ⟶ **2** (Scheme 2).



Scheme 2 *Reagents and conditions:* i, *hν*; ii, CH_2=$CHCO_2Me$

Our long-term goals required a source of dioxolanyl radicals which would be robust enough to tolerate many synthetic transformations. Although the Barton esters are excellent radical precursors, we foresaw problems in making them and in using them for certain types of substrates.

Hence, an alternative source was sought. A study of the literature showed that nitrate esters fragment to yield alkoxyl radicals in high yields,[5,6] and that nitrate esters are indeed robust. Furthermore, they are versatile intermediates since they can be converted into alkoxyl radicals by using either tributyltin radicals[7] or photochemical activation.[5] The plan was therefore as shown in Scheme 3: cleavage of the nitrate ester to give an alkoxyl radical would be followed by further fragmentation, affording the dioxolanyl radical. Cyclisation would generate the more favoured *cis*-ring junction geometry. Since the cyclisation precursors would be derived from tartrate, either enantiomer of any cyclised product should be accessible.



Scheme 3

The efficiency of fragmentation of alkoxyl radicals depends on the stability of the resulting carbon radical and on the degree of substitution and conjugation of the carbonyl by-product. Accordingly, we prepared two simple families of nitrate esters. These were the tertiary nitrates **3** derived from (+)-tartaric acid and the secondary nitrates **4** derived from (−)-tartaric acid. We initially sought to prepare diaryl nitrates (**3**, R′ = Ph) but were unable to isolate these highly reactive species. Therefore, the tertiary nitrates (**3**, R′ = Me) were adopted. In the first instance it was necessary to demonstrate that efficient cleavage of the nitrate ester and fragmentation could occur. Hence, nitrate ester **5** was prepared as shown in Scheme 4.

Results and discussion

Dimethyl *O*,*O*-isopropylidene tartrate was reduced with sodium boranuide to give a mixture of the alcohol **6** and the diol resulting from over-reduction. Protection of compound **6** with *tert*-butyldimethylsilyl chloride was followed by addition of methyllithium, and then nitration with acetic anhydride and

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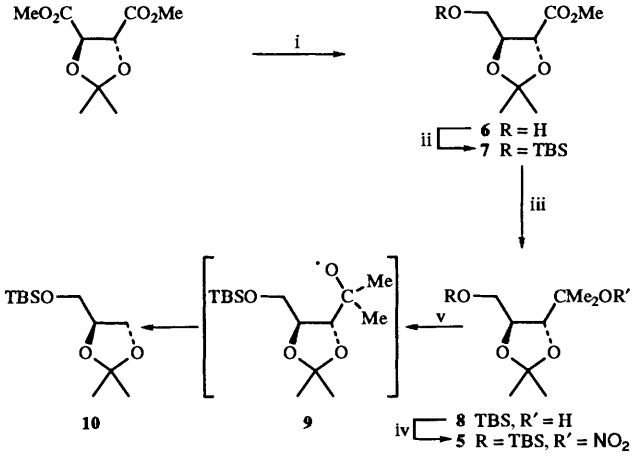


Scheme 4 *Reagents:* i, $NaBH_4$, MeOH; ii, Bu^tMe_2SiCl, imidazole, DMF; iii, MeLi, THF; iv, HNO_3, Ac_2O; v, TBTH, AIBN, C_6H_6

nitric acid. (**CAUTION:** The nitrating mixture is potentially explosive and affords acetyl nitrate). Treatment of nitrate **5** with tributyltin hydride (TBTH) and azoisobutyronitrile (AIBN) afforded the desired product **10** in 56% yield. No alcohol which would result from quenching of the radical **9** was detected. The volatility of product **10** suggested that some loss had occurred during purification.[8] These experiments indicated that nitrate esters were well suited precursors for dioxolanyl radicals.

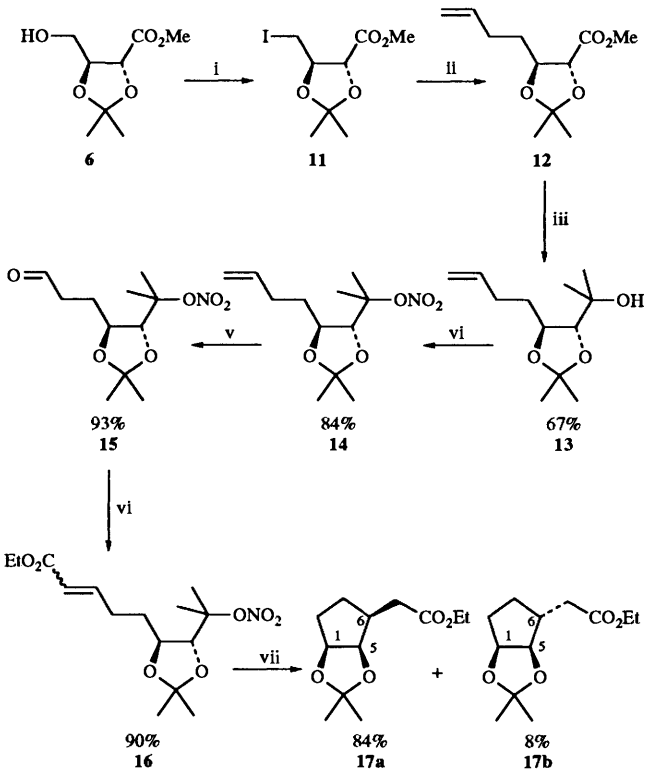
5-*Exo* cyclisations of the tertiary nitrates were then studied. Keck allylation[9] of the iodide **11** (Scheme 5) was optimised by using 2 molar equivalents of allyltributylstannane and 0.5 molar equivalents of AIBN at the start of the reaction. The alkene **14** was initially subjected to reaction with TBTH and AIBN, but no product was isolated, and it was surmised that this was due to the volatility of the product(s). Accordingly, the alkene was converted into substrates which would yield less volatile products. Alkene oxidation to aldehyde **15** and Wadsworth–Emmons conversion into ester **16** proceeded satisfactorily. Treatment with TBTH and AIBN led to two isomeric compounds which were separated. The ^1H spectra of the two compounds were significantly different; the ring-junction protons, at C-1 and C-5, corresponded to well defined and separated signals at δ 4.3–4.7. Examination of models of the two possible configurations at C-6 indicated that the ring junction proton at C-5 would possess a dihedral angle of ~0° with respect to the proton at C-6 in the *cis*-diastereoisomer **17a**, in contrast to an angle of near to 90° in *trans* case **17b**.

The low-field signals in the ^1H NMR spectrum of the major isomer clearly showed an apparent triplet at δ 4.55 corresponding to the C-5 proton, and so this compound was the all-*cis*-isomer **17a**. The corresponding signal for the minor isomer **17b** was a doublet at δ 4.3, reflecting a dihedral angle closer to 90° and one coupling constant of ~0 Hz. Both isomers exhibited apparent triplets at δ ~4.7, corresponding to the protons at C-1. Assignments of resonances were confirmed by ^1H–^1H and ^1H–^{13}C correlation spectra.

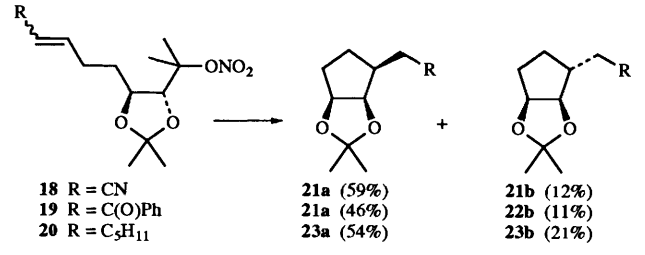
The success of this cyclisation, both in terms of the overall yield of 92%, and the stereoselectivity (84% of the all-*cis*-isomer as opposed to only 8% of the C-6 *trans*-isomer), prompted further investigation.

The aldehyde **15** was converted into three further alkenes **18–20**. The benzoyl, nitrile and amyl derivatives all underwent cyclisation, although with varying stereoselectivity. The products were separated in each case to give the purified diastereoisomers (Scheme 6).

Interestingly, the extremely high all-*cis* selectivity seen in the initial ethyl ester case (> 10:1) was not as marked in these other examples (~5:1–2.5:1). In addition, whilst both the ethyl ester and pentyl-substituted alkenes had undergone clean and



Scheme 5 *Reagents and conditions:* i, PPh_3, imidazole, I_2, PhMe, 60 °C; ii, allyltributyltin (2 mol equiv.), AIBN (0.5 mol equiv.), PhH; iii, MeLi (2.5 mol equiv.), −60 °C, THF; iv, fuming HNO_3, Ac_2O, 0 °C; v, OsO_4, $NaIO_4$, CH_2Cl_2; vi, $(EtO)_2POCH_2CO_2Et$, NaH; vii, TBTH (2.0 mol equiv.), AIBN (2.0 mol equiv.), PhH



Scheme 6

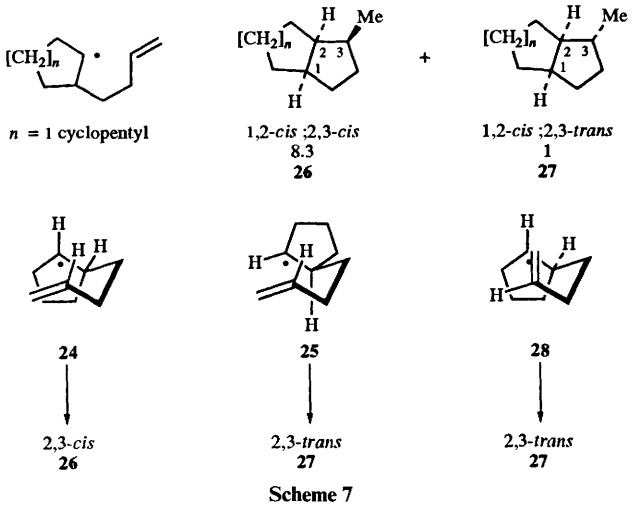
efficient conversions into the analogous cyclised compounds, examination of the crude product mixtures of the other cases indicated that other processes were probably taking place.

The general preference for *cis*-(2,3) stereochemistry in these examples is analogous to that observed in earlier examples of radical cyclisations to afford fused products.[10,11] In these cases high *cis* selectivity for the C-1/C-5 relative stereochemistries has been recorded (~8:1) in addition to the expected *cis*-ring fusion. Indeed, Curran has rationalised the results by considering the cyclohexane chair-like transition states **24** and **25** of the intermediate radicals.[10]

Of the two possible chair-like low-energy conformations shown in Scheme 7, approach of the carbon-centred radical onto the π^* orbital of the alkene would be more favourable in radical **24**. As a result this transition state is preferentially adopted over the alternative **25**, leading to predominantly all-*cis*-bicyclic compounds **26** over the *cis*–*trans*-products **27**.

Rajanbabu has obtained similar results but argues that the minor *trans* product may be derived from a boat-like transition state **28**,[11] since calculations have shown that the energy difference between chair-like and boat-like conformations in such radicals is less than 1 kcal mol^{-1}.†

† 1 cal = 4.184 J.



Scheme 7

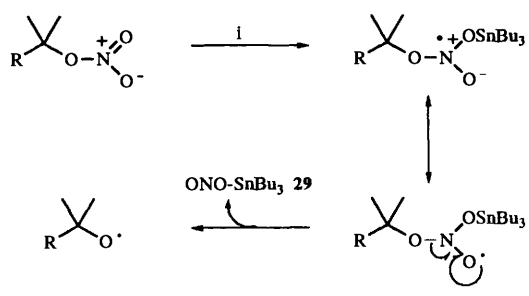
The reasons for the variable stereoselectivity in our cases are not yet completely clear, but it should be noted that whereas the α,β-unsaturated ester and ketone precursors were stereochemically pure *E*-isomers, the α,β-unsaturated nitrile was an *E*/*Z*-mixture, and the pentyl precursor appeared to be a single isomer, which from the conditions of formation was likely to be the *Z*-isomer. This stereochemical variation makes analysis of the results more difficult, and we do not wish to speculate at this stage.

Whilst no other identifiable products could be isolated from the decomposition of the nitrate ester **19**, TLC analysis of the crude mixture resulting from fragmentation of the nitrile-substituted alkene **18** indicated components running at much lower R_f-value than the expected bicycles **21a** and **21b**. Chromatographic separation revealed 2 apparently isomeric compounds exhibiting substantially different NMR characteristics to those of the expected bicycles, most obviously the presence of broad singlets at very low field ($\delta \sim 9$) in the ^{1}H NMR spectra. These signals were found not to correspond to any ^{13}C resonances by correlation spectroscopy, whilst other low-field quaternary signals were present in the ^{13}C spectra. The available NMR, IR and mass spectroscopic data were consistent with structures of the isomeric oximes **30a** and **30b**, isolated in 4% (all-*cis*) and 2% (C-2/C-3 *trans*) yields.

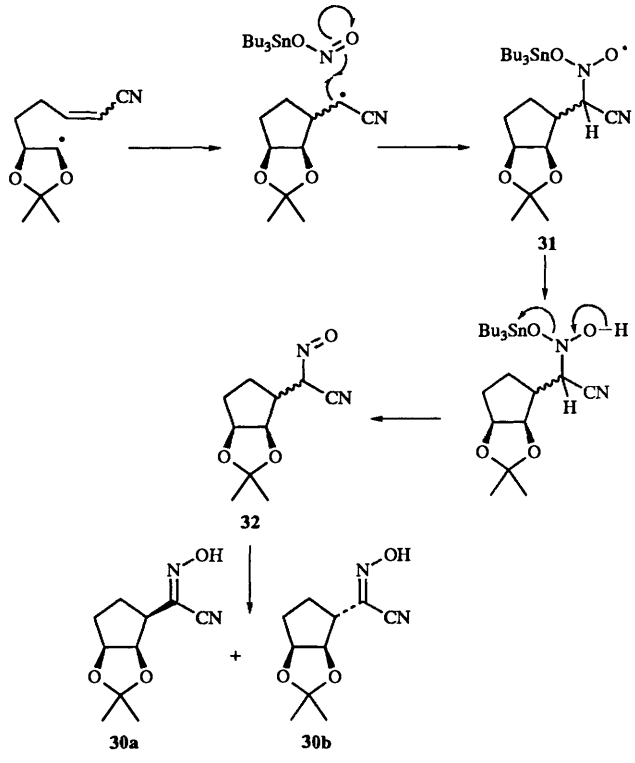
To explain this reaction which occurred under thermal (non-photochemical) activation with TBTH and AIBN, we proposed that an expected by-product of the reaction, tributyltin nitrite **29**, formed as shown in Scheme 8, was suffering attack in one of two possible ways. Either the tributyltin nitrite was undergoing thermal decomposition to NO which was acting as the trapping agent, or the carbon radical was attacking tributyltin nitrite directly, and the resulting intermediate **31** was breaking down to a nitroso product **32**, and hence the oximes **30**, either by a homolytic route or, following hydrogen-atom abstraction, by heterolytic means as shown in Scheme 9. Since nitroso compounds are truly excellent radical traps, nitrite esters should also react well with carbon-centred radicals. Further studies lend support to this theory on the origin of the observed oximes.[12] The structure of the oxime isomer **30a** was further confirmed by X-ray crystallography (see Fig. 1).

6-Membered rings

Having established that the 5-*exo* cyclisations proceeded well, 6-*exo* cyclisations were next attempted. Access to the required fumarate **33** and cinnamate **34** was straightforward. The *tert*-butyldimethylsilyl ether **5** was deprotected and coupled to form the appropriate ester. On exposure to TBTH and AIBN in



Scheme 8 *Reagents:* i, $Bu_2Sn^{\bullet}$



Scheme 9

refluxing benzene complete consumption of the nitrate esters was observed within 1.5–2.5 h (Scheme 10).

Chromatography afforded the pure products **35** (39%) and **36** (24%) as white solids. All spectra pointed to the presence of only one stereoisomer from each reaction. Careful recrystallisation of the fumarate-derived product **35** from (60–80 °C) light petroleum afforded material suitable for single-crystal X-ray analysis. The structure obtained from this analysis demonstrates a *cis*-stereochemical relationship between the three substituents on the six-membered ring, which rests in a boat conformation (Fig. 2). Comparison of the spectra, particularly the ^{1}H spectra, allows the cinnamate-derived product **36** to be assigned the analogous stereochemistry.

To compare the relative efficiencies of secondary and tertiary nitrates in these reactions, dimethyl D-tartrate was transformed into the diol **37** by treatment with 1.5 molar equivalents of sodium boranuide in methanol. Side-chain differentiation of this C_2-symmetric compound was effected by monoprotection with *tert*-butyldimethylsilyl chloride to the silyl ether **38**, which was then oxidised to the aldehyde **39** according to the procedure of Swern[13] (see Scheme 11).

