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REGIOSELECTIVE BOND CLEAVAGE AND COORDINATION EFFECTS IN THE REDUCTION OF SOME ACETALS WITH LITHIUM IN AMMONIA

A.D. Abell and R.A. Massy-Westropp*

Department of Organic Chemistry, University of Adelaide,
P.O. Box 498, Adelaide, South Australia, 5001

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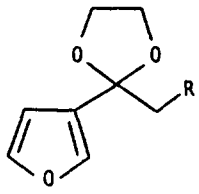
Abstract - Some benzylic-type acetals possessing the 2,8-dioxabicyclo[3.2.1]octane ring system are cleaved in a regioselective manner when treated with lithium in ammonia. The results from various reductions implicate coordination of lithium as a significant factor involved in reduction mechanisms.

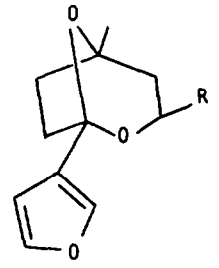
It is well documented that allylic and benzylic ethers, acetals, and to a lesser extent alcohols are reductively cleaved in metal in ammonia solutions.[1,2] Similar cleavages have been observed with related derivatives (referred to in this paper as benzylic derivatives) in the 2-substituted furan[3-5] and the 3-substituted furan[6-10] series. In addition to the observation that the 2-substituted compounds undergo reductive cleavage of the leaving group faster than in the 3-substituted series it was found that the outcome of the reduction in the latter series depended on whether or not the reduction was done in the presence of an added proton source. In particular, reduction of the benzylic acetal (**1a**) with lithium in ammonia in the presence of ethanol gave extensive reduction and cleavage of the furan ring.[10] In contrast, in the absence of an added proton source reduction gave a mixture of the monofission product 2-[1'-(furan-3"-yl)-nonyloxy]ethanol and the bisfission product, 3-nonylfuran in a ratio of approximately 3:1.[10] Hydrogenolysis of the first oxygen of the acetal is faster than hydrogenolysis of the second which cleaves at a rate comparable with that of the ether, 3-(1'-methoxynonyl)furan.[10] Consequently, the lithium alkoxide derived from the monofission product must have little influence on its subsequent cleavage.

Compounds prepared from the sesquiterpene eremoacetal (**2a**)[11] provide suitable models for the investigation of the metal in ammonia cleavage of the 2,8-dioxabicyclo[3.2.1]octane system. In particular, these compounds have a clearly defined stereochemistry and allow a study to be made of the selectivity of bond cleavage. Also, the possible influence of lithium chelation can be assessed by using a series of alcohols with an hydroxyl group in the side chain at C3. The results of these investigations are presented in this paper.

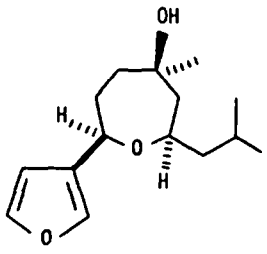
The reductions were done with lithium in ammonia at -33° under standardized conditions with no added proton source. Treatment of dihydroeremoacetal (**2b**)[11] for 15 min returned 97% of starting material. After a reaction time of 3 h starting material (63%), oxepanes (**3**) and (**4**) (17%) and diol (**5a**) (7%) were isolated and after a 7 h reduction starting material (30%) was recovered in addition to the oxepanes (20%) and diol (40%). The slowness of the cleavage



1a : R = C_7H_{15}
1b : R = CH_2OH
1c : R = $CH_2OCH_2C_6H_5$
1d : R = CH_2CH_2OH
1e : R = $CH_2CH_2OCH_2C_6H_5$
1f : R = $CH_2CH_2CH_2CH_2OH$
1g : R = $CH_2CH_2CH_2CH_2OCH_2C_6H_5$
1h : R = CO_2Et



2a : R = $CH{=}C(CH_3)_2$
2b : R = $CH_2CH(CH_3)_2$
2c : R = $CH_2CH_2CH_2$ 
2d : R = CH_2OH
2e : R = $CH_2OCH_2OCH_3$
2f : R = $CH_2C(OH)(CH_3)_2$
2g : R = $C(OH)(CH_3)_2$



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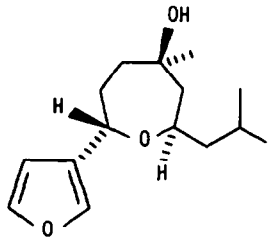

