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Intramolecular Reactions of Allyloxy Radicals Featuring Six-Centred Transition States; Regiochemistry and Stereochemistry.

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Abstract. *Intramolecular free-radical reactions of allyloxy radicals to form tetrahydropyrans and cyclopentanols have been studied; the cyclopentanols form stereoselectively with trans disposition of groups about the ring-forming bond.*

The chemistry of radical-induced epoxide opening (Figure 1) is now attracting a great deal of attention[1].

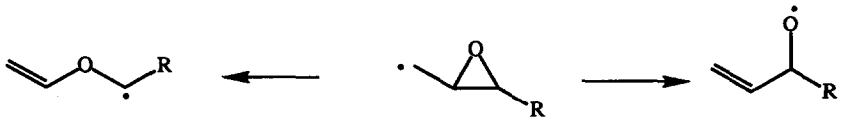


Figure 1

On opening of the ring (for R=alkyl), an allyloxy radical arises[2]. We have recently reported on the ability of allyloxy radicals to form tetrahydrofurans (Figure 2) and have used the reaction in a synthesis of lilac alcohols[3].

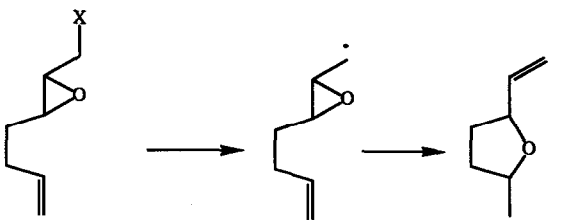


Figure 2

We now report their intramolecular reactions which go *via* 6-centred transition states. Surzur[4] reported

many years ago on the effects of structure variation on the intermolecular reactions of simpler oxygen-centred radicals with alkenes; in some cases hydrogen atom abstraction was observed, while in others addition to the double bond was seen. We have now investigated a number of cases where an intramolecular choice exists for these radicals as shown in figure 3.

The substrates (2a-d) for the radical reaction were formed in two easy steps from diethyl malonate. For the simplest case, (2a), both tetrahydropyran (4a) and cyclopentanol (6a) were formed in approximately equal amounts. Initially only one stereoisomer of the tetrahydropyran was isolated, and a series of nmr experiments demonstrated that in this isomer both the vinyl and methyl groups were equatorial. Specifically, a coupling constant consistent with vicinal axial-axial coupling was seen for both of the ring methine hydrogens (11.5 and 11.7 Hz respectively). Since this would be expected to result from the more stable of the possible transition states, this seemed unsurprising. However, on thorough examination of the crude nmr spectra from a number of trials of this experiment, it is clear that the second isomer is produced also although in much lesser amounts. The isolation of this minor diastereomer is apparently less efficient, and we have not succeeded in isolating a pure sample.

Regarding the cyclopentanols (6), the most notable fact was that only two of the four possible diastereoisomers were produced as judged by high-field nmr. The assignment of the stereochemistry of these compounds was not carried out at this stage (but see below).

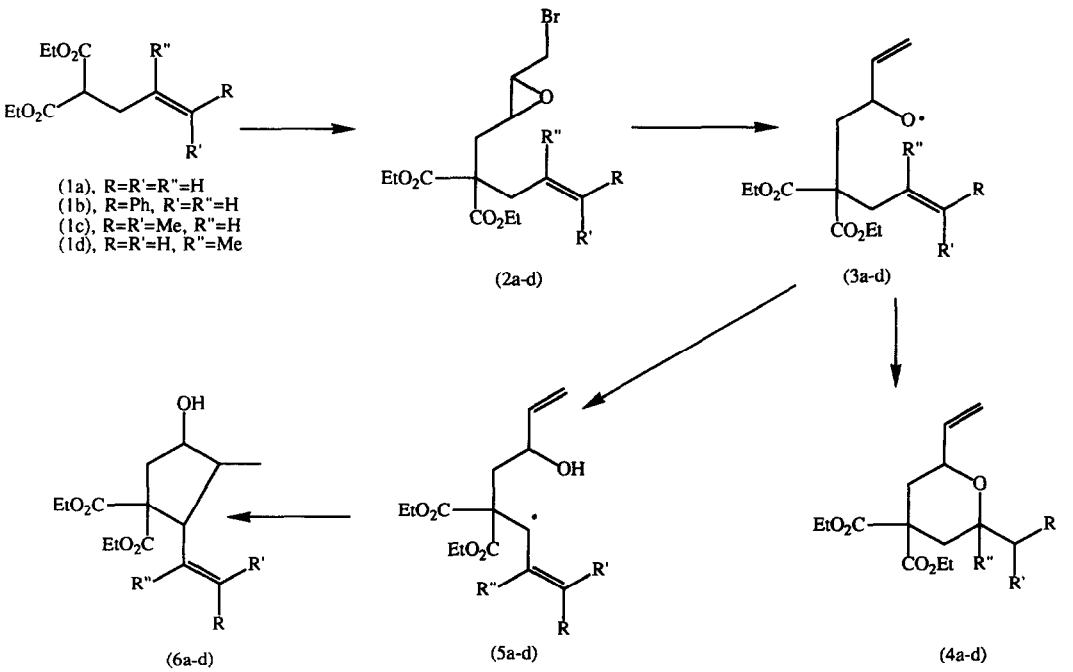


Figure 3

The cyclisation of the radical (3a) involves a transition state in which a primary radical is developing; on the other hand, the reaction path leading to the cyclopentanol (6a) goes *via* an allylic radical and so the transition

state leading to this species might be expected to enjoy some stabilisation associated with this incipient radical. If so, then the balance between the two pathways might be dramatically altered if the forming radical on the tetrahydropyran route were not primary but rather a radical with greater stability. To test this, the substrates (2b) and (2c) were prepared. Here the pathways leading through to the cyclopentanol pathway go through radicals with extensive allylic stabilisation as before, but now the tetrahydropyran routes feature development of tertiary and benzylic radicals. However, these cases also led to formation of 1:1 ratios of tetrahydropyrans to cyclopentanols, so the relative stabilisation of the incipient radicals appears unimportant in product development. This presumably reflects the fact that a very early transition state is featured in the tetrahydropyran ring formation. Both *cis* and *trans* tetrahydropyrans were produced, but, interestingly, only two of the four possible diastereoisomeric forms of the cyclopentanol were observed.

To attempt to bias the reaction towards the preferential formation of cyclopentanols, the epoxide (2d) was produced. In the reaction of this molecule, the intermediate radical faces a slower addition to the double bond to form the tetrahydropyran because of the extra steric barrier imposed by the methyl group (R"=Me). This effect has been precedented in a number of cases[5]. In this case the reaction was indeed biased towards the cyclopentanols, and only traces of the tetrahydropyrans could be detected in the spectrum of the crude product. Once again, however, only two cyclopentanols were seen. These compounds were isolated as an inseparable mixture and converted into their 3,5-dinitrobenzoate esters. Nmr indicated that the principal difference between the two isomers was at the newly esterified position (C4 in figure 4). Thus, the H4'-H5' coupling constant in one isomer was 3.8Hz while it was 9.3Hz in the other isomer. (The numbering used in this and other diagrams uses the site of the cyclising radical as carbon 1).