Since isolation of the pure aldehyde proved troublesome, treatment of the crude product with 1.2 molar equivalents of phenyllithium at low temperature afforded a diastereoisomeric

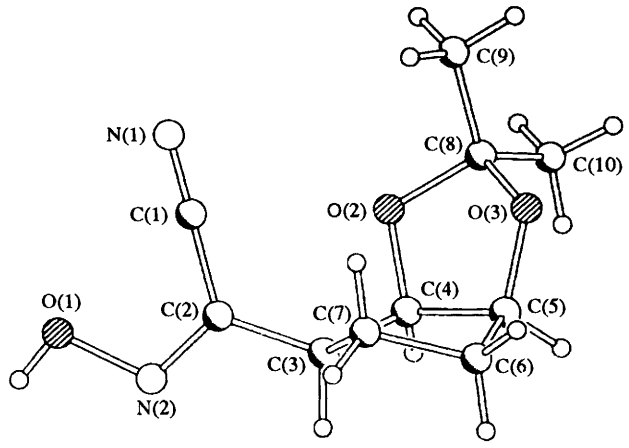


Fig. 1 X-Ray molecular structure of oxime **30a**, with crystallographic numbering scheme

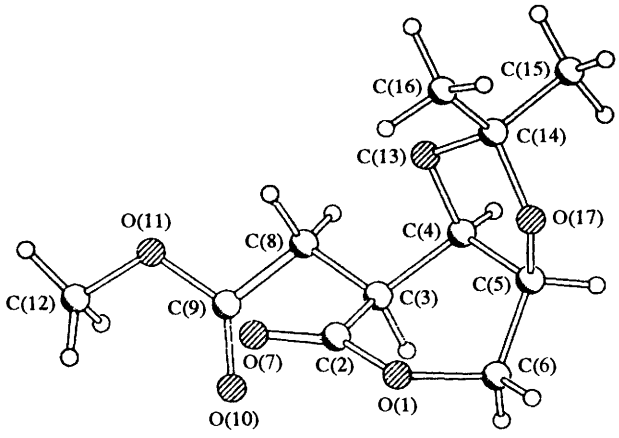
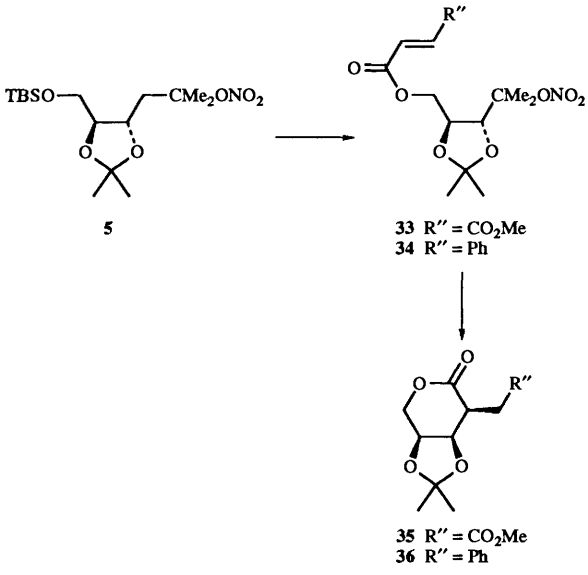


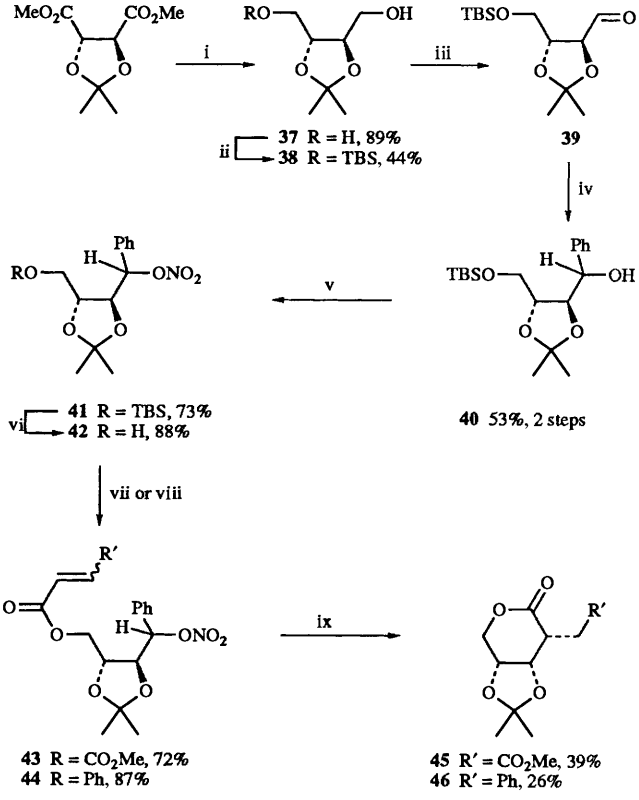
Fig. 2 X-Ray molecular structure of lactone **35**, with crystallographic numbering scheme



Scheme 10

mixture of the alcohol **40**, both diastereoisomers being readily isolated by column chromatography. This two-step procedure proved quite amenable to large-scale preparation, and gave an acceptable 53% overall conversion from the alcohol **38**. Subsequent nitration of the secondary alcohol by the standard procedure occurred smoothly to afford the required nitrate ester **41** in 73% yield. Removal of the *tert*-butyl dimethylsilyl (TBS) group and coupling of the derived alcohol **42** afforded the fumarate and cinnamate esters **43** and **44** respectively. Treatment with TBTH and AIBN afforded the lactones, **45** (39) and **46** (23%), the enantiomers of compounds **35** and **36**. These yields are comparable with those obtained from the tertiary nitrate, and so the relative efficiencies of fragmentation of the two types of nitrate esters appear similar under the conditions used.

The literature precedent for the successful cyclisation of carbon-centred radicals onto ester-containing side-chains to form 5- or 6-membered rings is sparse. There have been many unsuccessful attempts,[14] where failure to cyclise has been attributed to the esters' preference for a *trans* conformation rather than the *s-cis* conformation needed for cyclisation. In most of the successful examples,[15] the radicals generated were relatively stabilised, and therefore sufficiently long lived to allow the esters to adopt less stable conformations required for cyclisation. Nevertheless, both Clive and Beaulieu[16] and Camarasa *et al.*[17] were able to synthesize [3.3.0]-fused lactones



Scheme 11 *Reagents:* i, $NaBH_4$, MeOH; ii, Bu^tMe_2SiCl, imidazole, DMF; iii, $(COCl)_2$, Me_2SO, Et_3N; iv, PhLi, THF; v, Ac_2O, HNO_3; vi, TBAF, THF; vii, DCC, methyl hydrogen fumarate, DMAP, Et_2O; viii, cinnamoyl chloride, C_5H_5N, THF; ix, TBTH, AIBN, C_6H_6

as a result of successful 5-*exo*-trigonal cyclisations of unstabilised carbocyclic radicals onto ester side-chains.

However, to the authors' knowledge, only one example of the 6-*exo*-trigonal cyclisation of a carbocyclic radical onto an ester side-chain has been reported previously. Thus Chattopadhyaya[18] and co-workers employed phenyl selenides derived from furano- and pyrano-nucleosides as radical precursors, which were homolysed by treatment with TBTH and AIBN to afford novel [3.4.0]-*cis*-fused furo-pyrans and δ-lactones.

In summary, cyclisations of dioxolanyl radicals gave rise to *cis*-fused [5,5] and [5,6] bicyclic dioxolanes with complete control of ring-junction stereochemistry. Stereochemical induction at a third centre was observed, the magnitude of which was very sensitive to the nature of the substrate.

Experimental

General information

Mps were measured on a Kofler hot-stage apparatus and are uncorrected. Microanalyses were determined using a Perkin-Elmer 240B elemental analyser. IR spectra were obtained on a Perkin-Elmer 1720-X FTIR or a Pye-Unicam SP3-100 spectrometer. UV spectra were recorded on a Philips PU8700 series instrument. ^{1}H NMR spectra were recorded at 90 MHz on a Perkin-Elmer R32, at 250 MHz on a Bruker WM250, at 270 MHz on a JEOL EX270 or at 400 MHz on a Bruker AM400 machine. ^{13}C NMR spectra were recorded at 23 MHz on a JEOL FX90Q, at 63.5 MHz on a JEOL EX270 or at 100 MHz on a Bruker AM400 machine. NMR experiments were carried out in deuteriochloroform, [$^2H_4$]methanol, [$^2H_6$]acetone, [$^2H_3$]acetonitrile or [$^2H_6$]dimethyl sulfoxide with tetramethylsilane as internal reference. Coupling constants (J) are reported in hertz (Hz). In several cases mixtures of isomers were obtained. In cases where superimposition of the signals of two, or more, isomers occurred, the signals have been reported as multiplets (m), unless the coupling constants of each isomer could be ascertained. Mass spectra were recorded on a VG Micromass 70E or an AEI MS902 instrument. High-resolution FAB spectra were recorded at the EPSRC Mass Spectrometry Service Centre, Swansea. X-Ray crystallographic data appear at the end of this Experimental section. Optical rotations were measured on an Optical Activity Ltd type AA-10 polarimeter, and $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}.

Where necessary, solvents were dried and/or distilled before use. Tetrahydrofuran (THF) was distilled from sodium–benzophenone. Acetonitrile was distilled from phosphorus(v) oxide. Dichloromethane was distilled from calcium hydride. Diethyl ether, toluene and benzene were dried over sodium wire. Unless otherwise stated all light petroleum was of boiling range 40–60 °C and was distilled before use. Chromatography was performed using Sorbisil C60 (May and Baker), Kieselgel 60 (Art 9385) or Kieselgel HF254 silica gels.

(4*R*,5*R*)-Dimethyl-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate

(+)-Dimethyl L-tartrate (100.0 g, 0.56 mol) was treated with 2,2-dimethoxypropane (87.7 g, 0.84 mol) and toluene-*p*-sulfonic acid (0.34 g, 1.8 mmol) in benzene (400 cm^3) according to the procedure of Musich and Rapoport.[19] (4*R*,5*R*)-Dimethyl 2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate was isolated as a light green liquid (111.1 g, 91%); bp 98–104 °C at 1.2 mmHg (lit.,[19] 80 °C at 0.1 mmHg); $[\alpha]_D^{28}$ −55.5 (*c* 0.88, acetone) {lit.,[19] $[\alpha]_D^{32}$ −53.7 (neat)} (Found: M$^+$ − CH_3, 203.0509. Calc. for $C_8H_{11}O_6$: M − CH_3, 203.0556); *m*/*z* (200 °C) 203 (M$^+$ − CH_3, 25%), 159 (M$^+$ − $C_2H_3O_2$, 12), 59 ($C_2H_3O_2^+$, 40) and 43 ($C_2H_3O^+$, 100).

(4*R*,5*S*)-Methyl 5-hydroxymethyl-2,2-dimethyl-1,3-dioxolane-4-carboxylate 6

To a stirred solution of (4*R*,5*R*)-dimethyl 2,2-dimethyl-1,3-dioxolane dicarboxylate (27.91 g, 128 mmol) in methanol (100 cm^3), with cooling (ice-bath), was added, portionwise, sodium boranuide (2.91 g, 77 mmol, 0.6 mol equiv.) over a 1 hour period. The resulting mixture was then stirred at room temperature for a further 30 min before the solvent was removed under reduced pressure. The gummy residue was partitioned between water (50 cm^3) and ethyl acetate (3 × 100 cm^3) and the combined organic extracts were dried (Na_2SO_4) and evaporated to give a crude product. Chromatography on silica with diethyl ether–light petroleum (1:1) elution afforded diester starting material (8.35 g, 30% recovery). Further elution with diethyl ether–light petroleum (3:1) afforded (4*R*,5*S*)-dimethyl 5-hydroxymethyl-2,2-dimethyl-1,3-dioxolane-4-carboxylate **6** as an oil (8.48 g, 35%); $[\alpha]_D^{33}$ −18.6 (*c* 0.23, MeOH) {lit.,[19] $[\alpha]_D^{20}$ −19.2 (*c* 0.55, MeOH)} (Found: M$^+$ − CH_3, 175.0602. Calc. for $C_7H_{11}O_5$: M − CH_3, 175.0607); ν_{max}(film)/cm^{-1} 3505 (O–H), 2991 (C–H), 2939 (C–H), 1762 (C=O), 1385 [C(C–H_3)$_2$] and 1104 (C–O); δ_H(250 MHz; $CDCl_3$) 1.46 and 1.50 (6 H, 2 s, O–CMe_2–O), 2.21 (1 H, br s, CH_2OH), 3.76 [1 H, dd, *J* 12.2 and 3.9, CHC*H*(H)OH], 3.81 (3 H, s, CO_2Me), 3.97 [1 H, dd, *J* 12.2 and 2.9, CHCH(*H*)OH], 4.25 [1 H, m, CHC*H*(OR)CH_2] and 4.48 [1 H, d, *J* 7.7, MeO_2CC*H*-(OR)CH]; δ_C(68 MHz; $CDCl_3$) 24.9 (q), 26.1 (q), 51.7 (q), 61.1 (t), 74.3 (d), 78.9 (d), 110.6 (s) and 170.8 (s); *m*/*z* (200 °C) 175 (M$^+$ − CH_3, 100%), 159 (M$^+$ − CH_3O, 25), 131 (M$^+$ − $C_2H_3O_2$, 42) and 59 ($C_3H_7O^+$, 87). Further elution with ethyl acetate (100%) afforded (4*R*-*trans*)-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol as a very viscous oil (5.13 g, 25%).

(4*R*,5*S*)-Methyl 2,2-dimethyl-5-[(*tert*-butyldimethylsiloxy)-methyl]-1,3-dioxolane-4-carboxylate 7

Compound **6** (951 mg, 5.00 mmol), *tert*-butyldimethylsilyl chloride (904 mg, 6.00 mmol, 1.2 mol equiv.) and imidazole (851 mg, 12.5 mmol, 2.5 mol equiv.) were stirred together in dry dimethylformamide (DMF) (1.5 cm^3) at room temperature for 1 h. The mixture was partitioned between water (30 cm^3) and diethyl ether (2 × 20 cm^3). The combined organic extracts were dried (Na_2SO_4) and evaporated to yield the crude product (~ 1.7 g), which was chromatographed on silica and eluted with diethyl ether–(40–60°) light petroleum (1:10) to afford (4*R*,5*S*)-*methyl* 2,2-*dimethyl*-5-[(tert-*butyldimethylsiloxy*)*methyl*]-1,3-*dioxolane*-4-*carboxylate* **7** as an oil (1.52 g, 100%), $[\alpha]_D^{34}$ −15 (*c* 1.0, acetone) (Found: C, 55.4; H, 9.53. $C_{14}H_{28}SiO_5$ requires C, 55.23; H, 9.27%); ν_{max}(film)/cm^{-1} 2991, 2955, 2931, 2886, 2858, 1765, 1473, 1464, 1438, 1383, 1362, 1256 and 1110; δ_H(250 MHz; $CDCl_3$) 0.08 (6 H, s, O–$SiMe_2$), 0.90 (9 H, s, O–$SiMe_2C$*Me*$_3$), 1.45 and 1.46 (6 H, 2 × s, $OCMe_2O$), 3.77–3.92 (2 H, m, CHCH_2O), 3.79 (3 H, s, OMe), 4.21 [1 H, dt, *J* 7.4 and 3.8, CHC*H*(OR)CH_2] and 4.49 [1 H, d, *J* 7.4, MeO_2C(*RO*)-C*H*CH]; δ_C(23 MHz; $CDCl_3$) −5.4, −5.3, 18.4, 25.9, 26.0, 27.0, 52.2, 62.9, 75.6, 79.9, 111.4 and 171.4; *m*/*z* (170 °C) 289 (M$^+$ − CH_3, 12%), 247 (M$^+$ − Bu^t, 41), 89 ($OSiMe_3^+$, 54) and 73 ($SiMe_3^+$, 100).

2-[(4*R*,5*S*)-5-(*tert*-Butyldimethylsiloxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl]propan-2-ol 8

To a solution of compound **7** (5.97 g, 19.6 mmol) in dry, distilled, stirred THF (50 cm^3) under nitrogen, at −60 °C was added methyllithium (as a complex with LiBr, 33 cm^3 of 1.5 mol dm^{-3} solution in diethyl ether, 50 mmol, 2.5 mol equiv.) dropwise. The resulting mixture was stirred at −60 °C for 0.5 h, then was warmed to room temperature and quenched with water (20 cm^3). After partitioning, the aqueous phase was extracted with diethyl ether (50 cm^3) and the combined organic extracts were dried (Na_2SO_4), and evaporated under reduced pressure. The residue was chromatographed on silica with diethyl ether–light petroleum (1:6–1:4) elution to afford 3-[(4R,5S)-5-(tert-*butyldimethylsiloxymethyl*)-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]*propan*-2-*ol* **8** as an oil (5.65 g, 95%), $[\alpha]_D^{34}$ −10 (*c* 1.0, acetone) (Found: M$^+$ − CH_3, 289.1823. $C_{14}H_{29}O_4Si$ requires M − CH_3, 289.1835); ν_{max}(film)/cm^{-1} 3465, 2985, 2956, 2932, 2886, 2859, 1473, 1464, 1380 and 1370; δ_H(250 MHz; $CDCl_3$) 0.09 (6 H, s, $OSiMe_2$), 0.91 (9 H, s, Bu^t), 1.22, 1.26, 1.39 and 1.42 (12 H, 4 × s, 2 × CMe_2), 2.5 (1 H, br s, OH), 3.70–3.84 (2 H, m, CH_2O), 3.78 [1 H, d, *J* 7.8, (RO)C*H*CH] and 3.99 [1 H, ddd, *J* 7.8, 5.7 and 3.9, CHCH_X(OR)CH_AH$_B$]; δ_C(23 MHz; $CDCl_3$) −5.4, 18.5, 26.1, 26.4, 27.3, 64.7, 69.8, 77.8, 85.0 and 108.7; *m*/*z* (200 °C) 289 (M$^+$ − CH_3, 6%), 245 (M$^+$ − C_3H_7O, 2), 73 ($SiMe_3^+$, 70) and 59 ($C_3H_7O^+$, 100).