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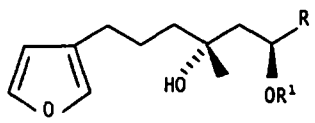
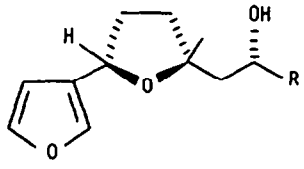


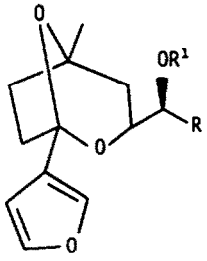
5a : R = $CH_2CH(CH_3)_2$; R^1 = H
5b : R = CH_2OH ; R^1 = H
5c : R = CH_2OAc ; R^1 = Ac
5d : R = $CH_2OCH_2OCH_3$; R^1 = H
5e : R = $CH_2C(OH)(CH_3)_2$; R^1 = H
5f : R = $C(OH)(CH_3)_2$; R^1 = H



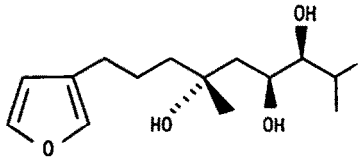
6a : R = $CH_2CH(CH_3)_2$
6b : R = $CH{=}C(CH_3)_2$

of the acetal (2b) is noteworthy, as is the fact that the tetrahydrofuran isomers, e.g. (6a), were not detected. Parallel results have been observed with the reduction of (2c).[12]

The following reductions were done on model alcohols where the hydroxyl group is present in a chain at C3 of the 2,8-dioxabicyclo[3.2.1]octane skeleton. Reduction of the primary alcohol (2d)[13] for 5.5 h gave starting material (42%), triol (5b) (41%) and a minor product (2%), tentatively assigned as an oxepane derivative. Reduction of the protected derivative (2e) for the same time gave more of the bisfission product (5d) (68%) and a smaller quantity of starting material (9%).



7a : R = $CH(CH_3)_2$; R^1 = H
7b : R = $CH(CH_3)_2$; R^1 = Ac
7c : R = CH_3 ; R^1 = H
7d : R = CH_3 ; R^1 = Ac



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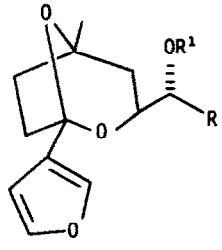
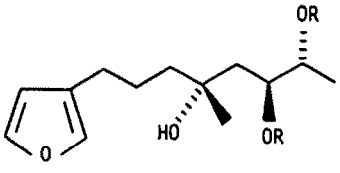


9a : R = CH_3 ; R^1 = H
9b : R = CH_3 ; R^1 = Ac



10a : R = H
10b : R = Ac

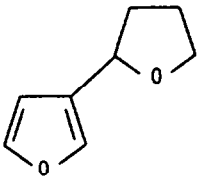
Reduction for 3 h of the secondary alcohol (7a)[13] gave starting material (40%) and triol (8) (37%). Under the same conditions the alcohol (9a) gave the corresponding bisfission product (10a) (79%) with only a trace of starting material. Under identical reduction conditions the tertiary alcohols (2f) and (2g) gave the following similar results: (2f) gave starting material (19%) and the triol (5e) (60%) while (2g) gave starting material (18%) and the triol (5f) (62%).

Two important points emerge from the results described. No tetrahydrofuran monocleavage products were detected in any of the lithium in ammonia reductions and the reduction rate and product composition is clearly dependent on the nature of the group at C3 of the 2,8-dioxabicyclo-[3.2.1]octane system. When this group does not contain an oxygenated substituent, e.g. (2b), the oxepane was isolated as the major product. However, when an oxygenated substituent is present the reduction rate is enhanced and little, if any, of the oxepane products were isolated.