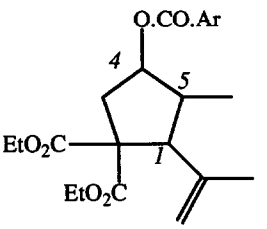


Figure 4

All other coupling constants showed very little variation between isomers. These diastereomeric dinitrobenzoates were not separable by tlc but were separated by hplc. One of the isomers (isomer 1) readily provided crystals for X-ray single crystal structure determination (figure 5). As shown, the cyclisation has occurred with 1,5-*trans* stereochemistry. The other isomer proved to be difficult to crystallise, but ultimately gave confirmation of the nmr findings (figure 6); i.e. that the diference between the two isomers resided at C4. From analogy of the nmr signals we believe that the pairs of cyclopentanols produced in each of the cases (4b, 4c, 4d) bear 1,5-*trans* stereochemistry.

The predominant 1,5 stereochemistry of radical cyclisations to form 5-membered rings is normally *cis*. This has been rationalised by Beckwith[6]. Stork[7] has previously observed a case where allylic radicals cyclised to give predominantly *trans* products, and has discussed whether this may be due to kinetic or other factors. By examination of models, we believe that our molecules should indeed form only the isomers seen. In figure 7, we see the difficulty in attaining the conformation needed for the formation of the normal *cis*

product (conformation (A)); working on the Beckwith hypothesis that cyclisation proceeds *via* a chair transition state, excessive steric interaction is seen in the starting radical between the axial ester group and the

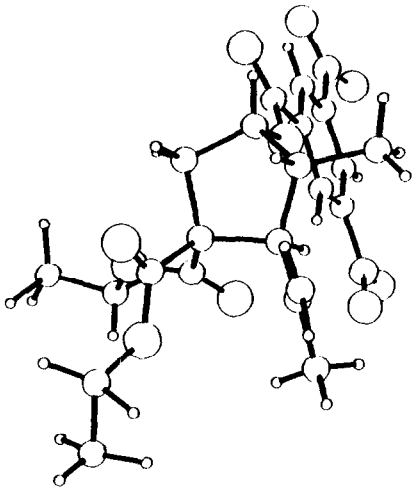


Figure 5

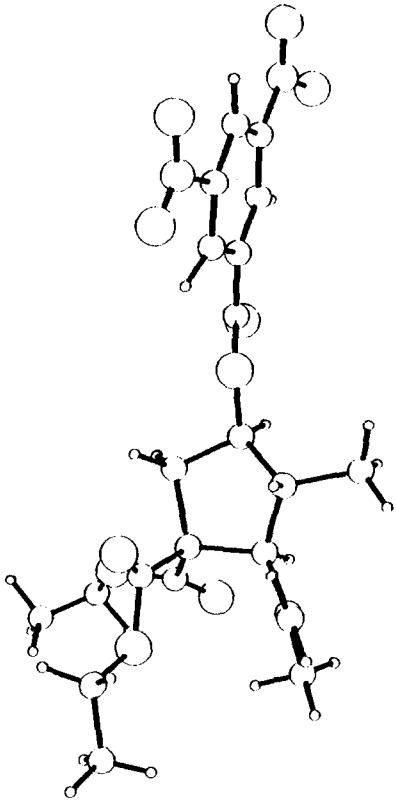
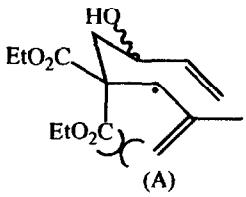
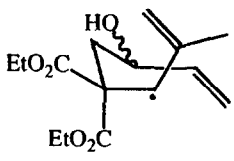


Figure 6

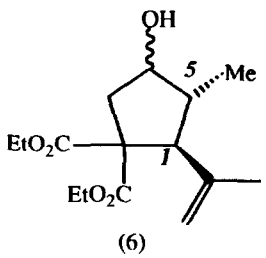
vinyl moiety; to maintain a chair transition state, the best compromise that can be made is to give the conformation (B) which leads to the observed products . This would predict that kinetic factors should dictate the formation of the observed isomers. If thermodynamic factors govern the formation of these products, then we should also expect that the more stable products should result as (6), since these feature the two major vicinal groups in the more stable *trans* arrangement.



(A)



(B)



(6)

Figure 7

The effects of complex substitution patterns on radical cyclisation reactions have only recently begun to be addressed[8]. The *trans/cis* ratio seen in these cyclisations is very pronounced (we cannot say that no *1,5-cis* product is formed, but the *trans/cis* ratio is certainly much greater than in Stork's case), and is complementary to what is expected from "normal" i. e. non-allylic radical cyclisations. This gives an exciting impetus to the development of *trans* stereochemical control in radical formation of 5-membered rings.

Experimental Section

Melting points were carried out on a Kofler hot stage apparatus and are uncorrected. Microanalyses were determined using a Perkin-Elmer 240B elemental analyser. Infrared spectra were obtained on a Perkin Elmer 1720-X FTIR or a Pye-Unicam SP3-100 spectrometer. Ultraviolet spectra were recorded on a Philips PU8700 series instrument. ^{1}H n.m.r. spectra were recorded at 90MHz on a Perkin-Elmer R32, at 250MHz on a Bruker WM250 or at 400MHz on a Bruker AM400 machine. ^{13}C n.m.r. spectra were recorded at 23MHz on a Jeol FX90Q, or at 100MHz on a Bruker AM400 machine. N.m.r. experiments were carried out in deuterochloroform, with tetramethylsilane as internal reference and chemical shifts are quoted in parts per million (δ p.p.m.). The following abbreviations are used for multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. Coupling constants (J) are reported in Hertz (Hz). In the case of ring systems, assignments are made according to the designated numbering system. Mass spectra were recorded on a VG Micromass 70E or an AEI MS902 instrument.

Where necessary, solvents were dried and/or distilled before use. Tetrahydrofuran was distilled from sodium-benzophenone. Pyridine was distilled from calcium hydride. Dichloromethane was distilled from calcium chloride. Diethyl ether, toluene and benzene were dried over sodium wire. Chromatography was performed using Sorbsil C60 (May and Baker), Fluka ACT, Kieselgel HF254 or Kieselgel 60 (Art 9385) silica gels.

1,4-Dibromo-2,3-epoxybutane

A solution of 1,4-dibromo-2-butene (10g, 47mmoles) and 3-chloroperoxybenzoic acid (13g, 80%, 60mmoles) in dichloromethane (250ml) was heated under reflux for seven days. After cooling the solution was washed successively with aqueous solutions of sodium sulphite (3 x 50ml), sodium bicarbonate (3 x 50ml), and brine (50ml). The organic material was dried ($MgSO_4$) and evaporated to dryness. Chromatography on silica gel with diethyl ether:hexane (1:4) afforded the desired epoxide as a colourless oil (7.6g, 70%); υ_{max} 1 220 (C-O, epoxide), 745 (C-Br)cm^{-1};δ_H (80 MHz) 3.2 - 3.6 (bm); δ_C (23MHz) 27.7, 30.9, 57.5 and 58.5 ppm; m/z 151 (M^+-Br, 54%) and 43 (50).