2-[(4*R*,5*S*)-5-(*tert*-Butyldimethylsiloxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl]propan-2-yl nitrate 5

Fuming, conc. nitric acid (2.0 cm^3, 47 mmol, ~5 mol equiv.) was added dropwise to stirred, cooled (ice-bath) acetic anhydride (10 cm^3, 0.11 mol, ~10 mol equiv.). The resulting solution was added dropwise to a solution of the alcohol **8** (2.05 g, 10.0 mmol) in acetic anhydride (10 cm^3) stirred in an ice-bath. The resulting mixture was stirred for 5 min and was then poured into saturated aq. sodium hydrogen carbonate (200 cm^3), which was then vigorously stirred for 0.5 h. The product was extracted into diethyl ether (2 × 100 cm^3) and the combined organic extracts were dried (Na_2SO_4), and evaporated under reduced pressure. The residue was chromatographed on silica and eluted with diethyl ether–light petroleum (1:20) to afford the 2-[(4R,5S)-5-(tert-*butyldimethylsiloxymethyl*)-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]*propan*-2-*yl nitrate* **5** as an oil (3.10 g, 89%), $[\alpha]_D^{32}$ −12 (*c* 1.0, acetone) (Found: C, 51.75; H, 8.9; N, 3.8. $C_{15}H_{31}NO_6Si$ requires C, 51.55; H, 8.94; N, 4.01%); ν_{max}(film)/cm^{-1} 2990, 2954, 2932, 2904, 2859, 1627, 1473, 1463, 1381, 1372 and 1254; δ_H(250 MHz; $CDCl_3$) 0.08 (6 H, s, $OSiMe_2$), 0.90 (9 H, s, $OSiMe_2Bu^t$), 1.40, 1.44, 1.61 and 1.62 (12 H, 4 × s, 2 × CMe_2), 3.68–3.85 (2 H, m, CH_2O), 4.03 [1 H, dt, *J* 7.0 and 4.0, CHC*H*(OR)CH_2] and 4.23 [1 H, d, *J* 7.0, C*H*(OR)CH]; δ_C(23 MHz; $CDCl_3$) −5.4, −5.3, 18.5, 20.9, 22.3, 26.0, 27.2, 27.6, 64.4, 78.5, 80.6, 90.8 and 110.1; *m*/*z* (200 °C) 334 ($M^+ - CH_3$, 2%) and 75 ($C_2H_7OSi^+$, 100).

(4*R*)-4-(*tert*-Butyldimethylsiloxymethyl)-1,3-dioxolane 10

To a stirred solution of nitrate **5** (87 mg, 0.25 mmol) in sodium-dried, deoxygenated benzene (50 cm^3) at reflux under nitrogen was added TBTH (80 mm^3, 0.30 mmol, 1.2 mol equiv.) in one portion, followed immediately by a solution of AIBN (8 mg, 0.05 mmol, 0.2 mol equiv.) in benzene (0.5 cm^3) in one portion, and the resulting mixture was refluxed for 16 h. More TBTH (80 mm^3) and AIBN (2 × 8 mg portions) were added over the following 23 h until complete consumption of starting material was achieved (TLC). The solvent was removed under reduced pressure and the residue was chromatographed on silica and eluted with diethyl ether–light petroleum (1:20) to obtain (4R)-4-(tert-*butyldimethylsiloxymethyl*)-1,3-*dioxolane* **10** as a light yellow liquid (34 mg, 56%), $[\alpha]_D$ +10 (*c* 0.68, acetone) (Found: M^+, 246.1584. $C_{12}H_{26}O_3Si$ requires M, 246.1651); ν_{max}(film)/cm^{-1} 2988, 2956, 2931, 2886, 2859, 1473, 1464, 1380, 1371, 1256 and 1099; δ_H(250 MHz; $CDCl_3$) 0.06 (6 H, s, $OSiMe_2$), 0.89 (9 H, s, Bu^t), 1.36 and 1.41 (6 H, 2 × s, $OCMe_2O$), 3.58 [1 H, dd, *J* 10.3 and 6.6, SiOCH(*H*)CH], 3.71 [1 H, dd, *J* 10.3 and 4.6, SiOC*H*(H)CH], 3.85 [1 H, dd, *J* 8.1 and 5.9, CHCH(*H*)OR], 4.04 [1 H, dd, *J* 8.1 and 6.3, CHCH(*H*)OR] and 4.15 [1 H, m, CH(H)C*H*(OR)CH(H)]; δ_C(100 MHz; $CDCl_3$) −5.3, 18.4, 25.5, 26.0, 26.8, 64.1, 66.9, 76.3 and 109.2; *m*/*z* 246 (M^+, 1%), 231 ($M^+ - CH_3$, 2) and 75 ($C_2H_7OSi^+$, 100).

(4*R*,5*R*)-Methyl 5-iodomethyl-2,2-dimethyl-1,3-dioxolane-4-carboxylate 11

Hydroxy ester **6** (6.9 g, 36.3 mmol), triphenylphosphine (14.74 g, 56.2 mmol, 1.55 mol equiv.) and imidazole (3.70 g, 54.4 mmol, 1.50 mol equiv.) were dissolved in toluene (150 cm^3). To the stirred mixture at 60 °C was added iodine (11.5 g, 45.3 mmol, 1.25 mol equiv.), and the resulting mixture was stirred at 60 °C for 45 min, then cooled to room temperature. Saturated aq. sodium hydrogen carbonate (50 cm^3) was added, followed by iodine until the colour of the organic layer persisted. The phases were separated and the organic layer was dried ($MgSO_4$), and evaporated under reduced pressure to yield a solid. Chromatography on silica and elution with dichloromethane afforded (4R,5R)-*Methyl* 5-*iodomethyl*-2,2-*dimethyl*-1,3-*dioxolane*-4-*carboxylate* **11** as an oil (10.6 g, 97%), $[\alpha]_D^{33}$ −12.3 (*c* 0.31, $CHCl_3$) (Found: $M^+ - CH_3$, 284.9656. $C_7H_{10}IO_4$ requires M − CH_3, 284.9624); ν_{max}(film)/cm^{-1} 2991 (C–H), 2954 (C–H), 1764 (C=O), 1382 (CMe_2) and 1103 (C–O); δ_H(250 MHz; $CDCl_3$) 1.45 and 1.54 (6 H, 2 × s, $OCMe_2O$), 3.40 [1 H, dd, *J* 10.9 and 4.8, IC*H*(H)CH], 3.53 [1 H, dd, *J* 10.9 and 4.4, ICH(*H*)CH], 3.82 (3 H, s, CO_2Me), 4.10 [1 H, dt, *J* 6.9 and 4.7, CH_2CH(OR)CH] and 4.31 [1 H, d, *J* 6.8, C(O)C*H*(OR)CH]; δ_C(68 MHz; $CDCl_3$) 7.2 (t), 26.4 (q), 27.4 (q), 52.9 (q), 77.7 (d), 79.5 (d), 112.1 (s) and 170.6 (s); *m*/*z* (200 °C) 285 ($M^+ - CH_3$, 83%), 241 ($M^+ - C_2H_3O_2$, 12) and 43 ($C_2H_3O^+$, 100).

(4*R*,5*S*)-Methyl 5-(but-3-enyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate 12

Iodo ester **11** (10.6 g, 35.3 mmol), allyltributyltin (23.4 g, 70.6 mmol, 2 mol equiv.), AIBN (2.9 g, 17.7 mmol, 0.5 mol equiv.) and sodium-dried toluene (100 cm^3) were stirred under nitrogen at 80 °C for 7 h. More AIBN (2.9 g, 17.7 mmol, 0.5 mol equiv.) was added in one portion and refluxing of the mixture was continued for a further 5 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica and eluted with diethyl ether–light petroleum (1:10) to afford (4R,5S)-*methyl* 5-(*but*-3-*enyl*)-2,2-*dimethyl*-1,3-*dioxolane*-4-*carboxylate* **12** as an oil (5.25 g, 69%), $[\alpha]_D^{33}$ −21.3 (*c* 0.15, acetone) (Found: $M^+ - CH_3$, 199.0967. $C_{10}H_{15}O_4$ requires M − CH_3, 199.0970); ν_{max}(film)/cm^{-1} 3080 (C–H), 2992 (C–H), 2940 (C–H), 1764 (C=O), 1643 (C=C), 1383 (CMe_2), 1102 (C–O), 996 (RCH=CH_2) and 917 (RCH=CH_2); δ_H(250 MHz; $CDCl_3$) 1.44 and 1.47 (6 H, 2 × s, $OCMe_2O$), 1.73–1.95 (2 H, m, CH_2CH_2CH=CH_2), 2.10–2.35 [2 H, m, (RO)CHCH_2CH_2], 3.79 (3 H, s, CO_2Me), 4.10–4.18 [2 H, m, (RO)C*H*C*H*(OR)], 4.97–5.11 (2 H, m, CH_2CH=CH_2) and 5.76–5.92 (1 H, ddt, *J* 17.0, 10.3 and 6.6, CH_2CH=CH_2); δ_C(68 MHz; $CDCl_3$) 25.6 (q), 27.1 (q), 29.7 (t), 32.5 (t), 52.3 (q), 78.4 (d), 78.9 (d), 110.8 (s), 115.1 (t), 137.5 (d) and 171.2 (s); *m*/*z* (200 °C) 199 ($M^+ - CH_3$, 100%), 139 ($C_8H_{11}O_2^+$, 14), 79 ($C_6H_7^+$, 63) and 59 ($C_3H_7O^+$, 48).

2-[(4*R*,5*S*)-5-(But-3-enyl)-2,2-dimethyl-1,3-dioxolan-4-yl]-propan-2-ol 13

To a stirred solution of ester **12** (1.55 g, 7.23 mmol) in dry, distilled THF (50 cm^3) under nitrogen at −60 °C was added dropwise methyllithium (as a complex with LiBr, 14.2 cm^3 of 1.4 mol dm^{-3} solution in diethyl ether, 19.8 mmol, 2.5 mol equiv.). The mixture was stirred at −60 °C for 15 min then was warmed to room temperature and quenched with water (50 cm^3). Diethyl ether (50 cm^3) was added and, after partitioning, the aqueous phase was extracted with more diethyl ether (200 cm^3). The combined organic extracts were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The residue was chromatographed on silica eluting with diethyl ether–light petroleum (1:4) to afford 2-[(4R,5S)-5-(*but*-3-*enyl*)-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]*propan*-2-*ol* **13** as an oil (1.04 g, 67%), $[\alpha]_D^{33}$ −32.2 (*c* 0.18, acetone) (Found: M^+, 214.1569. $C_{12}H_{22}O_3$ requires M, 214.1569); ν_{max}(film)/cm^{-1} 3474 (O–H), 3079 (C=CH_2), 2985 (C–H), 2936 (C–H), 1642 (C=C), 1375 (CMe_2), 997 (C=CH_2) and 914 (C=CH_2); δ_H(250 MHz; $CDCl_3$) 1.17, 1.25, 1.40 and 1.41 (12 H, 4 × s, 2 × CMe_2), 1.58–1.76 [2 H, m, CH_2CH_2CH(OR)], 2.10–2.37 (2 H, m, CH_2CH_2CH=CH_2), 3.55 [1 H, d, *J* 7.8, (RO)CHC*H*(OR)CMe_2], 3.97 [1 H, dt, *J* 8.0 and 3.7. CH_2CH(OR)CH(OR)], 4.95–5.10 (2 H, m, CH_2CH=CH_2) and 5.76–5.92 (1 H, ddt, *J* 16.9, 10.4 and 6.6, CH_2CH=CH_2); δ_C(68 MHz; $CDCl_3$), 24.6 (q), 27.0 (q), 27.3 (q), 27.4 (q), 30.3 (t), 34.5 (t), 69.6 (s), 76.2 (d), 86.7 (d), 108.1 (s), 114.8 (t) and 137.9 (d); *m*/*z* (200 °C), 214 (M^+, 1%), 199 ($M^+ - CH_3$, 24), 115 ($C_6H_{11}O_2^+$, 29) and 59 ($C_3H_7O^+$, 100).

2-[(4*R*,5*S*)-5-(But-3-enyl)-2,2-dimethyl-1,3-dioxolan-4-yl]-propan-2-yl nitrate 14

Fuming conc. nitric acid (0.75 cm^3, 18.0 mmol) was added

dropwise to stirred, cooled (ice-bath) acetic anhydride (3.9 cm^3, 41.0 mmol). A portion of this nitrating mixture (4.0 cm^3, 14.4 mmol based on conc. fuming nitric acid, 1.2 mol equiv.) was added dropwise to a solution of tertiary alcohol **13** (2.56 g, 11.96 mmol) in acetic anhydride (5 cm^3), with stirring and cooling (ice-bath). The resulting mixture was stirred for 15 min then was poured into saturated aq. sodium hydrogen carbonate (80 cm^3), and the mixture was vigorously stirred for 1 h. The product was extracted into diethyl ether (3 × 100 cm^3) and the combined organic extracts were dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed on silica and eluted with diethyl ether–light petroleum (1:40) to afford 2-[(4R,5S)-5-(*but*-3-*enyl*)-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]*propan*-2-*yl nitrate* **14** as an oil (2.6 g, 84%), $[\alpha]_D^{33}$ −30.5 (*c* 0.27, acetone) (Found: C, 55.6; H, 8.4; N, 5.4%. $C_{12}H_{21}NO_5$ requires C, 55.58; H, 8.16; N, 5.40%. Found: $M^+ - CH_3$, 244.1167. $C_{11}H_{18}NO_5$ requires $M - CH_3$, 244.1185); ν_{max}(film)/cm^{-1} 3081 (C=CH_2), 2990 (C–H), 2941 (C–H), 1629 (C=C) and (N=O), 1376 (CMe_2), 1295 (N=O), 1079 (C–O), 998 (C=CH_2) and 916 (C=CH_2); δ_H(250 MHz; $CDCl_3$) 1.37 and 1.38 (6 H, 2 × s, $OCMe_2O$), 1.56 and 1.59 (6 H, 2 × s, 2 × $OCMe_2ONO_2$), 1.64–1.76 [2 H, m, $CH_2CH_2CH(OR)$], 2.06–2.35 (2 H, m, $CH_2CH_2CH{=}CH_2$), 3.86 (1 H, d, *J* 7.4, $CHCH(OR)CMe_2$), 3.95 [1 H, ddd, *J* 9.6, 7.5 and 3.8, $CH_2CH(OR)CH$], 4.93–5.07 (2 H, m, $CH_2CH{=}CH_2$) and 5.72–5.88 (1 H, ddt, *J* 16.9, 10.5 and 6.6, $CH_2CH{=}CH_2$); δ_C(68 MHz; $CDCl_3$) 20.5 (q), 22.3 (q), 26.8 (q), 27.5 (q), 30.0 (t), 34.2 (t), 76.6 (d), 83.6 (d), 90.7 (s), 109.4 (s), 115.1 (t) and 137.6 (d); *m*/*z* (200 °C) 244 ($M^+ - CH_3$, 30%), 183 ($C_9H_{13}NO_3^+$, 30), 59 ($C_3H_7O^+$, 85) and 43 ($C_2H_3O^+$, 100).

2-[(4*R*,5*S*)-5-(2-Formylethyl)-2,2-dimethyl-1,3-dioxolan-4-yl]-propan-2-yl nitrate 15

Alkenyl nitrate **14** (60 mg, 0.23 mmol) was dissolved in an acetone–water (20 cm^3; 8:1) mixture and osmium(VIII) oxide (0.25 mmol; 5% in Bu^tOH) was added dropwise to the stirred solution at room temperature. After the mixture had been stirred for 15 min, sodium periodate (110 mg, 0.4 mmol) was added portionwise, and the mixture was stirred vigorously for a further 2 h. Water (20 cm^3) was then added, the aqueous phase was extracted with diethyl ether (2 × 50 cm^3), and the combined organic extracts were dried ($MgSO_4$), and evaporated under reduced pressure. The crude product was chromatographed on silica and eluted with diethyl ether–light petroleum (1:4) to afford 2-[(4R,5S)-5-(2-*formylethyl*)-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]*propan*-2-*yl nitrate* **15** as a light brown oil (56 mg, 93%), $[\alpha]_D^{29}$ −39.4 (*c* 0.11, acetone) (Found: $M^+ - CH_3$, 246.0966. $C_{10}H_{16}NO_6$ requires $M - CH_3$, 246.0978); ν_{max}(film)/cm^{-1} 2991 (C–H), 2939 (C–H), 1727 (C=O), 1624 (N=O), 1377 (CMe_2), 1296 (N=O) and 1084 (C–O); δ_H(250 MHz; $CDCl_3$) 1.38 and 1.39 (6 H, 2 × s, $OCMe_2O$), 1.62 and 1.63 (6 H, 2 × s, CMe_2ONO_2), 1.74–1.89 and 2.00–2.13 [2 H, m, $CH_2CH_2CH(OR)$], 2.68 (2 H, tt, *J* 7.0 and 1.0, $CH_2CH_2CH{=}O$), 3.88 [1 H, d, *J* 7.4, $CH(OR)CH(OR)CMe_2$], 3.98 [1 H, ddd, *J* 9.5, 7.4 and 2.9, $CH_2CH(OR)CH(OR)$] and 9.80 [1H, t, *J* 1.1, $CH_2C(H){=}O$]; δ_C(68 MHz; $CDCl_3$), 20.8 (q), 22.5 (q), 27.2 (q), 27.7 (t), 27.8 (q), 40.7 (t), 76.6 (d), 84.1 (d), 91.0 (s), 110.0 (s) and 201.9 (s); *m*/*z* (200 °C) 246 ($M^+ - CH_3$, 2%), 143 ($C_7H_{11}O_3^+$, 2), 59 ($C_3H_7O^+$, 21) and 43 ($C_2H_3O^+$, 100).