Regarding the absence of the tetrahydrofuran products from the reductions, it is possible that preferential cleavage of the C1-O8 bond had occurred to yield only oxepanes or, alternatively, the reductions of the tetrahydrofuran products arising from cleavage of the C1-O2 bond, e.g. (**6a**), if formed, occurred rapidly relative to the oxepanes, e.g. (**3**). Information about the relative rates of cleavage of tetrahydrofuran and oxepane derivatives was obtained by doing a reduction of a mixture (1:1) of the oxepane (**3**) and the tetrahydrofuran (**6a**) for 1 h. Isolation and characterisation of the products revealed that the tetrahydrofuran (**6a**) had been reduced to the diol (**5a**) to the extent of 95% whereas the oxepane (**3**) was resistant towards reduction (90% recovery). Therefore, if (**6a**) had been formed in the reduction of (**2b**) then it would have been rapidly reduced. These observations about the reduction of tetrahydrofuran and oxepane derivatives have been confirmed with model compounds and will be discussed later.

A competitive reduction of the epimeric oxepanes (**3**) and (**4**) for 3 h gave approximately equal reduction of each component and yielded the diol (**5a**) (10%), a yield comparable with that obtained (7%) from the similar reduction of dihydroeremoacetal (**2b**) after 3 h. The reduction of dihydroeremoacetal (**2b**), at least, would therefore appear to proceed predominantly, if not exclusively, via the oxepanes (**3**) and (**4**). It is likely that the conformation of the furan ring is a factor crucial for the preferential cleavage of the C1-O8 bond leading to the oxepanes.

The lithium cation is known to co-ordinate via 4,5 (most favourable) and 6-membered intermediates.[14,15] Enhanced rates of cleavage of the oxepanes bearing the extra oxygen substituent are unlikely because, as it has already been noted, the reductive cleavage of the monofission product from (**1a**) is slow even though it is possible in this case to have optimum co-ordination. Bearing in mind the slowness of the oxepane fission discussed above, it is considered that when the side-chain at C3 of the 2,8-dioxabicyclo[3.2.1]octane ring system is oxygenated the reduction proceeds significantly, or probably exclusively via the tetrahydrofuran intermediate which would then undergo further fast reduction to give the observed product, e.g. (**8**) from (**7a**). The oxygenated substituents in the side-chain of the reduction substrates (**2d**)-(**2g**), (**7a**) and (**9a**) offer the potential to co-ordinate lithium cations to the benzylic oxygen (O2) of the 2,8-dioxabicyclo[3.2.1]octane nucleus via a five or six membered ring. Co-ordination involving the other acetal oxygen (O8) would involve unfavourable seven or eight membered rings. In addition to facilitating electron addition to the furan ring, co-ordination would direct the cleavage of the C1-O2 bond to yield the intermediate tetrahydrofuran. Fast reduction would then produce the observed bisfission products.



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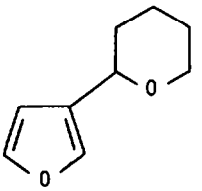

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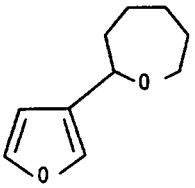

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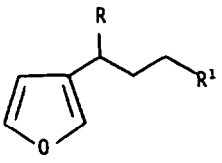
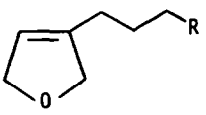
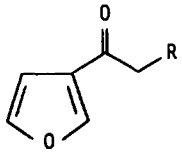




14a : R = H; R^1 = CH_2OH
14b : R = H; R^1 = CH_2CH_2OH
14c : R = H; R^1 = $CH_2CH_2CH_2OH$
14d : R = OCH_3; R^1 = nC_6H_{13}
14e : R = H; R^1 = OH
14f : R = OCH_2CH_2OH; R^1 = OH
14g : R = H; R^1 = CH_2OH
14h : R = OCH_2CH_2OH; R^1 = CH_2OH
14i : R = H; R^1 = $CH_2CH_2CH_2OH$
14j : R = OCH_2CH_2OH; R^1 = $CH_2CH_2CH_2OH$
14k : R = OH; R^1 = CH_2OH
14l : R = OH; R^1 = CH_2CH_2OH
14m : R = OH; R^1 = $CH_2CH_2CH_2OH$
14n : R = H; R^1 = nC_6H_{13}
14o : R = OH; R^1 = $CH_2OCH_2C_6H_5$
14p : R = OH; R^1 = $CH_2CH_2OCH_2C_6H_5$
14q : R = OH; R^1 = $CH_2CH_2CH_2OCH_2C_6H_5$