Ethyl 5-phenyl-2-ethoxycarbonyl-4-pentenoate (1b)

Diethyl malonate (5.27g, 5.0ml, 33mmoles) was added dropwise to a stirred slurry of THF rinsed sodium hydride (1.32g, 60% in mineral oil, 33 mmoles) in dry degassed THF (40ml) under N2. When all effervescence had ceased, cinnamyl bromide (6.49g, 33mmoles) was added dropwise to the clear yellow solution. The solution was stirred at room temperature for 16 hours after which time wet diethyl ether (30ml) was added cautiously. The solution was washed sequentially with water (2 x 30ml) and brine (30ml), dried (Na_2SO_4), and evaporated to dryness. Chromatography on silica gel with petrol 40/60: diethyl ether (15:1) yielded the desired alkene (1b) as a yellow oil (3.73g, 41%); (Found: C,69.59; H,7.34. $C_{16}H_{20}O_4$ requires

C, 69.53; H, 7.30 %); υ_{max} 2 882 (CH), 1 733 (C=O)cm^{-1}; δ_H (250MHz) 1.25 (6H, t, J 7Hz, $OCH_2C\underline{H}_3$); 2.79 (2H, t, J 7Hz, $C\underline{H}_2CH(CO_2Et)_2$); 3.49 (1H, t, J 7Hz $C\underline{H}(CO_2Et)_2$); 4.19 (4H, 2xq, J 7Hz, $OC\underline{H}_2CH_3$); 6.15 (1H, dt, J 16 and 7Hz, PhCH=C$\underline{H}$); 6.47 (1H, d, J 16Hz, PhC$\underline{H}$=CH); 7.3 (5H, m, Ph)ppm; δ_C 14.3, 32.39, 52.27, 61.54, 125.89, 126.38, 127.52, 128.66, 132.99, 137.38, 169.02ppm; m/z 276 (M^+,15.9%), 202 (33), 130 (14), 129 (100), 128 (36), 117 (51); (Found M^+, 276.134; $C_{16}H_{20}O_4$ requires M, 276.136).

Ethyl 5-methyl-2-ethoxycarbonyl-4-hexenoate (1c)

Diethyl malonate (11.4g, 71mmoles) was added dropwise to a stirred slurry of THF- rinsed sodium hydride (2.84g, 60% dispersion in mineral oil, 71mmoles) in dry THF (60ml) under N_2. After all effervescence had ceased, 4-bromo-2-methyl-2-butene (10.5g, 71mmoles) was slowly added to the clear yellow solution. The resulting solution was stirred at room temperature for 16 hours over which period a dense white precipitate formed. After cautious addition of wet diethyl ether (25ml) the reaction mixture was washed sequentially with water (25ml) and brine (25ml) dried ($MgSO_4$) and evaporated to dryness. Distillation yielded the alkene (1c) as a colourless oil (6.01g, 37%); (b.p. 86 - 90°C at 1.3mmHg); (Found: C, 62.79; H, 8.89. $C_{12}H_{20}O_4$ requires C, 63.12; H, 8.84%); υ_{max}: 2 982 (CH), 1 736 (C=O), 1 676 (C=C)cm^{-1}; δ_H (250MHz) 1.26 (6H, t, J 7Hz, $OCH_2C\underline{H}_3$); 1.63 (3H, s, $C\underline{H}_3$-C=CH); 1.68 (3H, s, $C\underline{H}_3$-C=CH); 2.59 (2H, (dd), J 8Hz, $C\underline{H}_2CH(CO_2Et)_2$); 3.33 (1H, t, J 8Hz, $C\underline{H}(CO_2Et)_2$); 4.19 (4H, q, J 7Hz, $OC\underline{H}_2CH_3$); 5.07 (1H, t, J 7Hz, C$\underline{H}$=C)ppm; δ_C 14.14, 17.76, 25.73, 27.68, 52.38, 61.27, 120.00, 134.72, 169.23ppm; m/z 228 (M^+, 13.4%), 160.1 (43.7), 115.0 (47.1), 81.1 (100), 69.1 (69.4); (Found: M^+, 228.136. $C_{12}H_{20}O_4$ requires M, 228.136).

Ethyl 4-methyl-2-ethoxycarbonyl-4-pentenoate (1d)

Diethyl malonate (17.7g, 110mmoles) was added dropwise to a stirred slurry of THF-rinsed sodium hydride (4.42g, 60% dispersion in mineral oil, 110mmoles) in dry THF (200ml) under N_2. After all effervescence had ceased, methallyl chloride (10g, 110mmoles) was slowly added to the clear yellow solution. The resulting solution was stirred at room temperature for 18 hours over which period a dense white precipitate formed. After cautious addition of wet diethyl ether (50ml) the reaction mixture was washed sequentially with water (50ml) and brine (50ml) dried ($MgSO_4$) and evaporated to dryness. Distillation yielded the alkene (1d) as a colourless oil (13.3g, 59%); (b.p. 82 - 86°C at 1.0mmHg); υ_{max} 2 983 (CH), 1 752 (C=O) 1 652 (C=C) cm^{-1}; δ_H (80MHz): 1.26 (6H, t, J 7Hz, $OCH_2C\underline{H}_3$); 1.75 (3H, s, $C\underline{H}_3$-C=CH_2); 2.61 (2H, d, J 8Hz, $C\underline{H}_2CH(CO_2Et)_2$); 3.57 (1H, t, J 8Hz, $C\underline{H}(CO_2Et)_2$); 4.19 (4H, q, J 7Hz, $OC\underline{H}_2CH_3$); 4.74 (2H, m, $C\underline{H}_2$=C)ppm; δ_C 14.19, 22.37, 36.67, 50.81, 61.48, 112.41, 141.93, 169.18 ppm; m/z 214 (M^+, 6%), 141 (100), 123 (80), 122 (57), 95 (78) (Found: M^+, 214.116. $C_{11}H_{18}O_4$ requires M, 214.120).

Ethyl 6-bromo-4,5-epoxy-2-ethoxycarbonyl-2-(2'-propenyl)-hexanoate (2a)

Ethyl 2-ethoxycarbonyl-4-pentenoate (1.04g, 5.6mmol) was added dropwise to a stirred slurry of THF-rinsed sodium hydride (0.22g, 60% dispersion in mineral oil, 5.6mmol) in dry THF (40ml). After all effervescence had ceased a solution of 1,4-dibromo-2,3-epoxybutane (1.28g, 5.6mmol) in dry THF (5ml) was slowly added to the clear yellow solution. The solution was heated under reflux for 14 hours over which time a dense white precipitate formed. After cooling, aqueous ether (5ml) was added and the mixture was washed sequentially with water (15ml) and saturated brine (15ml), dried and evaporated to dryness. Chromatography on silica gel with diethyl ether: hexane (1:9) afforded the desired epoxide (2a) as a colourless oil (1.10g, 56%); υ_{max} 1 725 (CO, ester), 1 645 (C=C), 650 (CBr); δ_H 1.27 (6H, t, J 7.2Hz,

($COCH_2CH_3)_2$); 1.98-2.45 (2H, m, $C(CO_2Et)_2CH_2C(O)$); 2.76 (2H, ddd, J 7.3, 1.2 and 1.2Hz, $CH_2CH=CH_2$); 2.94 (1H, ddd, J 6.8, 4.8 and 1.9Hz, CH-O-$CHCH_2Br$); 3.03 (2H, ddd, J 6.2, 5.6 and 1.9Hz, (O)$CHCH_2Br$); 3.26-3.38 (2H, bm, CH_2Br); 4.17-4.27 (4H, m, $(COCH_2CH_3)_2$); 5.10-5.20 (2H, m, $CH=CH_2$); 5.57-5.70 (1H, m, $CH=CH_2$); δ_C (23MHz) 14.0, 31.8, 35.1, 37.8, 56.1, 56.5, 57.1, 61.4,

119.5, 132.1, 170.3; m/z 350 (M^+, 17%), 348 (M^+, 16%), 275 (100), 223 (11), (Found: M^+, 350.055. $C_{14}H_{21}O_5Br$ requires M, 350.055; Found: M^+, 348.056. $C_{14}H_{21}O_5Br$ requires M, 348.057)