2-[(4*R*,5*S*)-5-(4-Ethoxycarbonylbut-3-enyl)-2,2-dimethyl-1,3-dioxolan-4-yl]propan-2-yl nitrate 16

Triethylphosphonoacetate (168 mg, 0.74 mmol) was added dropwise to a mixture of sodium hydride (36 mg, 0.39 mmol; 60% dispersion in oil) in dry THF (40 cm^3) over a 15 min period. The mixture was stirred for a further 30 min, and then the aldehyde nitrate **15** (194 mg, 0.74 mmol) was added dropwise. After being stirred at 60 °C for 15 min, the resulting mixture was dissolved in water (50 cm^3), and extracted with diethyl ether (2 × 100 cm^3). The organic layers were combined, dried ($MgSO_4$), and evaporated under reduced pressure. The crude product was chromatographed on silica and eluted with diethyl ether–light petroleum (1:6) to afford the 2-[(4R,5S)-5-(4-*ethoxycarbonylbut*-3-*enyl*)-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]-*propan*-2-*yl nitrate* **16** as a light yellow, viscous oil (221 mg, 90%), $[\alpha]_D^{31}$ −22.0 (*c* 0.41, acetone) (Found: $M^+ - CH_3$, 316.1342. $C_{14}H_{22}NO_7$ requires $M - CH_3$, 316.1396); ν_{max}(film)/cm^{-1} 2990 (C–H), 2940 (C–H), 1720 (C=O), 1627 (C=C) and (N=O), 1374 (CMe_2), 1296 (N=O), 1083 (C–O) and 982 (CHR=CHR); δ_H(250 MHz; $CDCl_3$) 1.28 (3 H, t, *J* 7.2, CO_2CH_2Me), 1.39 and 1.40 (6 H, 2 × s, $OCMe_2O$), 1.58 and 1.62 (6 H, 2 × s, CMe_2ONO_2), 1.65–1.88 [2 H, m, $CH_2CH_2CH(OR)$], 2.24–2.54 (2 H, m, CH_2CH_2CH), 3.87 [2 H, d, *J* 7.4, $CH(OR)CH(OR)CMe_2$], 3.96 [1 H, m, $CH_2CH(OR)CH$], 4.18 (2 H, q, *J* 7.1, CO_2CH_2Me), 5.85 [1 H, dt, *J* 15.7 and 1.6, $CH_2CH{=}CH(CO_2Et)$] and 6.97 [1 H, dt, *J* 15.7 and 6.9, $CH_2CH{=}CH(CO_2Et)$]; δ_C(68 MHz; $CDCl_3$) 14.2 (q), 20.3 (q), 22.6 (q), 26.8 (q), 27.5 (q), 28.7 (t), 33.4 (t), 60.2 (t), 76.5 (d), 83.6 (d), 90.6 (s), 109.6 (s), 121.9 (d), 147.8 (d) and 166.5 (s); *m*/*z* (200 °C) 316 ($M^+ - CH_3$, 78%), 255 ($M^+ - C_2H_5NO_2$, 80), 227 ($C_{12}H_{19}O_4^+$, 12) and 59 ($C_3H_7O^+$, 100).

Treatment of 2-[(4*R*,5*S*)-5-(4-ethoxycarbonylbut-3-enyl)-2,2-dimethyl-1,3-dioxolan-4-yl]propan-2-yl nitrate 16 with TBTH and AIBN

To a stirred, refluxing solution of compound **16** (188 mg, 0.566 mmol) in sodium-dried, deoxygenated benzene (150 cm^3) was added TBTH (220 mm^3, 0.849 mmol, 1.5 mol equiv.), in one portion, followed immediately by a solution of AIBN (139 mg, 0.849 mmol, 1.5 mol equiv.) in benzene (2 cm^3) in one portion. The resulting mixture was refluxed for 4 h, after which time further portions of TBTH (73 mm^3, 0.28 mmol, 0.5 mol equiv.) and AIBN (46 mg, 0.28 mmol, 0.5 mol equiv.) were added. After a total of 5.5 h, the starting material had been consumed, and the solvent was removed under reduced pressure. The residue was chromatographed on silica and eluted with diethyl ether–light petroleum (1:6), to afford the product as a pair of diastereoisomers. These were separated by chromatography on silica with dichloromethane as eluent (100%), to afford *ethyl* {(1S,5R,6S)-3,3-*dimethyl*-2,4-*dioxabicyclo*[3.3.0]*octan*-6-*yl*}*acetate* **17a** as a yellow oil (108 mg, 84%), $[\alpha]_D^{31}$ +45.1 (*c* 0.37, acetone) (Found: $M^+ - CH_3$, 213.1130. $C_{11}H_{17}O_4$ requires $M - CH_3$, 213.1127); ν_{max}(film)/cm^{-1} 2936 (C–H), 1736 (C=O), 1377 (CMe_2) and 1076 (C–O); δ_H(250 MHz; $CDCl_3$) 1.25 [3 H, t (partially obscured), *J* 7.1, CO_2CH_2Me], 1.28 and 1.41 (6 H, 2 × s, $OCMe_2O$), 1.43–1.88 [4 H, m, $CH(OR)CH_2CH_2CH(R)$], 1.95–2.10 [1 H, m, $CH(OR)CH(R)CH_2$], 2.39 (1 H, dd, *J* 16.4 and 7.1, $CHCH_2CO_2Et$), 2.61 (1 H, dd, *J* 16.4 and 7.4, $CHCH_2CO_2Et$), 4.13 (2 H, q, *J* 7.1, CO_2CH_2Me), 4.55 [1 H, t, *J* 5.3, $CHCH(OR)CH(R)$] and 4.63 [1 H, t, *J* 5.1, $CH_2CH(OR)CH$]; δ_C(68 MHz; $CDCl_3$) 14.6 (q), 24.2 (q), 26.2 (q), 28.2 (t), 32.5 (t), 33.9 (t), 41.0 (d), 60.6 (t), 81.2 (d), 81.3 (d), 109.5 (s) and 173.6 (s); *m*/*z* (200 °C) 213 ($M^+ - CH_3$, 100%), 183 ($M^+ - C_2H_5O$, 33), 153 ($C_9H_{13}O_2^+$, 56) and 59 ($C_3H_7O^+$, 34); and *ethyl* {(1S,5R,6R)-3,3-*dimethyl*-2,4-*dioxabicyclo*[3.3.0]*octan*-6-*yl*}*acetate* **17b** as a yellow oil (10 mg, 7.7%), $[\alpha]_D^{33}$ +32.5 (*c* 0.04, acetone) (Found: $M^+ - CH_3$, 213.1110; ν_{max}(film)/cm^{-1} 2982 (C–H), 2938 (C–H), 1736 (C=O), 1377 (CMe_2) and 1098 (C–O); δ_H(250 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.2, CO_2CH_2Me), 1.29 and 1.45 (6 H, 2 × s, $OCMe_2O$), 1.35–1.87 [3 H, m, $CH(H)CH_2CH(R)$], 1.98–2.08 [1 H, m, $CH(OR)CH(R)CH_2$], 2.15 (1 H, dd, *J* 15.1 and 8.5, $CHCH_2CO_2Et$), 2.27 (1 H, dd, *J* 15.1 and 7.6, $CHCH_2CO_2Et$), 2.46–2.55 [1 H, m, $C(H)HCH_2CH(R)$], 4.15 (2 H, q, *J* 7.1, CO_2CH_2Me), 4.31 [1 H, d, *J* 5.7,

CHC*H*(OR)CH(R)] and 4.66 [1 H, t, *J* 5.2, CH_2CH(OR)CH]; δ_C(100 MHz; $CDCl_3$) 14.3 (q), 24.2 (q), 26.5 (q), 27.9 (t), 30.9 (t), 36.4 (t), 41.9 (d), 60.6 (t), 80.6 (d), 85.5 (d), 109.9 (s) and 172.4 (s); *m/z* (200 °C) 213 ($M^+ - CH_3$, 59%), 171 ($C_9H_{15}O_3^+$, 22), 153 ($C_9H_{13}O_2^+$, 36), 125 ($C_7H_9O_2^+$, 99) and 43 ($C_2H_3O^+$, 100).

2-[(4*R*,5*S*)-5-(4-Cyanobut-3-enyl)-2,2-dimethyl-1,3-dioxolan-4-yl]propan-2-yl nitrate 18

Diethyl cyanomethylphosphonate (93 mg, 0.57 mmol) was added dropwise to a mixture of sodium hydride (28 mg, 0.69 mmol; 60% dispersion in oil) in dry THF (40 cm^3) over a period of 15 min. The mixture was stirred for a further 30 min, and then compound **15** (150 mg, 0.57 mmol) was added dropwise. The mixture was heated to 60 °C for 15 min, then was dissolved in water (50 cm^3), and extracted with diethyl ether (2 × 100 cm^3). The extracts were combined, dried ($MgSO_4$), and evaporated under reduced pressure. The crude product was chromatographed on silica and eluted with diethyl ether–light petroleum (1:5) to afford 2-[(4R,5S)-5-(4-*cyanobut*-3-*enyl*)-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]*propan*-2-*yl nitrate* **18** as a light yellow, viscous, oily inseparable pair of isomers (~3:2, *Z*:*E* alkenes) (159 mg, 98%), $[\alpha]_D^{31}$ −27.8 (*c* 0.16, acetone) (Found: $M^+ - CH_3$, 269.1062. $C_{12}H_{17}N_2O_5$ requires $M - CH_3$, 269.1137); ν_{max}(film)/cm^{-1} 2991 (C–H), 2939 (C–H), 2223 (CN), 1627 (C=C) and (N=O), 1377 (CMe_2), 1296 (N=O) and 1082 (C–O); δ_H(250 MHz; $CDCl_3$) 1.40–1.41 [12 H, 4 × s (overlapping), 2 × $OCMe_2O$], 1.59–1.65 [12 H, 4 × s (overlapping), 2 × CMe_2ONO_2], 1.68–1.91 [2 H, m, CH_2CH_2CH(OR)], 2.29–2.69 (2 H, m, CH_2CH_2CH=CH), 3.86 [1 H, 2 × d, *J* 7.5, CH(OR)C*H*(OR)CMe_2], 3.91–4.02 [1 H, m, CH_2CH(OR)CH], 5.34–5.43 [1 H, m, CH_2CH=C*H*(CN)], 6.55 [1 H, dt, *J* 10.9 and 7.8, CH_2CH=CH(CN) (*Z*-isomer)] and 6.76 [1 H, dt, *J* 16.3 and 7.1, CH_2CH=CH(CN) (*E*-isomer)]; δ_C(68 MHz; $CDCl_3$) 20.1 (q), 20.2 (q), 22.6 (q), 22.8 (q), 26.7 (q), 27.5 (q), 28.6 (t), 30.0 (t), 32.8 (t), 33.3 (t), 76.1 (d), 76.3 (d), 83.4 (d), 90.6 (s), 100.1 (d), 100.4 (d), 109.6 (s), 115.7 (s), 117.3 (s), 153.9 (d) and 154.7 (d); *m/z* (200 °C) 269 ($M^+ - CH_3$, 72%), 208 ($M^+ - C_2H_6NO_2$, 100), 180 ($C_{10}H_{14}NO_2^+$, 51) and 59 ($C_3H_7O^+$, 100).

2-[(4*R*,5*S*)-5-(4-Benzoylbut-3-enyl)-2,2-dimethyl-1,3-dioxolan-4-yl]propan-2-yl nitrate 19

Benzoylmethylene(triphenyl)phosphorane (366 mg, 0.96 mmol, 1.2 mol equiv.) and compound **15** (210 mg, 0.80 mmol) were dissolved in sodium-dried benzene (50 cm^3) and the stirred solution was heated under reflux for 10 h. The resulting solution was evaporated under reduced pressure; the residue was taken up in water (50 cm^3) and extracted with diethyl ether (2 × 50 cm^3). The organics were combined, dried ($MgSO_4$), and evaporated under reduced pressure. The crude product was chromatographed on silica and eluted with diethyl ether–light petroleum (1:7) to afford 2-[(4R,5S)-5-(4-*benzoylbut*-3-*enyl*)-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]*propan*-2-*yl nitrate* **19** as a light yellow viscous oil (203 mg, 70%), $[\alpha]_D^{31}$ −15.7 (*c* 1.22, acetone) [Found (FAB): $M^+ + H$, 364.1738. $C_{19}H_{26}NO_6$ requires $M + H$, 364.1760]; ν_{max}(film)/cm^{-1} 2990 (C–H), 2939 (C–H), 1672 (C=O), 1623 (C=C) and (N=O), 1376 (CMe_2), 1295 (N=O) and 1081 (C–O); δ_H(250 MHz; $CDCl_3$) 1.42 (6 H, s, CMe_2ONO_2), 1.60 and 1.64 (6 H, 2 × s, $OCMe_2O$), 1.75–1.96 [2 H, m, CH_2CH_2CH(OR)], 2.42–2.64 (2 H, m, CH_2CH_2-CH=CH), 3.91 [1 H, d, *J* 7.4, CHC*H*(OR)C$(Me)_2ONO_2$], 4.02 [1 H, ddd, *J* 8.8, 7.4 and 3.3, CH_2CH(OR)CH], 6.93 [1 H, d, *J* 15.5, PhC(O)C*H*=CH], 7.08 [1 H, dt, *J* 15.4 and 6.6, CH_2CH=CHC(O)Ph], 7.46 [2 H, t, *J* 7.3, 3- and 5-H (Ph)], 7.56 [1 H, t, *J* 7.3, 4-H (Ph)] and 7.93 [2 H, d, *J* 6.8, 2- and 6-H (Ph)]; δ_C(68 MHz; $CDCl_3$) 20.3 (q), 22.5 (q), 26.7 (q), 27.5 (q), 29.3 (t), 33.4 (t), 76.4 (d), 83.5 (d), 90.5 (s), 109.5 (s), 126.3 (d), 128.4 (d), 132.6 (d), 137.7 (s), 148.2 (d) and 190.5 (s); *m/z* (FAB + ve, MNBA)‡ 364 ($[M + 1]^+$, 6%), 348 ($M^+ - CH_3$, 9), 301 ($[M + 1]^+ - HONO_2$, 7), 287 ($M^+ - C_2H_6NO_2$, 9) and 105 ($C_7H_5O^+$, 100).

2-[(4*R*,5*S*)-2,2-Dimethyl-5-(non-3-enyl)-1,3-dioxolan-4-yl]-propan-2-yl nitrate 20

Hexyltriphenylphosphonium bromide (1.03 g, 2.4 mmol, 1.2 mol equiv.) was dissolved in dry, distilled THF (100 cm^3) and the solution was cooled to −30 °C. Butyllithium (1.36 cm^3, 2.2 mmol; 1.6 mol dm^{-3} in hexanes; 1.1 mol equiv.) was then added dropwise to the stirred solution, and the mixture was warmed to ambient temperature over a period of 30 min, resulting in a clear orange solution. Upon re-cooling of the solution to −78 °C, compound **15** (523 mg, 2.0 mmol) was added dropwise during 15 min, and the mixture was allowed to warm to room temp. over a period of 1 h. The resulting mixture was quenched with water (20 cm^3), filtered, and extracted with light petroleum (2 × 50 cm^3). The combined extracts were dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The crude product was chromatographed on silica, and elution with light petroleum–diethyl ether (30:1) afforded 2-[(4R,5S)-2,2-*dimethyl*-5-(*non*-3-*enyl*)-1,3-*dioxolan*-4-*yl*]*propan*-2-*yl nitrate* **20** as a clear liquid (591 mg, 90%), $[\alpha]_D^{28}$ −20.0 (*c* 0.45, acetone) (Found: $M^+ - CH_3$, 314.1973. $C_{16}H_{28}NO_5$ requires $M - CH_3$, 314.1967); ν_{max}(film)/cm^{-1} 2990 (C–H), 2931 (C–H), 2858 (C–H), 1626 (C=C) and (N=O), 1373 (CMe_2), 1295 (N=O) and 1079 (C–O); δ_H(250 MHz; $CDCl_3$) 0.88 (3 H, t, *J* 6.8, CH=CH$[CH_2]_4$Me), 1.23–1.38 (6 H, m, CH=CHCH_2-$[CH_2]_3$Me), 1.41 and 1.42 (6 H, 2 × s, $OCMe_2O$), 1.59 and 1.62 (6 H, 2 × s, $CHCMe_2ONO_2$), 1.63–1.69 [2 H, m, CH_2CH_2-CH(OR)], 2.00–2.08 (2 H, m, CH=C$HCH_2[CH_2]_3$Me), 2.17–2.28 [2 H, m, (RO)$CHCH_2CH_2CH$=CH], 3.89 [1 H, d, *J* 7.4, CHC*H*(OR)CMe_2], 3.90–3.98 [1 H, m, CH_2CH(OR)CH] and 5.30–5.47 (2 H, m, CH_2CH=C*H*CH_2); δ_C(68 MHz; $CDCl_3$) 14.0 (q), 20.6 (q), 22.3 (q), 22.6 (t), 23.9 (t), 26.9 (q), 27.2 (t), 27.6 (q), 29.3 (t), 31.5 (t), 35.2 (t), 76.8 (d), 83.6 (d), 90.8 (s), 109.4 (s), 128.3 (d) and 131.2 (d); *m/z* (200 °C) 314 ($M^+ - CH_3$, 3%), 266 ($M^+ - HONO_2$, 4), 225 ($M^+ - C_3H_6ONO_2$, 17), 211 ($C_{13}H_{22}O_2^+$, 5), 112 ($C_7H_{12}O^+$, 100) and 59 ($C_3H_7O^+$, 41).

Treatment of 2-[(4*R*,5*S*)-5-(4-cyanobut-3-enyl)-2,2-dimethyl-1,3-dioxolan-4-yl]propan-2-yl nitrate 18 with TBTH and AIBN

To a stirred, refluxing solution of compound **18** (570 mg, 2.0 mmol) in sodium-dried, deoxygenated benzene (450 cm^3) was added TBTH (0.8 cm^3, 3.0 mmol, 1.5 mol equiv.), in one portion, followed immediately by a solution of AIBN (0.49 g, 3.0 mmol, 1.5 mol equiv.) in benzene (10 cm^3) in one portion. The resulting mixture was refluxed for 4 h, after which time further portions of TBTH (0.27 cm^3, 1.0 mmol, 0.5 mol equiv.) and AIBN (0.17 g, 1.0 mmol, 0.5 mol equiv.) were added. After a total of 5.5 h, the starting material had been consumed, and the solvent was removed under reduced pressure. The residue was chromatographed on silica and eluted with diethyl ether–light petroleum (1:5) to afford the products as mixtures of diastereoisomers. These were separated by chromatography on silica and elution with ethyl acetate–light petroleum (1:5), to afford {(1S,5R,6S)-3,3-*dimethyl*-2,4-*dioxabicyclo*[3.3.0]*octan*-6-*yl*}*acetonitrile* **21a** as a yellow oil (215 mg, 59%), $[\alpha]_D^{33}$ 50.5 (*c* 0.22, acetone) (Found: $M^+ - CH_3$, 166.0867. $C_9H_{12}NO_2$ requires $M - CH_3$, 166.0868); ν_{max}(film)/cm^{-1} 2937 (C–H), 2870 (C–H), 2249 (CN), 1376 (CMe_2) and 1091 (C–O); δ_H(250 MHz; $CDCl_3$) 1.30 and 1.43 (6 H, 2 × s, $OCMe_2O$), 1.46–2.07 [5 H, m, CH(OR)CH_2CH_2CH(R)], 2.45 [1 H, dd, *J* 16.8 and 7.5, CHC(H)*H*CN], 2.58 [1 H, dd, *J* 16.8 and 7.5,

‡ *m*-Nitrobenzyl alcohol (MNBA) matrix.