Ethyl 6-bromo-4,5-epoxy-2-ethoxycarbonyl-2- (3'-phenyl-2'-propenyl)hexanoate (2b)
Ethyl 5-phenyl-2-ethoxycarbonyl-4-pentenoate, (1b), (1.1g, 4.2mmoles) was added dropwise to a stirred mixture of THF rinsed sodium hydride (0.17g, 60% in mineral oil, 4.2mmoles) in dry degassed THF (50ml) under N_2. When all effervescence had ceased, a solution of 1,4-dibromo-2,3- epoxybutane (0.92g, 4.0mmoles) in dry THF (2.5 ml) was added dropwise to the clear yellow solution. The solution was heated at reflux for 16 hours over which time a dense white precipitate was formed. On cooling wet diethyl ether (30 ml) was added cautiously. The solution was washed sequentially with water (2 x 30ml), and brine (30ml), dried (Na_2SO_4) and evaporated to dryness. Chromatography on silica gel G with petrol 40/60: diethyl ether (10:1) yielded the desired epoxide (2b) as a mixture of isomers (major isomer only quoted in following data) (1.21g, 72%); (Found C, 56.87; H, 6.06. $C_{20}H_{25}O_5Br$ requires C, 56.59; H, 5.94%); υ_{max} 2 982 (CH), 1 731 (C=O)cm^{-1}; δ_H(250 MHz) 1.26 (3H, t, J 7Hz, OCH_2CH_3); 1.27 (3H, t, J 7 Hz, OCH_2CH_3); 2.07 (1H, dd, J 15 and 7 Hz, HCHC(O)); 2.28 (1H, dd, J 15 and 5 Hz, HCHC(O)); 3.32 (2H, m, CH_2Br); 4.18-4.29 (4H, m, OCH_2CH_3); 5.98-6.10 (1H, m, PhCHCH); 6.49 (1H, d, J 15.8Hz, PhCH); 7.21-7.33 (5H, m, Ph)ppm; δ_C(23 MHz) 13.76, 31.55, 35.05, 36.88, 54.68, 54.86, 56.36, 56.78, 61.30, 61.39, 123.13, 125.89, 127.20, 128.20, 134.16, 136.55, 170.14, 170.19ppm; m/z 424 (M^+, 36%), 426 (M^+, 36), 353 (100), 351 (100), 327 (32), 352 (30) (Found: M^+, 424.090 and 426.087. $C_{20}H_{25}O_5Br$ requires M, 424.089 and 426.087).

Ethyl 6-bromo-4,5-epoxy-2-ethoxycarbonyl-2-(3'-methyl-2'-butenyl)hexanoate (2c)
Ethyl 5-methyl-2-ethoxycarbonyl-4-hexenoate, (1c),(1.0g, 4.38 mmoles) was added dropwise to a stirred slurry of THF rinsed sodium hydride (0.35g, 60% in mineral oil, 8.75mmoles) in dry degassed THF (50ml). When all effervescence had ceased, a solution of 1,4-dibromo- 2,3-epoxybutane (1.0g, 4.38mmoles) in dry degassed THF (5.0ml) was slowly added to the clear yellow solution. The solution was heated under reflux for 15 hours over which period a dense white precipitate formed. On cooling wet diethyl ether (30ml) was added. The solution was washed sequentially with water (2 x 20ml), and brine (20ml), dried (Na_2SO_4), and evaporated to dryness. Chromatography on silica gel G with petrol 40/60: diethyl ether (9:1) yielded the desired epoxide (2c) as a yellow oil (1.11g, 67%); (Found C, 51.17; H, 6.77; $C_{16}H_{25}O_5Br$ requires C, 51.05; H, 6.70%); υ_{max} 2 982 (CH), 1 731 (C=O); δ_H 1.26 (6H, 2xt, J 7Hz, OCH_2CH_3); 1.63 (3H, s, $CH_3C=CH$); 1.69 (3H, s, $CH_3C=CH$); 2.02 (1H, dd, J 15 and 7Hz, $C(CO_2Et)_2CH_2C(O)$); 2.19 (1H, dd, J 15 and 5Hz, $C(CO_2Et)_2CH_2C(O)$); 2.72 (2H, m, $CH_2CH=C$); 2.95 to 3.00 (2H, m, CH(O)$CHCH_2Br$); 3.32 (2H, m, CH_2-Br); 4.16-4.25 (4H, m, OCH_2CH_3); 4.96 (1H, tm, J 7Hz, $CH=CMe_2$)ppm; δ_C 14.2, 18.2, 26.2, 32.2, 32.3, 35.3, 56.5, 57.3, 61.6, 61.7, 117.5, 136.2, 171.1ppm; m/z 376 (M^+, 2%), 305 (44), 303 (43). (Found: M^+, 376.083. $C_{16}H_{25}O_5Br$ requires M, 376.089).

Ethyl 6-bromo-4,5-epoxy-2-ethoxycarbonyl-2-(2'-methyl-2'-propenyl)hexanoate (2d)
Ethyl 4-methyl-2-ethoxycarbonyl-4-pentenoate, (1d), (1.5g, 7.35mmoles) was added dropwise to a stirred slurry of THF rinsed sodium hydride (0.30g, 7.35mmoles, 60% dispersion in mineral oil) in dry degassed THF (75ml). When all effervescence had ceased, a solution of 1,4-dibromo-2,3-epoxybutane (1.67g,

7.35mmoles) in dry degassed THF (5.0ml) was slowly added to the clear yellow solution. The solution was heated under reflux for 15 hours over which period a dense white precipitate formed. On cooling wet diethyl ether (30ml) was added. The solution was washed sequentially with water (2 x 20ml), and brine (20ml), dried (Na_2SO_4), and evaporated to dryness. Chromatography on silica gel G with petrol 40/60: diethyl ether (9:1) yielded the desired epoxide (2d) as a yellow oil (1.65g, 63%); υ_{max} 2 982 (CH), 1 729 (C=O)cm^{-1}; δ_H 1.28 (6H, t, J 7Hz, OCH_2CH_3); 1.67 (3H, t, J 0.6Hz $CH_3C=CH_2$); 2.02 (1H, dd, J 15 and 7Hz, $C(CO_2Et)_2CH_2C(O)$); 2.25 (1H, dd, J 15 and 5Hz, $C(CO_2Et)_2CH_2C(O)$); 2.80-2.82 (2H, m, $CH_2C=CH_2$); 2.98-3.03 (2H, m, $CH_2CH(O)CHCH_2Br$); 3.32 (2H, m, CH_2-Br); 4.17-4.30 (4H, m, OCH_2CH_3); 4.78 (1H, m, HCH=CMe); 4.90 (1H, m, HCH=CMe)ppm; δ_C 13.98, 23.17, 28.87, 30.60, 31.96, 35.22, 41.00, 41.27, 55.03, 55.25, 55.47, 55.55, 56.78, 57.17, 61.59, 61.71, 116.13, 116.25, 140.23, 170.97.

2-Ethenyl-4,4-diethoxycarbonyl-6-methyltetrahydropyran (4a) and 2-methyl-3-ethenyl-4,4-dicarbethoxy-cyclopentanol (6a)

A solution of ethyl 6-bromo-4,5-epoxy-2-ethoxycarbonyl-2-(2'-propenyl)-hexanoate, (2a), (1.00g, 2.9mmol) and tri-n-butyltin hydride (1.0ml, 3.7mmol) in dry degassed THF (100ml) was heated to reflux under nitrogen. A solution of AIBN (50mg) in dry THF (5ml) was added dropwise over 1 hour. The mixture was heated under reflux for a further 3 hours. On cooling the solvent was removed under reduced pressure to afford a yellow oil which was chromatographed on alumina using hexane: diethyl ether (1:1). The fractions containing components of higher R_f were rechromatographed on silica gel with diethyl ether: hexane (1:3) to afford the 2-ethenyl-4,4-diethoxycarbonyl-6-methyl tetrahydropyran (4a) as a colourless oil (213mg, 27%). The fractions containing components of lower R_f were rechromatographed on silica gel with diethyl ether: hexane (1:1) to afford 2-methyl-3-ethenyl-4,4-dicarbethoxycyclopentanol (6a) as a colourless oil (249mg, 32%).

Tetrahydropyran (4a): υ_{max} 1 740 (CO, ester), 1 650 (C=C)cm^{-1}; δ_H (250MHz) 1.22-1.33 (9H, m, $(COCH_2CH_3)_2$, $CHCH_3$); 1.51-1.71 and 2.22-2.36 (4H, 2xm, $CH_2C(CO_2Et)_2CH_2$); 3.61 (1H, ddq, J 11.5, 6.2 and 1.9Hz, $CH(CH_3)$); 4.13-4.30 (4H, bm, $(COCH_2CH_3)_2$); 4.96 (1H, m, $CH(CH=CH_2)$); 5.16 (1H, ddd, J 10.5, 1.4 and 1.4Hz, $CH=CH_tH_c$); 5.30 (1H, ddd, J 17.3, 1.4 and 1.4Hz, $CH=CH_tH_c$); 5.85 (1H, ddd, J 17.3, 10.5 and 5.7Hz, $CH=CH_2$); δ_C (23Hz) 14.0, 21.9, 35.7, 37.4, 53.7, 61.6, 61.7, 70.1, 74.6, 115.6, 138.5, 170.7, 171.2; m/z 270 (M^+, 23%), 173 (100), 127 (51); (Found: M^+, 270.148. $C_{14}H_{22}O_5$ requires *M*, 270.147).

Cyclopentanol (6a): υ_{max} 3 520 (O-H), 3 100 (H-C), 1 725 (CO, ester), 1 645 (C=C)cm^{-1}; δ_H (250MHz) 0.99 and 1.06 (3H, 2xd, J 6.9 and 6.7Hz, CH_3); 1.17-1.29 (6H, bm, $(COCH_2CH_3)_2$); 1.65 (1H, s, OH); 1.80-2.01 (1H, bm, $CHCH_3$); 2.28-2.39 and 2.66-2.78 (2H, 2 x bm, CH_2); 2.66-2.78 and 3.16-3.24 (1H, 2 x bm, $CHCH=CH_2$); 3.72-3.78 and 4.07-4.29 (4H, 2 x bm, $(COCH_2CH_3)_2$); 5.10-5.24 (2H, bm, $CH=CH_2$); 5.51-5.75 (1H, bm, $CH=CH_2$); δ_C (23MHz) 11.8, 14.0, 16.0, 42.2, 43.3, 43.9, 46.5, 53.6, 55.1, 61.2, 61.3, 61.4, 61.9, 63.1, 74.6, 77.6, 117.5, 117.9, 134.1, 135.9, 136.4, 171.3, 171.8, 172.5; m/z 270 (M^+, 4%), 173 (100), 107 (26); (Found: M^+, 270.147. $C_{14}H_{22}O_5$ requires *M*, 270.147).

2-Ethenyl-4,4-diethoxycarbonyl-6-benzyltetrahydropyran (4b) and 2-methyl-3-styryl-4,4-dicarbethoxy-cyclopentanol (6b)

A solution of ethyl 6-bromo-4,5-epoxy-ethoxycarbonyl-2-(3'phenyl-2'-propenyl)hexanoate (2b) (0.2g, 0.47mmoles) in dry degassed THF (150ml) was heated to reflux under N_2. Separate solutions of AIBN (8mg) and tri-n-butyl tin hydride (0.14g, 0.13ml, 0.47mmoles) in THF (2.5ml each) were added simultaneously over a period of 2 hours. The solution was maintained at reflux for a further 2 hours. On cooling the solution was evaporated to dryness. Chromatography on neutral alumina with petrol 40/60:

diethyl ether (1:1) yielded two crude products free from most tin residues. Chromatography of the upper fraction from the alumina column on silica gel G with petrol 40/60: diethyl ether (10:1) yielded the desired tetrahydropyran (4b) as a mixture of isomers (32mg, 20%). Chromatography of this mixture afforded some separation of the isomers:

Isomer 1: υ_{max} 2 931 (CH), 1 734 (C=O)cm^{-1}; δ_H (400MHz) 1.23 (6H, 2xt, J 7Hz, OCH_2CH_3); 1.71 (1H, m, HCHCH(O)CH_2Ph); 2.18 (1H, m, HCHCH(O)CH=CH_2); 2.31 (1H, m, HCHCH(O)CH_2Ph); 2.40 (1H, m, HCHCH(O)CH=CH_2); 2.70 (1H, m, HCHPh); 2.88 (1H, m, HCHPh); 4.05-4.26 (5H, m, OCH_2CH_3 and CH of ring); 4.54 (1H, m, CH of ring); 5.02-5.08 (2H, m, CH_2=CH); 5.73 (1H, ddd, J 17, 11 and 4Hz, CH=CH_2); 7.18-7.30 (5H, m, Ph)ppm; δ_C 13.78, 13.88, 33.11, 34.55, 41.5, 61.39, 61.61, 115.63, 126.12, 128.16, 129.17, 137.23, 138.24, 170.94, 171.42ppm; m/z 346 (M^+, 1%), 255 (100), 209 (22), 181 (39) (Found: M^+, 346.175. $C_{20}H_{26}O_5$ requires M, 346.178)

Isomer 2: υ_{max} 2 916 (CH str), 1 732 (C=O)cm^{-1}; δ_H 1.18 (6H, t, J 8Hz, OCH_2CH_3); 1.22 (3H, t, J 8Hz, OCH_2CH_3); 1.57-1.71 (2H, m, CH_2CH(O)CH_2Ph); 2.22-2.28 (1H, dt, J 14 and 2Hz, Ph-HCH); 2.30-2.37 (1H, dt, J 14 and 2Hz, Ph-HCH); 2.71 (1H, dd, J 14 and 7Hz, HCHCH(O)CH=CH_2); 2.99 (1H, dd, J 14 and 6Hz, HCHCH(O)CH=CH_2); 3.64-3.75 (1H, m, CH(O)CH_2Ph); 3.93-4.01 (1H, m, CH(O)CH=CH_2); 4.10-4.21 (4H, m, CH_3CH_2O); 5.14 (1H, ddd, J 11 and 1Hz, HCH=CH); 5.30 (1H, ddd, J 17 and 2Hz, HCH=CH); 5.85 (1H, ddd, J 17.3, 10.6 and 5.5Hz, CH=CH_2); 7.17-7.31 (5H, m, Ph); δ_C 14.06, 35.21, 35.76, 42.54, 53.56, 61.52, 61.75, 74.44, 74.80, 115.45, 126.31, 128.32, 129.50, 138.08, 138.25, 170.55, 171.20; m/z 346 (M^+, 16%), 255 (100), 227 (19), 209 (24), 181 (67) 173 (47) (Found: M^+, 346.178. $C_{20}H_{26}O_5$ requires M^+, 346.178)