CHCH(*H*)CN], 4.52 [1 H, t, *J* 5.3, CHC*H*(OR)CH(R)] and 4.68 [1 H, t, *J* 5.1, CH_2CH(OR)CH]; δ_C(68 MHz; $CDCl_3$) 17.1 (t), 24.1 (q), 26.0 (q), 28.2 (t), 32.3 (t), 41.4 (d), 80.3 (d), 81.1 (d), 110.0 (s) and 119.7 (s); *m/z* (200 °C) 166 ($M^+ - CH_3$, 100%), 106 ($C_7H_8N^+$, 61) and 59 ($C_3H_7O^+$, 33); and {(1S,5R,6R)-3,3-*dimethyl*-2,4-*dioxabicyclo*[3.3.0]*octan*-6-*yl*}-*acetonitrile* **21b** as a yellow oil (43 mg, 12%); $[\alpha]_D^{33}$ 41.2 (*c* 0.02, acetone) (Found: $M^+ - CH_3$, 166.0865); ν_{max}(film)/cm^{-1} 2939 (C–H), 2249 (CN), 1377 (CMe_2) and 1.153 (C–O); δ_H(250 MHz; $CDCl_3$) 1.30 and 1.46 (6 H, 2 × s, $OCMe_2O$), 1.51–2.39 [7 H, m, $CHCH_2CH_2CH(CH_2CN)CH$], 4.34 [1 H, d, *J* 5.7, CH(OR)C*H*(OR)CH(R)] and 4.70 [1 H, t, *J* 5.3, CH_2CH-(OR)CH]; δ_C(100 MHz; $CDCl_3$) 19.6 (t), 24.2 (q), 26.6 (q), 27.9 (t), 30.6 (t), 42.2 (d), 80.5 (d), 84.8 (d), 110.7 (s) and 118.6 (s); *m/z* (200 °C) 166 ($M^+ - CH_3$, 81%), 106 ($C_7H_8N^+$, 58), 59 ($C_3H_7O^+$, 28) and 43 ($C_2H_3O^+$, 100). A further two fractions eluted at lower R_f were found to consist of 2-{(1S,5R,6R)-3,3-*dimethyl*-2,4-*dioxabicyclo*[3.3.0]*octan*-6-*yl*}-2-(*hydroxyimino*)-*acetonitrile* **30b** as a crystalline solid (10 mg, 2.4%), $[\alpha]_D^{25}$ +242.1 (*c* 0.08, acetone); mp 193–196 °C (Found: $M^+ - CH_3$, 195.0760. $C_9H_{11}N_2O_3$ requires $M - CH_3$, 195.0769); ν_{max}(KBr)/cm^{-1} 3251 (O–H), 3199 (O–H), 3034 (C–H), 2992 (C–H), 2978 (C–H), 2969 (C–H), 2946 (C–H), 2937 (C–H), 2872 (C–H), 2235 (CN), 1377 (CMe_2) and 1075 (C–O); δ_H(250 MHz; $CDCl_3$) 1.30 and 1.51 (6 H, 2 × s, $OCMe_2O$), 1.48–1.61 [1 H, m, (RO)CHCH(*H*)CH_2], 1.84 [1 H, m, CHC(H)*H*CH_2CH(R)], 2.12 [2 H, m, CH_2CH_2CH(R)], 3.15 [1 H, dt, *J* 12.7 and 6.0, CH_2CH(R)CH(OR)], 4.73 [1 H, t, *J* 5.0, CHC*H*(OR)CH(R)], 4.87 [1 H, t, *J* 5.5, CH_2CH(OR)CH] and 8.99 (1 H, br s, C=NOH); δ_C(100 MHz; [$^2H_6$]acetone) 23.9 (q), 25.7 (q), 26.3 (t), 31.9 (t), 41.7 (d), 80.9 (d), 81.2 (d), 110.3 (s), 115.6 (s) and 140.7 (s); *m/z* (170 °C) 195 ($M^+ - CH_3$, 41%), 152 ($C_8H_{10}NO_2^+$, 34), 92 ($C_6H_6N^+$, 37), 59 ($C_3H_7O^+$, 42) and 43 ($C_2H_3O^+$, 100); and 2-{(1S,5R,6S)-3,3-*dimethyl*-2,4-*dioxabicyclo*[3.3.0]*octan*-6-*yl*}-2-(*hydroxyimino*)*acetonitrile* **30a** as a crystalline solid (18 mg, 4.3%); $[\alpha]_D^{31}$ +119.6 (*c* 0.50, acetone); mp 126–130 °C (Found: $M^+ - CH_3$, 195.0744); ν_{max}(KBr)/cm^{-1} 3270 (O–H), 2983 (C–H), 2932 (C–H), 2877 (C–H), 2225 (CN), 1626 (C=N), 1.391 (CMe_2), 1382 (CMe_2) and 1083 (C–O); δ_H(400 MHz; $CDCl_3$) 1.31 and 1.50 (6 H, 2 × s, $OCMe_2O$), 1.52–1.62 [1 H, m, (RO)CHC*H*(H)CH_2], 1.78–1.84 [1 H, m, CH_2CH(H)CH(R)], 2.02 [1 H, m, (RO)CHCH(*H*)CH_2], 2.13 [1 H, m, CH_2CH(*H*)CH(R)], 2.72 [1 H, ddd, *J* 12.0, 5.9 and 5.6, CH(OR)C*H*(R)CH_2], 4.73 [2 H, m, CH_2CH(OR)C*H*(OR)CH(R)] and 9.44 (1 H, br s, C=NOH); δ_C(100 MHz; $CDCl_3$) 23.6 (q), 25.0 (q and t, overlapping), 31.6 (t), 46.1 (d), 80.4 (d), 80.9 (d), 109.6 (s), 110.5 (s) and 133.4 (s); *m/z* (200 °C) 195 ($M^+ - CH_3$, 7%), 152 ($C_8H_{10}NO_2^+$, 43), 92 ($C_6H_6N^+$, 60), 59 ($C_3H_7O^+$, 36) and 43 ($C_2H_3O^+$, 100).

Treatment of 2-[(4*R*,5*S*)-4-(benzoylbut-3-enyl)-2,2-dimethyl-1,3-dioxolan-4-yl]propan-2-yl nitrate 19 with TBTH and AIBN

To a stirred, refluxing solution of compound **19** (138 mg, 0.39 mmol) in sodium-dried, deoxygenated benzene (130 cm^3) was added a solution of TBTH (150 mm^3, 0.58 mmol, 1.5 mol equiv.) in one portion, followed immediately by a solution of AIBN (95 mg, 0.58 mmol, 1.5 mol equiv.) in benzene (2 cm^3) in one portion. The resulting mixture was refluxed for 4 h, after which time further portions of TBTH (50 mm^3, 0.19 mmol, 0.5 mol equiv.) and AIBN (32 mg, 0.19 mmol, 0.5 mol equiv.) were added. After a total of 6 h, the starting material had been consumed, and the solvent was removed under reduced pressure. The residue was chromatographed on silica with diethyl ether–light petroleum (1:5) as eluent to afford the product as a mixture of diastereoisomers. These were separated by chromatography on silica with dichloromethane–light petroleum (3:1) as eluent, to afford 2-{(1S,5R,6S)-3,3-*dimethyl*-2,4-*dioxabicyclo*[3.3.0]*octan*-6-*yl*}-1-*phenylethanone* **22a** as a yellow oil, which solidified on storage (45 mg, 46%), $[\alpha]_D^{31}$ +44.4 (*c* 1.1, acetone); mp 69–71 °C (Found: $M^+ - CH_3$, 245.1173. $C_{15}H_{17}O_3$ requires $M - CH_3$, 245.1178); ν_{max}(KBr)/cm^{-1} 2996 (C–H), 2978 (C–H), 2958 (C–H), 2933 (C–H), 2900 (C–H), 2864 (C–H), 1687 (C=O), 1373 (CMe_2), 759 (Ar–H) and 695 (Ar–H); δ_H(400 MHz; $CDCl_3$) 1.28 and 1.43 (6 H, 2 × s, $OCMe_2O$), 1.49–1.89 [4 H, m, CH(OR)CH_2CH_2CH(R)], 2.23–2.29 [1 H, m, CH(OR)C*H*(R)CH_2], 3.07 [1 H, dd, *J* 17.8 and 6.3, CHC*H*(H)C(O)Ph], 3.33 [1 H, dd, *J* 17.8 and 7.3, CHCH(*H*)C(O)Ph], 4.64–4.68 [2 H, m, CH_2CH(OR)C*H*-(OR)CH(R)], 7.46 [2 H, t, *J* 7.6, 3- and 5-H (Ph)], 7.56 [1 H, t, *J* 7.4, 4-H (Ph)] and 8.01 [2 H, d, *J* 7.2, 2- and 6-H) (Ph)]; δ_C(68 MHz; $CDCl_3$) 23.8 (q), 25.9 (q), 28.0 (t), 32.2 (t), 37.8 (t), 39.7 (d), 80.7 (d), 81.1 (d), 108.9 (s), 128.1 (d), 128.4 (d), 132.8 (d), 137.2 (s) and 199.7 (s); *m/z* (200 °C) 245 ($M^+ - CH_3$, 14%), 202 ($C_{13}H_{14}O_2^+$, 8), 105 ($C_7H_5O^+$, 100) and 59 ($C_3H_7O^+$, 5); and 2-{(1S,5R,6R)-3,3-*dimethyl*-2,4-*dioxa*[3.3.0]*bicyclooctan*-6-*yl*}-1-*phenylethanone* **22b** as a yellow oil, which solidified on storage (12 mg, 11%), $[\alpha]_D^{31}$ +31.3 (*c* 0.62, acetone); mp 55–57 °C (Found: $M^+ - CH_3$, 245.1156); ν_{max}(KBr)/cm^{-1} 2993 (C–H), 2979 (C–H), 2961 (C–H), 2952 (C–H), 2935 (C–H), 2912 (C–H), 2872 (C–H), 1673 (C=O), 1375 (CMe_2), 754 (Ar–H) and 690 (Ar–H); δ_H(400 MHz; $CDCl_3$) 1.29 and 1.45 (6 H, 2 × s, $OCMe_2O$), 1.40–1.44 [1 H, m, CH(OR)C*H*(H)CH_2], 1.76–1.88 [2 H, m, CH(OR)CH(*H*)CH(*H*)CH(R)], 2.06–2.15 [1 H, m, CHCH(*H*)CH(R)], 2.68 [1 H, m, CH_2CH(R)CH(OR)], 2.81 [1 H, dd, *J* 16.0 and 8.0, CHC*H*(H)C(O)Ph], 2.95 [1 H, dd, *J* 16.1 and 7.2, CHCH(*H*)C(O)Ph], 4.37 [1 H, d, *J* 5.8, CHC*H*(OR)CH(R)], 4.69 [1 H, t, *J* 5.9, CH_2CH(OR)CH], 7.46 [2 H, t, *J* 7.6, 3- and 5-H (Ph)], 7.56 [1 H, t, *J* 7.3, 4-H (Ph)] and 7.95 [2 H, d, *J* 7.1, 2- and 6-H (Ph)]; δ_C(68 MHz; $CDCl_3$) 24.1 (q), 26.5 (q), 27.9 (t), 31.0 (t), 40.2 (t), 41.3 (d), 80.5 (d), 85.8 (d), 109.9 (s), 128.1 (d), 128.6 (d), 133.1 (d), 136.8 (s) and 198.8 (s); *m/z* (200 °C) 245 ($M^+ - CH_3$, 25%), 202 ($C_{13}H_{14}O_2^+$, 8), 105 ($C_7H_5O^+$, 100) and 59 ($C_3H_7O^+$, 6).

Treatment of 2-[(4*R*,5*S*)-2,2-dimethyl-5-(non-3-enyl)-1,3-dioxolan-4-yl]propan-2-yl nitrate 20 with TBTH and AIBN

To a stirred, refluxing solution of compound **20** (591 mg, 1.80 mmol) in sodium-dried, deoxygenated benzene (450 cm^3) was added TBTH (700 mm^3, 2.70 mmol, 1.5 mol equiv.), in one portion, followed immediately by a solution of AIBN (443 mg, 2.70 mmol, 1.5 mol equiv.) in benzene (10 cm^3) in one portion. The resulting mixture was refluxed for 4 h, after which time further portions of TBTH (233 mm^3, 0.90 mmol, 0.5 mol equiv.) and AIBN (148 mg, 0.90 mmol, 0.5 mol equiv.) were added. After a total of 5.5 h, the starting material had been consumed, and the solvent was removed under reduced pressure. The residue was chromatographed on silica with diethyl ether–light petroleum (1:50) as eluent, to afford the product diastereoisomers (1S,5R,6R)-6-*hexyl*-3,3-*dimethyl*-2,4-*dioxabicyclo*[3.3.0]*octane* **23a** as a yellow liquid (218 mg, 54%), $[\alpha]_D^{31}$ +42.9 (*c* 2.7, acetone) (Found: C, 74.8; H, 12.1. $C_{14}H_{26}O_2$ requires C, 74.29; H, 11.58%) (Found: $M^+ - CH_3$, 211.1700. $C_{13}H_{23}O_2$ requires $M - CH_3$, 211.1698); ν_{max}(film)/cm^{-1} 2957 (C–H), 2928 (C–H), 2857 (C–H), 1379 (CMe_2), 1371 (CMe_2) and 1043 (C–O); δ_H(250 MHz; $CDCl_3$) 0.88 (3 H, m, $CH_2[CH_2]_4Me$), 1.21–1.64 {14 H, m, $CHCH_2$-$[CH_2]_4Me$ and (OR)CH$[CH_2]_2$CH(R)}, 1.29 and 1.42 (6 H, 2 × s, $OCMe_2O$), 1.72–1.81 [1 H, m, CH(OR)C*H*(R)CH_2], 4.46 [1 H, t, *J* 5.1, (OR)C*H*CH(R)CH_2] and 4.61 [1 H, t, *J* 5.1, CH(OR)C*H*(OR)CH_2]; δ_C(68 MHz; $CDCl_3$) 14.0 (q), 22.6 (t), 23.8 (q), 25.8 (q), 27.9 (t), 28.5 (t), 28.6 (t), 29.6 (t), 31.8 (t), 32.4 (t), 45.1 (d), 80.7 (d), 81.4 (d) and 108.6 (s); *m/z* (200 °C) 211 ($M^+ - CH_3$, 100%), 151 ($C_{11}H_{19}^+$, 79) and 59 ($C_3H_7O^+$, 30); and (1S,5R,6S)-6-*hexyl*-3,3-*dimethyl*-2,4-*dioxabicyclo*[3.3.0]-*octane* **23b** as an orange liquid (87 mg, 21%), $[\alpha]_D^{31}$ +17.3 (*c* 1.7, acetone) (Found: C, 73.9; H, 12.0%) (Found: $M^+ -$

CH_3, 211.1691. $C_{13}H_{23}O_2$ requires M − CH_3, 211.1698); ν_{max}(film)/cm^{-1} 2927 (C–H), 2857 (C–H), 1379 (CMe_2), 1371 (CMe_2) and 1044 (C–O); δ_H(250 MHz; $CDCl_3$) 0.88 (3 H, m, $CH_2[CH_2]_4Me$), 1.05–1.56 (10 H, m, $CHCH_2[CH_2]_4Me$), 1.29 and 1.45 (6 H, 2 × s, $OCMe_2O$), 1.68–2.01 [5 H, m, (OR)CH-CH_2CH_2CH(R)], 4.26 [1 H, d, *J* 5.8, (RO)CHCH(OR)CH(R)] and 4.62 [1 H, m, (RO)CHCH(OR)CH_2]; δ_C(68 MHz; $CDCl_3$) 14.0 (q), 22.6 (t), 24.0 (q), 26.5 (q), 27.7 (t), 27.9 (t), 29.3 (t), 30.9 (t), 31.4 (t), 31.8 (t), 45.0 (d), 80.6 (d), 86.2 (d) and 109.4 (s); *m/z* (200 °C) 211 (M^+ − CH_3, 59%), 151 ($C_{11}H_{19}^+$, 56), 67 ($C_5H_7^+$, 100) and 59 ($C_3H_7O^+$, 26).

2-[(4*R*,5*S*)-5-Hydroxymethyl-2,2-dimethyl-1,3-dioxolan-4-yl] propan-2-yl nitrate

To a stirred solution of compound **5** (2.80 g, 8.01 mmol) in dry, distilled THF (30 cm^3) was added tetrabutylammonium fluoride (TBAF) (8.40 cm^3 of a 1.0 mol dm^{-3} solution in THF; 8.40 mmol, 1.05 mol equiv.) dropwise at room temp. After 5 min, saturated aq. ammonium chloride (10 cm^3) was added, followed by water (10 cm^3) and the phases were separated. The aqueous phase was extracted with diethyl ether (20 cm^3) and the combined organic layers were dried (Na_2SO_4), and evaporated under reduced pressure. The residue was chromatographed on silica with diethyl ether–light petroleum (2:3–1:1) as eluent to afford 2-[(4R,5S)-5-*hydroxymethyl*-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]*propan*-2-*yl nitrate* as an oil (1.87 g, 100%), $[\alpha]_D^{33}$ −17 (*c* 1.0, acetone) (Found: M^+ − CH_3, 220.0773. $C_8H_{14}NO_6$ requires M − CH_3, 220.0821); ν_{max}(film)/cm^{-1} 3446, 2991, 2940, 1625, 1459, 1374 and 1251; δ_H(400 MHz; $CDCl_3$) 1.43, 1.45, 1.49 and 1.51 (12 H, 4 × s, 2 × CMe_2), 2.20 (1 H, br s, OH), 3.66–3.88 (2 H, m, CH_2OH), 4.07 [1 H, d, *J* 7.8, (RO)C*H*CH] and 4.12 (1 H, m, CH_2CH); δ_C(100 MHz; $CDCl_3$) 20.5, 22.5, 26.9, 27.5, 63.4, 77.8, 80.0, 90.3 and 110.0; *m/z* (180 °C) 220 (M^+ − CH_3, 1%), 155 (M^+ − H_2NO_4, 30), 131 (M^+ − $C_3H_6NO_3$, 6) and 59 ($C_3H_7O^+$, 100).