Chromatography of the lower fraction, from the alumina column, on silica gel G with petrol 40/60; diethyl ether (9:1, 7:1, then 4:1) yielded the desired cyclopentanol (6b) as a mixture of isomers (60mg, 37%); υ_{max} 3 522 (OH), 2 981 (CH_2), 1 732 (C=O)cm^{-1}; (signals due to one of the two cyclopentanol isomers are denoted by *). δ_H 1.01-1.28 (9H, m, OCH_2CH_3, *OCH_2CH_3, $CHCH_3$ and *$CHCH_3$); 1.92-1.98 (1H, m, CH-Me); 2.03-2.11 (1H, m, *CHMe); 2.35 (1H, d, J 15Hz, *HCHCHOH); 2.43 (2H, d, 7Hz, CH_2CHOH); 2.80 (1H, dd, J 15 and 4.6Hz, *HCHCHOH); 2.93 (1H, dd, J 11 and 9Hz, Ph-CH=CH-CH); 3.40 (1H, dd, J 12 and 9Hz, *Ph-CH=CH-CH); 3.78 (1H, q, J 7Hz, CH-OH); 4.01-4.28 (5H, m, *CH-OH, *OCH_2CH_3 and OCH_2CH_3); 5.99 (1H, dd, J 16 and 9Hz, *PhCH=CHCH); 6.08 (1H, dd, J 16 and 9Hz, PhCH=CHCH); 6.52 (1H, d, J 16Hz, Ph-CH=CH); 6.55 (1H, d, J 16Hz, *Ph-CH=CH); 7.18-7.35 (5H, m, Ph and *Ph)ppm; δ_C 11.71, 13.82, 16.13, 29.47, 42.07, 43.02, 44.47, 47.03, 52.58, 54.30, 61.17, 61.23, 61.42, 62.17, 63.26, 74.68, 77.55, 125.95, 125.97, 127.04, 127.12, 127.30, 127.79, 128.26, 132.33, 132.95, 136.92, 137.03, 171.14, 171.75, 172.37ppm; m/z 346 (M^+, 2%), 181 (50), 144 (51), 129 (100), 91 (55) (Found: M^+, 346.180. $C_{20}H_{26}O_5$ requires M^+, 346.178).

2-Ethenyl-4,4-diethoxycarbonyl-6-isopropyl tetrahydropyran (4c) and 2-methyl-3-(2'-methylpropenyl-4,4-dicarbethoxycyclopentanol (6c)

A solution of ethyl 6-bromo-4,5-epoxy-2-ethoxycarbonyl-2-(3'-methyl-2'-butenyl) hexanoate (0.23g, 0.61mmoles) in dry degassed THF (150ml) was heated to reflux under N_2. Separate solutions of AIBN (10mg) and tri-n-butyl tin hydride (0.18g, 0.16ml, 0.62mmoles) in THF (2.5ml each) were added simultaneously over a period of 3 hours. The solution was maintained at reflux for a further hour. On cooling the solution was evaporated to dryness. Chromatography on neutral alumina with petrol 40/60: diethyl ether (1:1) yielded two crude products free from most tin residues. Chromatography of the upper fraction, from the alumina column, on silica gel G with petrol 40/60: diethyl ether 10:1 yielded the desired tetrahydropyran (4c) as a mixture of isomers (40mg, 22%); Chromatography on silica gel G with petrol 40/60: diethyl ether (15:1) afforded some separation of isomers:

Isomer 1: υ_{max}2 980 (CH), 1 734 (C=O)cm^{-1}; δ_H(400 MHz), 0.92 (3H, d, J 7Hz, CH_3); 0.95 (3H, d, J 7Hz, CH_3); 1.24 (3H, t, J 7Hz, OCH_2CH_3); 1.27 (3H, t, J 7Hz, OCH_2CH_3); 1.55-1.74 (3H, m, CH_2 of ring and $CH(Me)_2$); 2.32 (2H, m, CH_2 of ring); 3.11-3.15 (1H, m, CH-O); 3.91-3.95 (1H, m, CH-O); 4.14-4.29 (4H, m, OCH_2CH_3); 5.11 (1H, dd, J 11 and 2Hz, $RCH=CH_2$); 5.28 (1H, dd, J 17 and 2Hz, $RCH=CH_2$); 5.8-5.87 (1H, m, $RCH=CH_2$)ppm; δ_C (100MHz) 14.26, 14.34, 18.41, 18.70, 32.83, 33.21, 36.12, 53.85, 61.66, 61.87, 74.58, 78.97, 115.23, 138.76, 170.96, 171.64ppm; m/z 298 (M^+, 10%), 255 (16), 181 (25), 173 (100), 169 (33), 127 (28); (Found: M^+, 298.175. $C_{16}H_{26}O_5$ requires M, 298.178)

Isomer mixture: υ_{max} 2 979 (CH), 1 732 (C=O)cm^{-1}; δ_H(* denotes signals due to one of the two tetrahydropyran isomers) 0.91- 0.97 (6H, m, CH_3 and $^*CH_3$); 1.23-1.30 (6H, m, OCH_2CH_3 and $^*OCH_2CH_3$); 1.61 (2H, m, $^*CH_2$ ring); 1.68-1.79 (3H, m, $^*CH(Me)_2$ + CH_2 ring); 2.1-2.15 (1H,m , $CH(Me)_2$); 2.27-2.40 (2H, m, CH_2 ring and $^*CH_2$ ring); 3.11-3.16 (1H, m, *CH-O); 3.54-3.59 (1H,m , CH-O); 3.91-3.95 (1H, m, *CH-O); 4.1-4.3 (8H, m, OCH_2CH_3 and $^*OCH_2CH_3$); 4.45-4.47 (1H, m, CH-O); 5.1-5.32 (2H, m,=CH_2 and *=CH_2); 5.75-5.89 (1H, m, CH= and *CH=)ppm; δ_C 13.94, 13.99, 14.01, 14.10, 18.17, 18.47, 18.58, 31.75, 31.94, 32.59, 32.97, 33.32, 35.26, 51.05, 53.61, 61.43, 61.46, 61.63, 70.34, 73.10, 74.34, 76.75, 115.00, 115.56, 137.88, 138.52, 170.72, 171.25, 171.40, 171.71ppm; m/z 298 (M^+, 4%), 255 (67), 209 (36), 181 (64), 173 (100) (Found: M^+, 298.179. $C_{16}H_{26}O_5$ requires M, 298.1780)

Chromatography of the lower fraction from the alumina column, on silica gel G with petrol 40/60; diethyl ether (9:1, 2:1) yielded the desired cyclopentanol (6c) as a mixture of isomers (61mg, 30%); υ_{max} 3 513 (OH), 2 964 (CH), 1 726 (C=O)cm^{-1};(signals due to one of the two cyclopentanol isomers are denoted by *) δ_H 0.94 (3H, d, J 7Hz, $^*CH_3CH$); 1.00 (3H, d, J 7Hz, CH_3); 1.17-1.27 (6H, m, OCH_2CH_3 and $^*OCH_2CH_3$); 1.71-1.75 (7H, m, $CH_3C=CH$, $^*CH_3C=CH$, $CHCH_3$ and $^*CHCH_3$); 2.23 (1H, s, OH and *OH); 2.31 (1H, dd, J 15 and 1Hz, *HCHCHOH); 2.39 (2H, m CH_2CHOH); 2.77 (H, dd, J 15 and 4Hz, *HCHCHOH); 3.07 (1H, t, J 11Hz, $CHCH=CMe_2$); 3.54 (1H, t, J 11Hz, $^*CHCH=CMe_2$); 3.69 (1H, m, CHOH); 4.07-4.25 (5H, m, $^*OCH_2CH_3$ and OCH_2CH_3 and *CHOH); 4.81 (1H, m, $^*CH=CMe_2$ and $CH=CMe_2$)ppm; δ_C 11.9, 14.0, 14.1, 16.1, 18.3, 18.4, 26.1, 42.5, 43.4, 46.4, 48.1, 49.1, 49.8, 61.1, 61.2, 61.3, 61.4, 63.4, 75.0, 77.5, 123.0, 123.4, 135.4, 135.9, 171.5, 171.8, 172.1, 173.1ppm; m/z 298 (M^+, 33%), 224 (63), 209 (58), 173 (100), 161 (79) (Found: M^+, 298.179. $C_{16}H_{26}O_5$ requires M, 298.178).

2-Methyl-3-(1'-methylethenyl)-4,4-dicarbethoxy-cyclopentanol (6d).

A solution of ethyl 6-bromo-4,5-epoxy-2-ethoxycarbonyl-2-(2'-methyl-2'-propenyl) hexanoate (2d), (0.74g, 2mmoles) in dry degassed THF (250ml) was heated to reflux under N_2. A solution of AIBN (30mg) and tri-n-butyltin hydride (0.59g, .55ml, 2mmoles) in THF (10ml) was added over a period of 4 hours. The solution was maintained at reflux for a further two hours. On cooling the solution was evaporated to dryness. Chromatography on neutral alumina with petrol 40/60: diethyl ether (1:1) yielded crude products free from most tin residues. Chromatography on silica gel G with diethyl ether: 40/60 petrol (1:3, 1:1, 1:0) yielded the cyclopentanol (6d) as a mixture of two diastereomers (175mg, 31%); υ_{max} 3 462 (OH), 2 980 (CH), 1 718 (C=O)cm^{-1}; δ_H 0.98 (3H, d, J 7Hz, $^*CH_3CH$); 1.03 (3H, d, J 7Hz, CH_3CH); 1.18-1.29 (6H, m, CH_3CH_2O and $^*CH_3CH_2O$); 1.75 (3H, s, $CH_3C=CH_2$); 1.79 (3H, s, $CH_3C=CH_2$); 1.92-1.99 (1H, m, CHMe); 2.08-2.14 (1H, m, CHMe); 2.20 (1H, d, J 15Hz, *HCHCHOH); 2.32 (1H, dd, J 14 and 8Hz, HCHCHOH); 2.53 (1H, dd, J 14 and 8Hz, HCHCHOH); 2.89 (1H, dd, J 15 and 4Hz, $CHC(Me)=H_2$); 2.91 (1H, d, J 12Hz, *HCHCHOH); 3.35 (1H, d, J 13Hz, $^*CHC(Me)=CH_2$); 3.66 (1H, q, J 8Hz, CHOH); 3.98-4.28 (5H, m, OCH_2CH_3, $^*OCH_2CH_3$ and *CHOH); 4.76-4.92 (2H, m, CH_2=CMe and $^*CH_2$=CMe);

δ_C 11.96, 13.86, 14.01, 15.98, 23.53, 24.07, 42.60, 43.23, 43.41, 45.64, 54.16, 55.72, 61.29, 61.42, 61.48, 61.78, 63.71, 74.91, 76.97, 112.76, 113.39, 142.61, 143.15, 171.09, 171.59, 172.16, 173.18ppm; m/z 284 (M^+, 12), 220 (39), 210 (35), 193 (63), 192 (82), 173 (100) (Found: M^+, 284.160. $C_{15}H_{24}O_5$ requires M, 284.162).

Dinitrobenzoate esters of the cyclopentanols (6d)

3,5 Dinitrobenzoyl chloride (103mg, 0.45mmoles) and the cyclopentanols (6d) (127mg, 0.45mmoles) were dissolved in pyridine (5ml) and the solution stirred at room temperature for sixteen hours. Diethyl ether (20ml) was added and the solution was washed with aqueous copper sulphate until no pyridine remained, sodium bicarbonate (2 x 5ml), water (3 x 5ml), and brine (5ml), dried (Na_2SO_4) and evaporated to dryness to yield the dinitrobenzoate ester as a white crystalline solid (210mg, 98%). A portion of the mixture of diastereomers was dissolved in the minimum amount of solvent and separated by hplc on a 20x250mm YMC packed column, S043 (S-15Sil) with dichloromethane: petrol 40/60 (3:2), flow rate of 9.0ml/min to yield a sample of each isomer for X-ray crystallographic analysis.

Isomer 1

m.p. 95-96°C υ_{max} 1 729 (C=O)cm^{-1}; δ_H 1.07 (3H, d, J 6.5Hz, CH_3CH); 1.23 (3H, t, J 7.1Hz, $CH_3CH_2(O)O$); 1.27 (3H, t, J 7.1Hz, CH_3CH_2O); 1.82 (3H, s, CH_3CCH_2); 2.41-2.52 (1H, m, $CHCH_3$); 2.67 (1H, dd, J 14.2 and 8.2Hz, $CH_2C(CO_2Et)_2$); 2.79 (1H, dd, J 14.2 and 8.7Hz, $CH_2C(CO_2Et)_2$); 3.07 (1H, d, J 12.6Hz, $CHC(Me)CH_2$); 4.0-4.3 (4H, m, CH_3CH_2O); 4.86 (1H, s, HCH=C); 4.94 (1H, q, J 9.3Hz, CH-OAr); 5.01 (1H, m, HCH=C); 9.18 (2H, d, J 2.1Hz, ortho-ArH); 9.26 (1H, t, J 2.1Hz, para-ArH); δ_C 13.68, 14.00, 15.43, 23.66, 29.70, 38.67, 41.62, 53.93, 61.27, 61.65, 61.79, 80.61, 113.83, 122.49, 129.50, 133.63, 141.90, 148.72, 162.53, 170.38, 171.63, 180.68

Isomer 2

δ_H 0.99 (3H, d, J 6.7Hz, CH_3CH); 1.23 (6H, t, J 7.2Hz, CH_3CH_2O); 1.84 (3H, s, CH_3CCH_2); 2.42 (2H, d, J 15.4Hz, $CH_2C(CO_2Et)_2$); 3.15 (1H, dd, J 15.3 and 4.2Hz, $CHCH_3$); 3.54 (1H, d, J 12.4Hz, $CHC(Me)CH_2$); 3.99-4.36 (4H, m, CH_3CH_2O); 4.82 (1H, s, HCH=C); 5.00 (1H, s, HCH=C); 5.65 (1H, t, J 3.9Hz, CH-OAr); 9.11 (2H, d, J 2.1Hz, ortho-ArH); 9.26 (1H, t, J 2.1Hz, para-ArH); m/z 478 (M^+, .3%), 405 (8), 404 (8), 387 (7), 267 (21), 220 (50), 195 (50), 192 (100) (Found: M^+, 478.161. $C_{22}H_{26}O_{10}N_2$ requires M^+, 478.159).

Crystallographic analysis of dinitrobenzoates, isomers 1 and 2.