Methyl hydrogen but-2-enedioate[20]

This compound was obtained from maleic anhydride by treatment with thionyl dichloride in methanol according to the procedure of Eisner, Elvidge and Linstead.[20] The product was obtained as a crystalline solid, mp 141–142 °C (lit.,[20] 141 °C) (Found: C, 46.4; H, 4.6. Calc. for $C_5H_6O_4$: C, 46.16; H, 4.65%); ν_{max}(KBr)/cm^{-1} 3400–2600, 1722, 1688, 1635, 1440 and 1000; δ_H(400 MHz; CD_3OD) 3.80 (3 H, s, OMe) and 6.80 (2 H, s, CH=CH); δ_C(100 MHz; CD_3OD) 52.8, 134.1, 135.4, 167.0 and 167.9; *m/z* (200 °C) 130 (M^+, 9%), 99 (M^+ − OCH_3, 100) and 85 (M^+ − CO_2H, 94).

2-{[(4*R*,5*S*)-5-[3-(Methoxycarbonyl)propenoyloxymethyl]-2,2-dimethyl-1,3-dioxolan-4-yl]}propan-2-yl nitrate 33

To a stirred mixture of 2-[(4*R*,5*S*)-2,2-dimethyl-5-hydroxymethyl-1,3-dioxolan-4-yl]propan-2-yl nitrate (235 mg, 1.00 mmol) and methyl hydrogen but-2-eneoate (130 mg, 1.0 mmol) in sodium-dried diethyl ether (10 cm^3) were added, at 0 °C (ice-bath), a solution of 4-(dimethylamino)pyridine (DMAP) (12 mg, 0.098 mmol, 0.1 mol equiv.) in diethyl ether (1 cm^3), and then a solution of dicyclohexylcarbodiimide (DCC) (206 mg, 1.00 mmol) in diethyl ether (2 cm^3), both dropwise. The mixture was allowed to warm to room temp. and was stirred for 4 h. Diethyl ether (20 cm^3) was added, the precipitate was removed by filtration, and the filtrate was washed successively with saturated aq. sodium hydrogen carbonate (10 cm^3) and then saturated brine (10 cm^3). The organic phase was dried (Na_2SO_4), and the solvent was removed under reduced pressure. The residue was chromatographed on silica with diethy ether–light petroleum (1:5) as eluent to afford the *title compound* **33** as a solid (251 mg, 74%); mp 45 °C, $[\alpha]_D^{33}$ −21 (*c* 1.0, acetone) (Found: M^+ − CH_3, 332.0936. $C_{13}H_{18}NO_9$ requires M − CH_3, 332.0981); ν_{max}(KBr)/cm^{-1} 3083, 2996, 2954, 2907, 1718, 1627, 1443, 1373 and 1252; δ_H(400 MHz; $CDCl_3$) 1.42, 1.46, 1.64 and 1.67 (12 H, 4 × s, 2 × CMe_2), 3.82 (3 H, s, OMe), 4.07 [1 H, d, *J* 7.7, (RO)C*H*CH], 4.24–4.30 [2 H, m, $CHCH$(OR)CH(H)O], 4.50 [1 H, dm, *J* 8.8, CHCH(*H*)O] and 6.91 [2 H, s, OC(O)CH=CH(O)CO]; δ_C(100 MHz; $CDCl_3$) 20.2, 22.6, 26.9, 27.3, 52.4, 65.9, 75.3, 80.6, 90.2, 110.9, 133.0, 164.6 and 165.1; *m/z* (200 °C) 332 (M^+ − CH_3, 3%) and 113 ($C_5H_5O_3^+$, 100).

2-[(4*R*,5*S*)-5-Cinnamoyloxymethyl-2,2-dimethyl-1,3-dioxolan-4-yl]propan-2-yl nitrate 34

To a solution of 2-[(4*R*,5*S*)-5-hydroxymethyl-2,2-dimethyl-1,3-dioxolan-4-yl]propan-2-yl nitrate (235 mg, 1.00 mmol) and pyridine (174 mg, 2.20 mmol, 2.2 mol equiv.) in dry, distilled THF (1.5 cm^3) under nitrogen at room temp. was added a solution of cinnamoyl chloride (183 mg, 1.10 mmol, 1.1 mol equiv.) in THF (1.5 cm^3) and the mixture was stirred for 20 h. More cinnamoyl chloride (83 mg, 0.50 mmol, 0.5 mol equiv.) was added and the mixture was stirred at room temperature under nitrogen for a further 4 h, then was poured into saturated aq. sodium hydrogen carbonate (20 cm^3) and extracted with diethyl ether (2 × 30 cm^3). The combined organic extracts were washed successively with water (10 cm^3) and saturated brine (10 cm^3), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was chromatographed on silica and eluted with dichloromethane–light petroleum (1:1) to afford 2-[(4R,5S)-5-*cinnamoyloxymethyl*-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]*propan*-2-*yl nitrate* **34** as a thick oil that solidified on refrigeration as a solid (292 mg, 80%), mp 60–61 °C, $[\alpha]_D^{33}$ −22 (*c* 1.0, acetone) (Found: M^+ − CH_3 − HNO_3, 287.1286. $C_{17}H_{19}O_4$ requires M − CH_3 − HNO_3, 287.1283); ν_{max}(KBr)/cm^{-1} 2994, 2947, 1699, 1632, 1497, 1452 and 1373; λ_{max}(EtOH)/nm 279 (ε 28 000); δ_H(250 MHz; $CDCl_3$) 1.45, 1.47, 1.65 and 1.67 (12 H, 4 × s, 2 × CMe_2), 4.12 [1 H, d, *J* 7.1, (RO)C*H*CH], 4.22–4.34 [2 H, m, $CHCH$(OR)CH(H)O], 4.49 [1 H, dd, *J* 11.1 and 2.6, CHCH(*H*)O], 6.49 [1 H, d, *J* 16.0, OC(O)C*H*=CHPh (*E*)], 7.38–7.55 (5 H, m, Ph) and 7.74 [1 H, d, *J* 16.0, OC(O)CH=C*H*Ph (*E*)]; δ_C(100 MHz; $CDCl_3$) 20.4, 22.3, 27.0, 27.3, 65.4, 75.6, 80.9, 90.2, 110.8, 117.3, 128.2, 128.9, 130.5, 134.2, 145.8 and 166.6; *m/z* (200 °C) 287 (M^+ − CH_4NO_3, 6%), 131 ($C_9H_7O^+$, 100) and 103 ($C_8H_7^+$, 32).

Methyl 2-{(3a*S*,7*S*,7a*R*)-2,2-dimethyl-6-oxo-3a,6,7,7a-tetrahydro-4*H*-1,3-dioxolo[4,5-*c*]pyran-7-yl}acetate 35

To a stirred, refluxing solution of compound **33** (84 mg, 0.25 mmol) in sodium-dried, deoxygenated benzene (50 cm^3) was added TBTH (110 mm^3, 0.41 mmol, 1.6 mol equiv.), in one portion, followed immediately by a solution of AIBN (62 mg, 0.38 mmol, 1.5 mol equiv.) in benzene (2 cm^3) in one portion. The resulting mixture was refluxed for 1.5 h, and then the solvent was removed under reduced pressure. The residue was chromatographed on silica and eluted with diethyl ether–light petroleum (5:1) to afford *methyl* 2-{(3aS,7S,7aR)-2,2-*dimethyl*-6-*oxo*-3a,6,7,7a-*tetrahydro*-4H-1,3-*dioxolo*[4,5-c]*pyran*-7-*yl*} *acetate* **35** as a solid (23 mg, 39%), mp 86–89 °C; $[\alpha]_D^{30}$ +120 (*c* 2.4, $CHCl_3$) (Found: C, 54.2; H, 6.4. $C_{11}H_{16}O_6$ requires C, 54.09; H, 6.60%); ν_{max}(KBr)/cm^{-1} 2993, 2979, 2956, 2938, 2924, 2906, 1747, 1437 and 1377; δ_H(250 MHz; $CDCl_3$) 1.32 and 1.42 (6 H, 2 × s, CMe_2) 2.63 [1 H, dd, *J* 19.4 and 9.0, $CHCH$(H)CO_2Me], 3.05 [1 H, m, $CHCH$(COR)CH(H)], 3.08 [1 H, dd (partly obscured), *J* 19.4 and 6.5, CHCH(*H*)CO_2Me], 3.73 (3 H, s, OMe), 4.23 [1 H, dd, *J* 13.0 and 1.4, OCH(H)CH], 4.45 [1 H, d, *J* 13.0, OCH(*H*)CH], 4.55 [1 H, d, *J* 7.7, (RO)C*H*CH] and 4.68 [1 H, dd, *J* 7.7 and 2.9, CHC*H*-(OR)CH]; δ_C(100 MHz; $CDCl_3$) 24.1, 25.9, 31.0, 40.2, 52.0, 67.8, 72.5, 73.9, 109.7, 170.7 and 172.2; *m/z* (200 °C) 229 (M^+ − CH_3, 39%), 213 (M^+ − CH_3O, 14) and 43 ($C_2H_3O^+$, 100).

(3a*S*,7*S*,7a*R*)-7-Benzyl-2,2-dimethyl-3a,6,7,7a-tetrahydro-4*H*-1,3-dioxolo[4,5-*c*]pyran-6-one 36

To a stirred, refluxing solution of compound **34** (92 mg, 0.25 mmol) in sodium-dried, deoxygenated benzene (50 cm^3) under nitrogen was added TBTH (100 mm^3, 0.37 mmol, 1.5 mol equiv.), in one portion, followed immediately by a solution of AIBN (62 mg, 0.38 mmol, 1.5 mol equiv.) in benzene (2 cm^3) in one portion. The resulting mixture was refluxed for 2.5 h, and then the solvent was removed under reduced pressure. The residue was chromatographed on silica and eluted with diethyl ether–light petroleum (1:1) to afford (3aS,7S, 7aR)-7-*benzyl*-2,2-*dimethyl*-3a,6,7,7a-*tetrahydro*-4H-1,3-*dioxolo*[4,5-c]*pyran*-6-*one* **36** as a solid (16 mg, 24%); mp 106–109 °C, $[\alpha]_D^{30}$ +128 (*c* 1.7, $CHCl_3$) (Found: M^+, 262.1207. $C_{15}H_{18}O_4$ requires M, 262.1205); ν_{max}(KBr)/cm^{-1} 2992, 2939, 2914, 1735, 1606, 1498, 1380, 1369, 750 and 702; δ_H(400 MHz; $CDCl_3$) 1.31 and 1.48 (6 H, 2 × s, CMe_2), 2.58 [1 H, ddd, *J* 10.3, 4.6 and 2.6, CHC*H*(COR)CH(H)], 2.95 [1 H, dd, *J* 14.0 and 10.3, CHC*H*(H)Ph], 3.34 [1 H, dd, *J* 14.0 and 4.6, CHCH(*H*)Ph], 4.07 [1 H, dd, *J* 13.0 and 1.7, OC*H*(H)CH], 4.40 [3 H, m, OCH(*H*)C*H*(OR)C*H*(OR)CH] and 7.25–7.35 (5 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 24.2, 26.0, 32.1, 45.3, 67.9, 72.5, 109.6, 126.7, 128.7, 129.4 and 138.6; *m*/*z* (200 °C) 262 (M^+, 8%), 247 ($M^+ - CH_3$, 35), 148 ($C_9H_8O_2^+$, 68), 131 ($C_9H_7O^+$, 87), 91 ($C_7H_7^+$, 100) and 43 ($C_2H_3O^+$, 81).

(4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-dimethanol 37

To a stirred, cooled (ice-bath) solution of dimethyl (4*S*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (55.38 g, 0.25 mol) in methanol (1000 cm^3) was added sodium boranuide (14.3 g, 0.38 mol, 1.5 mol equiv.) portionwise over a 1 h period. A further portion of sodium boranuide (4.8 g, 0.13 mol, 0.5 mol equiv.) was added, and the resulting mixture was stirred at room temp. for a further 2 h, until the starting material had been consumed. The solvent was removed under reduced pressure, the residue was partitioned between water (100 cm^3) and ethyl acetate (3 × 100 cm^3), and the combined organic phases were dried (Na_2SO_4) and evaporated to give a crude product. Chromatography on silica and elution with ethyl acetate (100%) afforded (4R,5R)-2,2-*dimethyl*-1,3-*dioxolane*-4,5-*dimethanol* **37** as a very viscous oil (36.7 g, 89%), $[\alpha]_D^{29}$ −4.9 (*c* 0.74, $CHCl_3$) (Found: $M^+ - CH_3$, 147.0745. $C_6H_{11}O_4$ requires M − CH_3, 147.0657); ν_{max}(film)/cm^{-1} 3400 (O–H), 2988 (C–H), 2936 (C–H), 1373 (CMe_2) and 1112 (C–O); δ_H 250 MHz; $CDCl_3$) 1.43 (6 H, s, $OCMe_2O$), 2.63 (2 H, br s, 2 × CH_2OH), 3.76 (4 H, m, 2 × $CHCH_2OH$) and 4.00 [2 H, m, 2 × (RO)C*H*CH_2OH]; δ_C(68 MHz; $CDCl_3$) 26.8 (q), 62.1 (t), 78.3 (d) and 109.2 (s); *m*/*z* (200 °C) 147 ($M^+ - CH_3$, 35%) and 59 ($C_3H_7O^+$, 100).

(4*R*,5*R*)-5-(*tert*-Butyldimethylsiloxymethyl)-2,2-dimethyl-1,3-dioxolane-4-methanol 38

(4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-dimethanol **37** (17.3 g, 110 mmol), *tert*-butyldimethylsilyl chloride (17.7 g, 120 mmol, 1.1 mol equiv.) and imidazole (18.2 g, 270 mmol, 2.5 mol equiv.) were stirred together in dry, distilled DMF (25 cm^3) at room temp. for 1 h. The mixture was partitioned between water (50 cm^3) and ethyl acetate (3 × 50 cm^3). The combined organic phases were dried (Na_2SO_4) and evaporated, and the crude product was chromatographed on silica, and eluted with diethyl ether–light petroleum (1:4) to afford the diprotected diol as a clear liquid (13.42 g, 32%), followed by elution with diethyl ether–light petroleum (2:3) to afford (4R,5R)-5-(tert-*butyldimethylsiloxymethyl*)-2,2-*dimethyl*-1,3-*dioxolane*-4-*methanol* **38** as an oil (13.0 g, 44%), $[\alpha]_D^{30}$ +7.1 (*c* 0.56, acetone) (Found: $M^+ - CH_3$, 261.1510. $C_{12}H_{25}O_4Si$ requires M − CH_3, 261.1522); ν_{max}(film)/cm^{-1} 3468 (O–H), 2986 (C–H), 2953 (C–H), 2930 (C–H), 2859 (C–H), 1371 (CMe_2) and 1082 (Si–O); δ_H(250 MHz; $CDCl_3$) 0.09 (6 H, s, $OSiMe_2CMe_3$), 0.90 (9 H, s, Bu^t), 1.40 and 1.42 (6 H, 2 × s, $OCMe_2O$), 2.52 (1 H, br s, CH_2OH), 3.64–3.71 (2 H, m, $CHCH_2OSi$), 3.75–3.92 (3 H, m) and 4.00 (1 H, dt, *J* 7.5 and 4.5, C*H*CH_2); δ_C(68 MHz; $CDCl_3$) −5.5 (q), 18.3 (s), 25.8 (q), 26.9 (q), 27.0 (q), 62.7 (t), 63.7 (t), 78.1 (d), 80.1 (d) and 109.1 (s); *m*/*z* (200 °C) 261 ($M^+ - CH_3$, 12%), 219 [$M^+ - C(CH_3)_3$, 12], 131 ($C_5H_7O_4^+$, 92), 89 [$OSi(CH_3)_3^+$, 11], 75 ($C_2H_7OSi^+$, 100) and 73 [$Si(CH_3)_3^+$, 72].

(4*S*,5*R*)-5-(*tert*-Butyldimethylsiloxymethyl)-2,2-dimethyl-1,3-dioxolane-4-carbaldehyde 39

This compound was prepared from compound **38** (2.33 g, 8.4 mmol), oxalyl dichloride (0.84 cm^3, 9.3 mmol), dimethyl sulfoxide (DMSO) (1.43 cm^3, 18.5 mmol) and triethylamine (5.89 cm^3, 42.1 mmol) in dichloromethane (20 cm^3) according to the procedure of Swern,[13] to afford (4S,5R)-5-(tert-*butyldimethylsiloxymethyl*)-2,2-*dimethyl*-1,3-*dioxolane*-4-*carbaldehyde* **39** as a light yellow oil (2.3 g, crude), which was used directly in the subsequent step (Found: $M^+ - CH_3$, 259.1375. $C_{12}H_{23}O_4Si$ requires M − CH_3, 259.1366); δ_H(270 MHz; $CDCl_3$) 0.00 (6 H, s, $OSiMe_2CMe_3$), 0.82 (9 H, s, Bu^t), 1.34 and 1.40 (6 H, 2 × s, $OCMe_2O$), 3.72 [2 H, d, *J* 4.3, (RO)CHC*H*$_2$OSi], 4.04 [1 H, dt, *J* 7.3 and 4.3, (RO)C*H*-CH_2OSi], 4.25 [1 H, dd, *J* 7.3 and 1.3, (RO)C*H*C(H)O] and 9.69 [1 H, d, *J* 1.3, (RO)CHC*H*O]; *m*/*z* (200 °C) 259 ($M^+ - CH_3$, 1%), 159 ($C_6H_{11}O_3Si^+$, 15), 89 ($OSiMe_3^+$, 9), 75 ($C_2H_7OSi^+$, 100) and 73 ($SiMe_3^+$, 49).