Crystal data. Isomer 1. C 22 H 26 N 2 O 10, M=478.44, Triclinic, a=7.187(4), b=10.722(6) , c = 16.945(4) Å, α = 100.65(3),β = 96.45 (3), γ = 100.05(4)° , U = 1249.34 $Å^3$, z = 2 ,Dc = 1.27 g cm^{-3} , F (000) = 504, Space Group P1, Cu-k_α radiation λ = 1.54178 Å, μ = (Cu-k_α) = 8.70 cm^{-1}. Crystal data. Isomer 2 C 22 H 26 N 2 O 10, M = 478.44, Monoclinic, a = 22.660(9), b = 15.411(7) , c = 7.724(3) Å, β = 90.36(3)° U = 2697.27 $Å^3$ z = 4, Dc = 1.18 g cm^{-3} , F (000) = 1008 , Space group $P2_1/c$, Mo-k_α radiation λ = 0.70926Å , μ (Mo-k_α) = 1.01 cm^{-1}

Crystals of approximate dimensions 0.45 x 0.15 x 0.15 mm for 1 and 0.5 x 0.5 x 0.07 mm for 2 were mounted on an Enraf Nonius CAD4 and a Hilger and Watts Y290 diffractometer respectively and 25 (1) and 12 (2) reflections were used to determine accurate lattice parameters. Intensity data were collected with an

$\omega/2\theta$ scan. Totals of 3700 (1) and 3287 (2) independent reflections were measured of which 2090 and 1552 respectively had $I>3\sigma(I)$ and were considered observed and used in the subsequent refinement. Crystals of (2), with a β angle very close to 90°, were found to be twinned on the (001) plane, indeed early samples apparently showed perfect orthorhombic symmetry. Eventually a crystal was selected of one predominant twin, but some intensities were clearly in error for the residual twin. The data were corrected for Lorentz and polarisation factors but no absorption corrections were made. Crystallographic calculations were performed using a CRYSTALS[9] system of programs. The structures were solved by direct methods using the MULTAN[10] program. Least squares refinement including anisotropic thermal parameters for non-hydrogen atoms and isotropic refinement of hydrogen atoms located in a difference Fourier synthesis terminated at R 0.0514 (R_w 0.0657) for (1). The crystal structure of (2) was found to contain disordered solvent molecules of petroleum, located in channels parallel to the c axis at approximately 0.05, 0.25, z throughout the crystal with about a third of a petrol per molecule accounting for the difference in density above. This disorder together with the twinning, did not allow refinement of the hydrogen atoms and terminated at the very high residuals R 0.0139, (R_w0.1349), but nevertheless allowed confirmation of the gross molecular structure. Final difference maps showed no features in excess of 0.3eÅ^{-3} for (1), and 0.4eÅ^{-3} for (2).

The refined fractional atomic coordinates are shown in Tables 1 and 2 respectively and the resulting molecular structures are illustrated in figures 5 and 6. In (1) the cyclopentanol ring adopts the half-chair conformation with C(5) 0.63Å out of the plane. The H(4)-C(4)-C(5)-H(5) torsion angle is 63° in (1) and 155° in (2) accounting for the different nmr coupling constants. The geometric data for both structures are unexceptional. Observed and calculated structure factors, thermal parameters, bond lengths and bond angles are all listed in a Supplementary Publication. See Notice to Authors, Tetrahedron 40(2), ii (1984).

Table 1
Fractional atomic coordinates for Isomer 1

Atom	x/a	y/b	z/c
C(1)	0.4510(6)	0.1216(4)	0.7871(3)
C(2)	0.4705(5)	0.2707(3)	0.8217(2)
C(3)	0.6549(5)	0.3354(4)	0.7935(3)
C(4)	0.6958(6)	0.2337(4)	0.7277(2)
C(5)	0.6435(6)	0.1093(4)	0.7576(3)
C(6)	0.6412(9)	-0.0142(6)	0.6980(4)
C(7)	0.3790(8)	0.0329(4)	0.8410(3)
C(8)	0.493(1)	-0.0099(6)	0.8904(4)
C(9)	0.167(1)	-0.0070(7)	0.8333(6)
C(10)	0.4898(6)	0.2996(4)	0.9131(2)
O(11)	0.6363(5)	0.3225(4)	0.9588(2)
O(12)	0.3193(4)	0.2926(3)	0.9377(2)
C(13)	0.3165(9)	0.3137(7)	1.0251(3)
C(14)	0.120(1)	0.310(2)	1.0388(7)
C(15)	0.2981(5)	0.3199(4)	0.7867(2)
O(16)	0.1628(4)	0.2556(3)	0.7406(2)
O(17)	0.3231(3)	0.4464(2)	0.8124(2)
C(18)	0.1696(7)	0.5079(5)	0.7837(4)
C(19)	0.2344(9)	0.6493(5)	0.8135(5)
O(20)	0.5575(3)	0.2217(3)	0.6544(2)
C(21)	0.6039(6)	0.2947(4)	0.6013(2)
O(22)	0.7552(4)	0.3647(3)	0.6048(2)
C(23)	0.4381(5)	0.2800(4)	0.5360(2)

Table 2
Fractional atomic cooordinates for Isomer 2

Atom	x/a	y/b	z/c
C(1)	0.7793(6)	0.444(1)	0.688(3)
C(2)	0.7582(7)	0.459(1)	0.498(2)
C(3)	0.6939(7)	0.415(1)	0.493(3)
C(4)	0.6820(6)	0.388(1)	0.673(2)]
C(5)	0.7432(7)	0.368(1)	0.760(3)
C(6)	0.7421(7)	0.361(1)	0.956(3)
C(7)	0.8432(8)	0.438(1)	0.726(3)
C(8)	0.8719(8)	0.356(2)	0.732(3)
C(9)	0.8774(8)	0.520(2)	0.737(4)
C(10)	0.7984(8)	0.400(2)	0.380(3)
O(11)	0.7972(6)	0.3312(9)	0.343(2)
O(12)	0.8468(6)	0.4593(9)	0.334(2)
C(13)	0.8896(9)	0.412(2)	0.233(3)
C(14)	0.939(1)	0.482(2)	0.222(5)
C(15)	0.7570(8)	0.554(1)	0.443(3)
O(16)	0.7641(6)	0.6121(9)	0.538(2)
O(17)	0.7381(6)	0.5604(8)	0.284(2)
C(18)	0.731(1)	0.648(2)	0.217(4)
C(19)	0.745(2)	0.655(2)	0.059(6)
O(20)	0.6461(4)	0.3094(6)	0.684(2)
C(21)	0.5874(7)	0.319(1)	0.706(3)
O(22)	0.5654(5)	0.3877(9)	0.717(3)
C(23)	0.5577(7)	0.238(1)	0.737(3)

Table 1 (continued)
Fractional atomic coordinates for Isomer 1

Atom	x/a	y/b	z/c
C(24)	0.2545(6)	0.2190(4)	0.5428(3)
C(25)	0.1092(5)	0.2126(4)	0.4804(2)
C(26)	0.1371(7)	0.2625(4)	0.4130(3)
C(27)	0.3198(7)	0.3219(4)	0.4087(2)
C(28)	0.4707(6)	0.3327(4)	0.4689(2)
N(29)	-0.0858(5)	0.1467(4)	0.4877(3)
O(30)	-0.1086(5)	0.0978(4)	0.5454(2)
O(31)	-0.2139(5)	0.1456(5)	0.4335(3)
N(32)	0.3574(7)	0.3746(4)	0.3368(2)
O(33)	0.5127(7)	0.4425(4)	0.3391(2)
O(34)	0.2297(7)	0.3491(4)	0.2792(2)

Table 2 (continued)
Fractional atomic cooordinates for Isomer 2

Atom	x/a	y/b	z/c
C(24)	0.5020(8)	0.240(1)	0.806(3)
C(25)	0.4745(8)	0.161(1)	0.832(3)
C(26)	0.499(1)	0.081(1)	0.779(3)
C(27)	0.5526(7)	0.084(1)	0.710(3)
C(28)	0.5815(6)	0.161(1)	0.678(2)
N(29)	0.4159(9)	0.163(2)	0.911(4)
O(30)	0.3929(9)	0.096(2)	0.935(4)
O(31)	0.3987(7)	0.232(1)	0.985(3)
N(32)	0.5762(8)	0.005(1)	0.632(3)
O(33)	0.6215(8)	0.006(1)	0.566(3)
O(34)	0.5497(9)	-0.058(1)	0.646(4)

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