[(4*R*,5*R*)-5-(*tert*-Butyldimethylsiloxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl]phenylmethanol 40

Compound **39** [2.30 g (crude), 8.4 mmol] was dissolved in THF (60 cm^3) and phenyllithium (5.6 cm^3, 10.0 mmol; 1.8 mol dm^{-3} in diethyl ether, 1.2 mol equiv.) added dropwise to this solution cooled to −60 °C. The resulting mixture was stirred for a further 10 min, warmed to room temp., and quenched with water (10 cm^3). The aqueous phase was extracted with diethyl ether (2 × 50 cm^3), and the combined organic extracts was dried (Na_2SO_4) and evaporated to yield a crude product, which was chromatographed on silica with dichloromethane (100%) elution, to afford [(4R,5R)-5-(tert-*butyldimethylsiloxymethyl*)-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]*phenylmethanol* **40** as a pair of diastereoisomers (1.57 g, 53% over 2 steps) (Found: $M^+ - CH_3$, 337.1842. $C_{18}H_{29}O_4Si$ requires M − CH_3, 337.1835); ν_{max}(film)/cm^{-1} 3436 (O–H), 2986 (C–H), 2955 (C–H), 2931 (C–H), 2858 (C–H), 1381 (CMe_2), 1083 (C–O), 779 (Ar–H) and 703 (Ar–H); *m*/*z* (200 °C) 337 ($M^+ - CH_3$, 5%), 245 ($C_{15}H_{21}OSi^+$, 23), 117 ($C_4H_9O_2Si^+$, 100), 75 ($C_2H_7OSi^+$, 52) and 73 ($SiMe_3^+$, 66).

Although the diastereoisomeric mixture was used for chemical transformations, small quantities of the two diastereoisomers were separated for determination of spectroscopic properties as follows:

Diastereoisomer A (major) was isolated as a light yellow, crystalline solid, $[\alpha]_D^{25}$ +2.4 (*c* 0.17, acetone), mp 39–43 °C; δ_H(250 MHz; $CDCl_3$) −0.01 and 0.03 (6 H, 2 × s, $OSiMe_2$), 0.89 (9 H, s, Bu^t), 1.38 and 1.42 (6 H, 2 × s, $OCMe_2O$), 3.20 [1 H, dd, *J* 10.7 and 3.6, (RO)CHC*H*(H)OSi], 3.56 [1 H, br s, CH(Ph)O*H*], 3.51 [1 H, dd, *J* 10.7 and 4.4, (RO)CHCH-(*H*)OSi], 4.01–4.07 [1 H, m, CH(OR)C*H*(OR)CH_2], 4.14 [1 H, dd, *J* 7.8 and 5.3, CHC*H*(OR)CH(Ph)OH], 4.86 [1 H, d, *J* 5.2, CHC*H*(Ph)OH] and 7.24–7.41 (5 H, m, Ph); δ_C(68 MHz; $CDCl_3$) −5.7 (q), −5.6 (q), 18.3 (s), 25.8 (q), 26.9 (q), 27.0 (q), 63.5 (t), 73.0 (d), 78.1 (d), 81.5 (d), 109.0 (s), 126.3 (d), 127.7 (d), 128.2 (d) and 139.7 (s).

Diastereoisomer B (minor) was isolated as a yellow, viscous oil; $[\alpha]_D^{25}$ +18.0 (*c* 0.10, acetone); δ_H(250 MHz; $CDCl_3$) −0.05 and −0.02 (6 H, 2 × s, $OSiMe_2$), 0.85 (9 H, s, $OSiMe_2CMe_3$), 1.41 (6 H, s, $OCMe_2O$), 3.15 [1 H, dd, *J* 10.8

and 5.0, (RO)CHC(H)*H*OSi], 3.29 [1 H, br d, *J* 4.7, CH(OR)CH(Ph)O*H*], 3.40 [1 H, dd, *J* 10.8 and 4.4, CH(OR)-C*H*(H)OSi], 3.85 [1 H, dt, *J* 7.8 and 4.3, C*H*(OR)CH(H)OSi], 4.18 [1 H, dd, *J* 7.8 and 6.1, CH(OR)C*H*(OR)CH(Ph)], 4.69 [1 H, br t, *J* 5.1, CH(OR)C*H*(Ph)OH] and 7.27–7.39 (5 H, m, Ph); δ_C(68 MHz; $CDCl_3$) −5.6 (q), −5.5 (q), 18.3 (s), 25.8 (q), 27.1 (q), 27.2 (q), 63.1 (t), 74.7 (d), 78.0 (d), 81.5 (d), 109.5 (s), 126.9 (d), 128.1 (d), 128.4 (d) and 139.9 (s).

[(4*S*,5*R*)-5-(*tert*-Butyldimethylsiloxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl]phenylmethyl nitrate 41

Fuming, conc. nitric acid (0 2 cm^3, 4.7 mmol) was added dropwise to stirred, cooled (ice-bath) acetic anhydride (10 cm^3, 11.0 mmol). Of the resulting stirred, cooled (ice-bath) solution, a portion (0.65 cm^3, 2.5 mmol based on fuming conc. nitric acid, ~ 3 mol equiv.) was added to a solution of compound **40** (0.31 g, 0.87 mmol) in acetic acid (1 cm^3) dropwise. The resulting mixture was stirred for 5 min and was then poured into saturated aq. sodium hydrogen carbonate (20 cm^3) and the mixture was vigorously stirred for 20 min. The aq. solution was extracted into diethyl ether (3 × 30 cm^3) and the combined extracts were dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed on silica and eluted with diethyl ether–light petroleum (1:5) to afford [(4S,5R)-5-(tert-*butyldimethylsiloxymethyl*)-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]*phenylmethyl nitrate* **41** as a pair of diastereoisomers (0.253 g, 73%) (Found: $M^+ - CH_3$, 382.1693. $C_{18}H_{28}NO_6Si$ requires $M - CH_3$, 382.1686); ν_{max}(film)/cm^{-1} 2988 (C–H), 2955 (C–H), 2931 (C–H), 2859 (C–H), 1641 (N=O), 1382 (CMe_2), 1372 (CMe_2), 1089 (C–O), 780 (Ar–H) and 701 (Ar–H); *m*/*z* (200 °C) 382 ($M^+ - CH_3$, 1%), 245 ($C_{12}H_{25}O_3Si^+$, 6), 169 ($C_8H_{13}O_2Si^+$, 70) and 75 ($C_2H_7OSi^+$, 100).

Although the diastereoisomeric mixture was used for chemical transformations, small quantities of the two diastereoisomers were separated for determination of spectroscopic properties as follows:

Diastereoisomer A was isolated as a yellow oil, $[\alpha]_D^{24}$ +30.8 (*c* 0.01, acetone); δ_H(250 MHz; $CDCl_3$) 0.04 and 0.06 (6 H, 2 × s, $OSiMe_2$), 0.91 (9 H, s, Bu^t), 1.15 and 1.38 (6 H, 2 × s, $OCMe_2O$), 3.58 [1 H, dd, *J* 10.5 and 4.2, CH(OR)C*H*(H)OSi], 3.67 [1 H, dd, *J* 10.6 and 5.4, CH(OR)CH(*H*)OSi], 3.89 [1 H, m, CHC*H*(OR)CH_2], 4.37 [1 H, dd, *J* 8.0 and 3.8, CHC*H*(OR)CH(Ph)], 6.05 [1 H, d, *J* 3.8, C*H*(Ph)CH(OR)] and 7.35–7.42 (5 H, m, Ph); δ_C(68 MHz; $CDCl_3$) −5.6 (q), −5.5 (q), 18.3 (s), 25.9 (q), 26.5 (q), 27.2 (q), 63.5 (t), 77.5 (d), 78.5 (d), 83.9 (d), 110.4 (s), 127.9 (d), 128.4 (d), 129.1 (d) and 133.6 (s).

Diasteroisomer B was isolated as a yellow oil, $[\alpha]_D^{24}$ +21.3 (*c* 0.08, acetone); δ_H(250 MHz; $CDCl_3$) −0.08 and −0.04 (6 H, 2 × s, $OSiMe_2$), 0.84 (9 H, s, Bu^t), 1.42 and 1.47 (6 H, 2 × s, $OCMe_2O$), 2.77 [1 H, dd, *J* 11.2 and 3.6, (RO)CHC(H)-*H*OSi], 3.38 [1 H, dd, *J* 11.2 and 3.4, (RO)CHCH(*H*)OSi], 3.85 [1 H, dt, *J* 7.8 and 3.5, CH(RO)C*H*CH_2], 4.41 [1 H, t, *J* 7.7, CH(RO)C*H*CH(Ph)], 5.82 [1 H, d, *J* 7.5, (RO)CHC*H*(Ph)] and 7.40 (5 H, s, Ph); δ_C(68 MHz; $CDCl_3$) −5.7 (q), −5.5 (q), 18.2 (s), 25.8 (q), 27.0 (q), 62.0 (t), 76.4 (d), 78.5 (d), 86.1 (d), 110.2 (s), 127.7 (d), 128.9 (d), 129.8 (d) and 133.9 (s).

[(4*S*,5*R*)-5-Hydroxymethyl-2,2-dimethyl-1,3-dioxolan-4-yl]-phenylmethyl nitrate 42

Compound **41** (0.20 g, 0.50 mmol) was taken up in THF (10 cm^3), and a stirred solution of TBAF (0.6 cm^3, 0.6 mmol, 1.2 mol equiv.; 1.0 mol dm^{-3} in THF) was added dropwise to the first solution stirred at room temp. After the mixture had been stirred for a further 10 min, saturated aq. ammonium chloride (10 cm^3) was added, followed by diethyl ether (20 cm^3). The aqueous layer was extracted with ethyl acetate (3 × 20 cm^3), and the combined organics were dried, and evaporated under reduced pressure. The crude product was chromatographed on silica with diethyl ether–light petroleum (1:1) elution to afford [(4S,5R)-5-*hydroxymethyl*-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]-*phenylmethyl nitrate* **42** as a pair of diastereoisomers (126 mg, 88%) (Found: $M^+ - CH_3$, 268.0814. $C_{12}H_{14}NO_6$ requires $M - CH_3$, 268.0821); ν_{max}(film)/cm^{-1} 3436 (O–H), 2990 (C–H), 2937 (C–H), 1635 (N=O) and 1374 (CMe_2); *m*/*z* (200 °C) 268 ($M^+ - CH_3$, 9%), 131 ($C_6H_{11}O_3^+$, 71), 107 ($C_7H_6O^+$, 9) and 59 ($C_3H_7O^+$, 100).

Although the diastereoisomeric mixture was used for chemical transformations, small quantities of the two diastereoisomers were separated for determination of spectroscopic properties as follows:

Diastereoisomer A was isolated as a clear oil; $[\alpha]_D^{25}$ +16.4 (*c* 0.06, acetone); δ_H(250 MHz; $CDCl_3$) 1.32 and 1.41 (6 H, 2 × s, $OCMe_2O$), 2.09 (1 H, br s, CH_2OH), 3.32 [1 H, dd, *J* 12.1 and 4.2, (RO)CHC(H)*H*OH], 3.66 [1 H, dd, *J* 12.1 and 3.1, (RO)CHC(*H*)HOH], 4.12 [1 H, m, CH(RO)C*H*CH_2OH], 4.31 [1 H, dd, *J* 8.1 and 4.9, CH(RO)C*H*CH(Ph)], 6.01 [1 H, d, *J* 4.9, (RO)CHC*H*(Ph)] and 7.32–7.52 (5 H, m, Ph); δ_C(68 MHz; $CDCl_3$) 26.0 (q), 26.6 (q), 61.5 (t), 76.6 (d), 77.4 (d), 82.7 (d), 109.3 (s), 126.4 (d), 128.2 (d), 128.8 (d) and 133.3 (s).

Diastereoisomer B was isolated a clear oil, $[\alpha]_D^{25}$ +64.5 (*c* 0.03, acetone); δ_H(250 MHz; $CDCl_3$) 1.46 and 1.47 (6 H, 2 × s, $OCMe_2O$), 2.68 [1 H, dd, *J* 12.3 and 4.2, (RO)CHC(H)-*H*OH], 3.20 [1 H, dd, *J* 12.3 and 2.6, (RO)CHC(*H*)HOH], 3.85–3.91 [1 H, ddd, *J* 8.1, 4.1 and 2.7, CHC*H*(OR)CH_2], 4.30 [1 H, t, *J* 8.2, CH(RO)C*H*CH(Ph)], 5.80 [1 H, d, *J* 8.3, (RO)CHC*H*(Ph)] and 7.37–7.44 (5 H, m, Ph); δ_C(68 MHz; $CDCl_3$) 26.7 (q), 27.0 (q), 61.2 (t), 75.9 (d), 78.3 (d), 86.3 (d), 110.4 (s), 127.4 (d), 129.1 (d), 130.1 (d) and 133.3 (s).

{(4*S*,5*R*)-5-[3-(Methoxycarbonyl)propenoyloxymethyl]-2,2-dimethyl-1,3-dioxolan-4-yl}phenylmethyl nitrate 43

To a stirred mixture of compound **42** (236 mg, 0.83 mmol) and methyl hydrogen but-2-enedioate (108 mg, 0.83 mmol) in sodium-dried diethyl ether (10 cm^3) was added, at 0 °C (ice-bath), a solution of DMAP (10.2 mg, 0.083 mmol, 0.1 mol equiv.) in diethyl ether (2 cm^3), then a solution of DCC (172 mg, 0.83 mmol) in diethyl ether (2 cm^3), dropwise. The mixture was allowed to warm to room temperature and was stirred continuously for 4 h. Diethyl ether (20 cm^3) was added, the precipitate was removed by filtration, and the filtrate was washed successively with saturated aq. sodium hydrogen carbonate (10 cm^3), and then saturated brine (10 cm^3). The organic phase was dried (Na_2SO_4), and the solvent was removed under reduced pressure. The residue was chromatographed on silica and eluted with diethyl ether–light petroleum (1:5) to afford {(4S,5R)-5-[3-(*methoxycarbonyl*)*propenoyloxymethyl*]-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*}*phenylmethyl nitrate* **43** as a light yellow viscous oil containing a mixture of diastereoisomers (230 mg, 72%) (Found: $M^+ - CH_3$, 380.0938. $C_{17}H_{18}NO_9$ requires $M - CH_3$, 380.0982); ν_{max}(film)/cm^{-1} 2989 (C–H), 2955 (C–H), 2935 (C–H), 2859 (C–H), 1729 (C=O), 1642 (N=O), 1383 (CMe_2) and 1374 (CMe_2); *m*/*z* (200 °C) 380 ($M^+ - CH_3$, 2%), 185 ($C_8H_9O_5^+$, 73) and 113 ($C_5H_5O_3^+$, 100).

These diastereoisomers did not prove separable by chromatography, and subsequent reactions were performed with mixtures of the diastereoisomers. To obtain pure samples of the separate diastereoisomers for assignment of spectroscopic properties, the individual diastereoisomers of the alcohol **42** were separately converted into the corresponding single isomer of diester **43**.

Compound **43** diastereoisomer A; δ_H(250 MHz; $CDCl_3$) 1.33 and 1.40 (6 H, 2 × s, $OCMe_2O$), 3.81 (3 H, s, CH=CHCO_2*Me*), 3.97–4.03 [1 H, m, (RO)C*H*CH_2OCO], 4.21–4.29 [3 H, m, CH(RO)C*H*CH(OR)C*H*$_2$OCO], 5.99 [1 H, d, *J* 4.3, (RO)-CHC*H*(Ph)], 6.83 [1 H. d, *J* 16.5, OC(O)C*H*=C*H*–CO_2Me (*E*)], 6.76 [1 H, d, *J* 16.7, OC(O)C*H*=C*H*CO_2Me (*E*)] and 7.34–7.44 (5 H, m, Ph); δ_C(68 MHz; $CDCl_3$) 26.6 (q), 27.1 (q), 52.4 (q),

64.7 (t), 75.5 (d), 78.1 (d), 83.0 (d), 111.1 (s), 126.8 (d), 128.9 (d), 129.5 (d), 132.8 (d), 133.6 (s), 134.0 (d), 164.4 (s) and 165.1 (s).

Compound **43** diastereoisomer B; δ_H(250 MHz; $CDCl_3$) 1.44 and 1.46 (6 H, 2 × s, OMe_2O), 3.44 [1 H, dd, *J* 12.1 and 5.2, (RO)CHC*H*(H)OCO], 3.81 (3 H, s, CH=CHCO$_2$Me), 3.82 [1 H, m (partially obscured by adjacent peak), (RO)CHC(H)-*H*OCO], 4.01–4.09 [1 H, m, (RO)CH(RO)C*H*CH$_2$], 4.21–4.31 [1 H, m, CH(RO)C*H*CH(Ph)], 5.83 [1 H, d, *J* 8.0, (RO)-CHC*H*(Ph)], 6.86 [2 H, s, OC(O)C*H*=C*H*CO$_2$Me (*E*)] and 7.34–7.44 (5 H, m, Ph); δ_C(68 MHz; $CDCl_3$) 25.8 (q), 27.0 (q), 52.4 (q), 63.8 (t), 75.7 (d), 80.1 (d), 85.6 (d), 111.1 (s), 127.3 (d), 129.2 (d), 130.2 (d), 132.8 (d), 133.1 (s), 133.9 (d), 164.1 (s) and 165.1 (s).

[(4*S*,5*R*)-5-Cinnamoyloxymethyl-2,2-dimethyl-1,3-dioxolan-4-yl]phenylmethyl nitrate 44

To a solution of compound **42** (107 mg, 0.38 mmol) and pyridine (78 mg, 0.99 mmol, 2.2 mol equiv.) in dry, distilled THF (2 cm^3) at room temp. was added a solution of cinnamoyl chloride (112 mg, 0.67 mmol, 1.5 mol equiv.) in THF (2 cm^3) and the mixture was stirred for 13 h. More cinnamoyl chloride was added (37 mg, 0.22 mmol, 0.3 mol equiv.) and the mixture was stirred at room temp. under nitrogen for a further 5 h, then was poured into saturated aq. sodium hydrogen carbonate (20 cm^3) and extracted with diethyl ether (2 × 30 cm^3). The combined extracts were washed successively with water (10 cm^3) and saturated brine (10 cm^3), dried ($MgSO_4$), and evaporated under reduced pressure. The crude product was chromatographed on silica and eluted with dichloromethane–light petroleum (1 : 1) to afford [(4S,5R)-5-*cinnamoyloxymethyl*-2,2-*dimethyl*-1,3-*dioxolan*-4-*yl*]*phenylmethyl nitrate* **44** as a clear oil, containing a mixture of diastereoisomers (126 mg, 87%) (Found: M$^+$ − CH_3, 398.1250. $C_{21}H_{20}NO_7$ requires M − CH_3, 398.1240); ν_{max}(film)/cm^{-1} 3065 (Ar–H), 3032 (Ar–H), 2989 (C–H), 2937 (C–H), 1718 (C=O), 1641 (N=O), 1383 (CMe) and 1374 (CMe_2); *m*/*z* (200 °C) 398 (M$^+$ − CH_3, 1%), 261 ($C_{15}H_{17}O_4^+$, 9), 203 ($C_{12}H_{11}O_3^+$, 76), 131 ($C_9H_7O^+$, 100), 103 ($C_8H_7^+$, 75) and 59 ($C_3H_7O^+$, 13).

Diastereoisomer A; δ_H(250 MHz; $CDCl_3$) 1.32 and 1.43 (6 H, 2 × s, OMe_2O), 4.03–4.11 [1 H, m, (RO)C*H*CH$_2$OCO], 4.24–4.32 [3 H, m, (RO)CHC*H*$_2$OCO and CH(RO)-C*H*CH(Ph)], 6.01 [1 H, d, *J* 3.6, (RO)CHC*H*(Ph)], 6.45 [1 H, d, *J* 16.1, OC(O)C*H*=CHPh (*E*)], 7.35–7.55 (10 H, m, Ph) and 7.73 [1 H, d, *J* 16.0, OC(O)CH=C*H*Ph (*E*)]; δ_C(68 MHz; $CDCl_3$) 26.5 (q), 27.1 (q), 64.2 (t), 75.7 (d), 78.2 (d), 83.2 (d), 111.0 (s), 117.1 (d), 127.1 (d), 128.1 (d), 128.8 (d), 128.9 (d), 129.4 (d), 130.5 (d), 133.5 (s), 134.1 (s), 145.7 (d) and 166.4 (s).

Diastereoisomer B; δ_H(250 MHz; $CDCl_3$) 1.47 and 1.48 (6 H, 2 × s, OMe_2O), 3.50 [1 H, dd, *J* 12.1 and 5.3, (RO)CHC(H)*H*OCO], 3.85 [1 H, dd, *J* 12.1 and 3.1, (RO)CHC(*H*)HOCO], 4.04–4.14 [1 H, m, (RO)C*H*CH$_2$OCO], 4.24–4.34 [1 H, m, CH(RO)C*H*CH(Ph)], 5.86 [1 H, d, *J* 7.8, (RO)CHC*H*(Ph)], 6.37 [1 H, d, *J* 16.0, OC(O)C*H*=CHPh (*E*)], 7.33–7.54 (10 H, m, Ph) and 7.65 [1 H, d, *J* 16.0, OC(O)CH=C*H*Ph (*E*)]; δ_C(68 MHz; $CDCl_3$) 26.8 (q), 27.0 (q), 63.1 (t), 75.9 (d), 77.1 (d), 85.6 (d), 110.9 (s), 117.1 (d), 127.3 (d), 128.0 (d), 128.7 (d), 128.8 (d), 129.1 (d), 130.0 (d), 133.2 (s), 133.5 (s), 145.5 (d) and 166.1 (s).

Methyl {(3a*R*,7*R*,7a*S*)-2,2-dimethyl-6-oxo-3a,6,7,7a-tetrahydro-4*H*-1,3-dioxolo[4,5-*c*]pyran-7-yl}acetate 45

To a stirred, refluxing solution of compound **43** (114 mg, 0.296 mmol) in sodium-dried, deoxygenated benzene (50 cm^3) was added TBTH (119 mm^3, 0.44 mmol, 1.5 mol equiv.), in one portion, followed immediately by a solution of AIBN (73 mg, 0.44 mmol, 1.5 mol equiv.) in benzene (2 cm^3) in one portion. The resulting mixture was refluxed for 2 h, then the solvent was removed under reduced pressure. The residue was chromatographed on silica and eluted with diethyl ether–light petroleum (5 : 1) to afford *methyl* {(3aR,7R,7aS)-2,2-*dimethyl*-6-*oxo*-3a,6,7,7a-*tetrahydro*-4H-1,3-*dioxolo*[4,5-c]*pyran*-7-*yl*}*acetate* **45** as a solid (27 mg, 39%), $[\alpha]_D^{25}$ −129 (*c* 0.02, $CHCl_3$); mp 101–102 °C (Found: M$^+$ − CH_3, 229.0703. $C_{10}H_{13}O_6$ requires M − CH_3, 229.0712); ν_{max}(KBr)/cm^{-1} 2993 (C–H), 2980 (C–H), 2957 (C–H), 2938 (C–H), 2925 (C–H), 2907 (C–H), 1742 (C=O) and 1380 (OCOCH); δ_H(400 MHz; $CDCl_3$) 1.33 and 1.43 (6 H, 2 × s, OMe_2O), 2.64 [1 H, m, CHC*H*(H)CO$_2$Me], 3.05–3.08 [2 H, m, C*H*CH(*H*)CO$_2$Me], 3.74 (3 H, s, OMe), 4.22 [1 H, dd, *J* 13.0 and 1.8, COOC*H*(H)CH], 4.45 [1 H, dd, *J* 13.6 and 0.8, COCH(*H*)CH], 4.55 [1 H, dt, *J* 7.7 and 1.2, CH$_2$(RO)C*H*CH(OR)] and 4.69 [1 H, dd, *J* 7.7 and 3.1, (RO)CHC*H*(OR)CH]; δ_C(100 MHz; $CDCl_3$) 24.3 (q), 26.0 (q), 31.1 (t), 40.4 (d), 52.1 (q), 67.9 (t), 72.6 (d), 74.1 (d), 109.9 (s), 170.7 (s) and 172.4 (s); *m*/*z* (200 °C) 229 (M$^+$ − CH_3, 35%), 213 (M$^+$ − CH_3O, 12) and 43 ($C_2H_3O^+$, 100).

(3a*R*,7*R*,7a*S*)-7-Benzyl-2,2-dimethyl-3a,6,7,7a-tetrahydro-4*H*-1,3-dioxolo[4,5-*c*]pyran 46

To a stirred, refluxing solution of compound **44** (121 mg, 0.29 mmol) in sodium-dried, deoxygenated benzene (50 cm^3) under nitrogen was added TBTH (118 mm^3, 0.44 mmol, 1.5 mol equiv.) in one portion, followed immediately by a solution of AIBN (72 mg, 0.44 mmol, 1.5 mol equiv.) in benzene (2 cm^3) in one portion. The resulting mixture was refluxed for 5 h, after which time the solvent was removed under reduced pressure.

Table 1 Crystal data

Compound	**30a**	**35**
Formula	$C_{10}H_{14}N_2O_3$	$C_{11}H_{16}O_6$
M	210.23	244.24
System	orthorhombic	monoclinic
a/Å	8.097(2)	5.899(1)
b/Å	9.148(1)	10.745(1)
c/Å	15.247(1)	9.766(1)
β/°	90	90.53(1)
V/Å^3	1129.4(1)	619.0(1)
No. of reflections for lattice	25	25
θ range/°	26.2–27.3	28–33
Space group	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)
Z	4	2
D_x/g cm^{-3}	1.24	1.31
F(000)	448	260
μ(Cu-Kα)/cm^{-1}	7.7	9.1
Crystal size	0.4 × 0.5 × 0.55	0.25 × 0.5 × 0.75
Scan mode	2θ/ω	2θ/ω
θ_{max}/°	60	76
No. of checks/interval	3, 1 h	1, 1 h
Drop of check intensity/%	7	2
Total data	1673	1366
Unique data	1647[a]	1366
h-range	−9→9	−7→7
k-range	−10→10	0→13
l-range	−16→17	0→12
Structure solution method	direct	direct
Software	SHELXS-86[21]	MULTAN-80[22]
Structure refinement software	SHELXL-93[23]	CRYSTALS[24]
No. of data used	1638	1279[b]
No. of variables	145	218
Refinement against	F^2	*F*
Weighting scheme	2-term Chebyshev	4-term Chebyshev[25]
Extinction correction	empirical[c]	none
$R = \Sigma[\|F_o\| - \|F_c\|]/\Sigma\|F_o\|$	0.041[d]	0.033
w*R*	0.114[e]	0.039[f]
Δρ max/e Å^3	0.15	0.15
Max shift/e.s.d.	0.003	0.11

[a] Including 649 Friedel pairs. [b] $I > 3\sigma(I)$. [c] F_c multiplies by $[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-\frac{1}{4}}$, where *x* was refined to 0.019(2). [d] For 1489 data with $I > 2\sigma(I)$; $R = 0.051$ for all data. [e] Based on F^2. [f] Based on *F*.

The crude product was chromatographed on silica and eluted with diethyl ether–light petroleum (1 : 1) to afford (3aR,7R,7aS)-*7-benzyl-2,2-dimethyl-*3a,6,7,7a-*tetrahydro-*4H-1,3-*dioxolo* [4,5-c]*pyran* **46** as a light brown solid (20 mg, 26%); $[\alpha]_D^{26}$ −133.0 (*c* 0.02, $CHCl_3$), mp 106–109 °C (Found: M^+, 262.1171. $C_{15}H_{18}O_4$ requires M, 262.1205); ν_{max}(KBr)/cm^{-1} 2992 (C–H), 2939 (C–H), 2915 (C–H), 1735 (C=O), 750 (Ar–H) and 702 (Ar–H); δ_H(400 MHz; $CDCl_3$) 1.31 and 1.48 (6 H, 2 × s, $OCMe_2O$), 2.58 [1 H, ddd, *J* 10.3, 4.6 and 2.6, CHC*H*-(CH_2Ph)CO], 2.95 [1 H, dd, *J* 14.0 and 10.3, CHC*H*(H)Ph], 3.35 [1 H, dd, *J* 14.0 and 4.5, CHCH(*H*)Ph], 4.07 [1 H, d, *J* 11.7, CO_2CH(H)CH], 4.40 [3 H, m, CO_2CH(*H*)C*H*(OR)C*H*-(OR)CH] and 7.25–7.35 [5 H, m, (Ph), Ar–H]; δ_C(100 MHz; $CDCl_3$) 24.3 (q), 26.1 (q), 32.2 (t), 45.4 (d), 67.9 (t), 72.5 (d), 109.6 (s), 126.7 (d), 128.7 (d), 129.4 (d), 138.6 (s) and 171.5 (s); *m/z* (200 °C) 262 (M^+, 14%), 247 ($M^+ - CH_3$, 34), 148 ($C_9H_8O_2^+$, 61) and 91 ($C_7H_7^+$, 100).

X-Ray crystallography

Single-crystal X-ray diffraction experiments were performed at ambient temperature on the Enraf-Nonius CAD-4 four-circle diffractometer (Ni-filtered Cu-Kα radiation λ = 1.541 78 Å). Crystal data and experimental details are listed in Table 1. In both structures, all non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms, located by difference Fourier, were refined in isotropic approximation for compound **35**. For compound **30a**, hydroxy H-atom was refined isotropically; other H-atoms were treated in a riding model (CH_3 groups—as rotating bodies). The absolute configuration of neither compound could be determined reliably from anomalous dispersion data, and was assigned according to the configuration of the original L-(+)-tartrate, retained at the C(5) atom in compounds **30a** and **35**.§

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§ *Supplementary publication:* The additional material, available from the Cambridge Crystallographic Data Centre, comprises atomic coordinates and displacement parameters, and bond distances and angles (see Instruction for Authors, Issue No. 1).

References

1 B. Giese, *Radicals in Organic Synthesis*, Pergamon Press, Oxford, 1986, p. 150. For some of the many examples, see A. L. J. Beckwith, D. M. O'Shea and D. H. J. Roberts, *J. Chem. Soc., Chem. Commun.*, 1983, 1445; D. L. J. Clive, D. R. Cheshire and L. Set, *J. Chem. Soc., Chem. Commun.*, 1987, 353; G. Stork, R. Mook, Jr., S. A. Biller and S. D. Rychnovsky, *J. Am. Chem. Soc.*, 1983, **105**, 3741; A. L. J. Beckwith, G. Phillipou and A. K. Serelis, *Tetrahedron Lett.*, 1981, **22**, 2811; D. A. Burnett, J.-K. Choi, D. J. Hart and Y.-M. Tsai, *J. Am. Chem. Soc.*, 1984, **106**, 8201; G. Stork and M. J. Sofia, *J. Am. Chem. Soc.*, 1986, **108**, 6826; D. P. Curran and S.-C. Kuo, *J. Am. Chem. Soc.*, 1986, **108**, 1106. See also references 10 and 11, this paper.
2 For a preliminary account of this work, see M. J. Begley, R. J. Fletcher, J. A. Murphy and M. S. Sherburn, *J. Chem. Soc., Chem. Commun.*, 1993, 1723. This research was first reported at the Royal Society of Chemistry, Heterocyclic Group Meeting, King's College, London, January 1991.
3 For a recent report of cyclisations of dioxolanyl radicals, see F. E. Ziegler and P. G. Harran, *J. Org. Chem.*, 1993, **58**, 2768.
4 D. H. R. Barton, A. Gateau-Olesker, S. D. Gero, B. Lacher, C. Tachdjian and S. Z. Zard, *J. Chem. Soc., Chem. Commun.*, 1987, 1790.
5 R. W. Binkley and D. J. Koholic, *J. Org. Chem.*, 1979, **44**, 2047; *J. Carbohydr. Chem.*, 1984, **3**, 85; J. Honeyman and J. W. W. Morgan, *Adv. Carbohydr. Chem.*, 1957, **12**, 117.
6 N. Hussain, D. O. Morgan, C. R. White and J. A. Murphy, *Tetrahedron Lett.*, 1994, **35**, 5069.
7 J. C. Lopez, R. Alonso and B. Fraser-Reid, *J. Am. Chem. Soc.*, 1989, **111**, 6471; G. D. Vite and B. Fraser-Reid, *Synth. Commun.*, 1988, **18**, 1339.
8 M. J. Shiao, C. Y. Yang, S. H. Lee and T. C. Wu, *Synth. Commun.*, 1988, **18**, 359.
9 G. E. Keck and J. B. Yates, *J. Am. Chem. Soc.*, 1982, **104**, 5829.
10 D. P. Curran and D. M. Rakiewicz, *Tetrahedron*, 1985, **41**, 3943.
11 T. V. Rajanbabu, T. Fukunaga and G. S. Reddy, *J. Am. Chem. Soc.*, 1989, **111**, 1759.
12 R. J. Fletcher, M. Kizil and J. A. Murphy, *Tetrahedron Lett.*, 1995, **36**, 323.
13 For a review see A. J. Mancuso and D. Swern, *Synthesis*, 1981, 165.
14 J. E. Baldwin, R. M. Adlington, M. B. Mitchell and J. Robertson, *Tetrahedron*, 1991, **47**, 5901; J. E. Brumwell, N. S. Simpkins and N. K. Terrett, *Tetrahedron Lett.*, 1993, **34**, 1219.
15 A. L. J. Beckwith and P. E. Pigou, *J. Chem. Soc., Chem. Commun.*, 1986, 85; D. P. Curran and C. T. Chang, *J. Org. Chem.*, 1989, **54**, 3140; H. Oumar-Mahamat, C. Moustrou, J.-M. Surzur and M. P. Bertrand, *J. Org. Chem.*, 1989, **54**, 5684; *Tetrahedron Lett.*, 1989, **30**, 331; H. Nagashima, K. Seki, N. Ozaki, H. Wakamatsu, K. Itoh, Y. Tomo and J. Tsuji, *J. Org. Chem.*, 1990, **55**, 985; S. A. Kates, M. A. Dombroski and B. B. Snider, *J. Org. Chem.*, 1990, **55**, 2427; R. Di Fabio, S. Hannessian, J.-F. Marcoux and M. Prud'homme, *J. Org. Chem.*, 1990, **55**, 3436; D. P. Curran and J. Tamine, *J. Org. Chem.*, 1991, **56**, 2746.
16 D. L. J. Clive and P. L. Beaulieu, *J. Chem. Soc., Chem. Commun.*, 1983, 307.
17 M.-J. Camarasa, S. Huss and S. Velazquez, *J. Chem. Soc., Chem. Commun.*, 1991, 1263.
18 P. Agback, J. Chattopadhyaya, A. Sandstrom and Z. Xi, *Tetrahedron*, 1991, **47**, 9675.
19 J. A. Musich and H. Rapoport, *J. Am. Chem. Soc.*, 1978, **100**, 4865.
20 U. Eisner, J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 1951, 1501.
21 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
22 P. Main, S. L. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declerq and M. M. Woolfson, MULTAN, Universities of York (UK) and Louvain (Belgium), 1980.
23 G. M. Sheldrick, SHELX-93, Program for the refinement of crystal structures, University of Göttingen, Germany, 1993.
24 D. J. Watkin, J. R. Carruthers and P. W. Betteridge, CRYSTALS Users Guide, Chemical Crystallography Lab., University of Oxford, 1985.
25 J. R. Carruthers and D. J. Watkin, *Acta Crystallogr., Sect. A*, 1979, **35**, 698.

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