15a : R = OH
15b : R = CH_2OH



16a : R = $CH_2CH_2OC_6H_5$
16b : R = $CH_2CH_2CH_2OCH_2C_6H_5$
16c : R = $CH_2CH_2CH_2CH_2OCH_2C_6H_5$
16d : R = CO_2Et

In order to confirm the results found with the reduction of the complex substrates, tetrahydrofuran (**6a**) and oxepane (**3**), the three simple benzylic ethers (**11**)-(**13**) were prepared to investigate their relative rates of reduction. Some model compounds with an hydroxyl group at varying chain lengths from the benzylic dioxolane ring were also prepared. These reductions were carried out under standardized conditions with lithium in ammonia, using tetrahydrofuran as co-solvent without an added proton source. The crude ether extracts from the reductions were analysed directly by GLC and the products were subsequently isolated and characterized. A number of substrates were reduced under competitive conditions in order to assess their relative rates of reduction.

The results showed that after 15 min reduction the tetrahydrofuran (**11**) was reductively cleaved substantially faster to yield the product (**14a**) (93% by GLC; 90% isolated) than either the tetrahydropyran (**12**) to alcohol (**14b**) (18% by GLC; 17% isolated) or the oxepane (**13**) to the compound (**14c**) (13% by GLC and isolation). A competitive experiment for 11 min gave (by GLC): (**11**) 100%, (**12**) 10% and (**13**) 8% reduction. In a further competitive reduction the tetrahydropyran (**12**) reduced at twice the rate of the methyl ether (**14d**). A possible explanation for these results can be found in the combustion data[16] which show that tetrahydrofuran possesses about 18.7 kJ/mole more strain energy than tetrahydropyran. The ability of the ethers to co-ordinate the lithium cation may be significant but attempts to rank the basicities of the cyclic ethers have been conflicting.[17]

The following results were found for the reduction (15 min) of each of the alcohols (**1b**), (**1d**) and (**1f**). (**1b**) gave a mixture of the bisfission alcohol (**14e**) (55%), the monofission diol (**14f**) (13%), the 2,5-dihydrofuran (**15a**) (10%) and starting material (5%). The higher homologue (**1d**) yielded the analogous products (**14g**) (48%), (**14h**) (10%), (**15b**) (5%) and starting material (28%). Significantly less reduction of (**1d**) relative to (**1b**) had occurred, a result confirmed by a competitive reduction of these two substrates. In a competitive reduction of (**1b**) and (**1f**)

it was found that (**1f**) gave the alcohol (**14i**) (41%), the diol (**14j**) (13%) and starting material (43%).

It is clear that the rate of acetal cleavage and the quantity of the dihydrofuran are dependent on the position of the hydroxyl group. Although it is known[10] that the furan ring is reduced rapidly in the presence of an added proton source, it is unlikely that the enhanced rate of reduction of (**1b**) relative to both (**1d**) and (**1f**) is attributable to the amount of furan reduction. Reduction of the benzyl ether (**1c**) for 15 min gave the parent alcohol (**1b**) (4%), monocleavage product (**14f**) (13%) and the biscleavage product (**14e**) (70%). The alcohol (**1b**) can be prepared preparatively from (**1b**) at -78°, indicating a fast cleavage of the benzyl ether relative to the acetal. Significantly, at -33°, fast hydrogenolysis of the acetal was still observed but no dihydrofuran was detected, showing that its formation was dependent on the presence of a proton source other than ammonia. The fact that the amount of dihydrofuran decreases as the distance of the hydroxyl group from the acetal increases in the series (**1b**), (**1d**) and (**1f**) suggests that the hydroxyl proton is transferred by an intramolecular mechanism in one of the reduction intermediates leading to the dihydrofuran. This is supported by the results of the reduction of dihydroeremoacetal (**2b**) in the presence of an equivalent t-butyl alcohol. The same product ratio was observed with no reduction of the furan ring. Because both the alcohol (**1b**) and its benzyl ether (**1c**) (effectively the alkoxide in the reduction medium) are cleaved faster than (**1d**) and (**1f**) it is likely that lithium co-ordination is important. Here co-ordination, involving a six membered ring, would be more favourable and promote electron addition to the furan ring and subsequent cleavage. In addition to the significance of co-ordination in acetal cleavage, it should be noted that in all examples with an additional side-chain oxygen substituent (hydroxyl, methoxymethyl ether and benzyl ether) significantly less monofission product was observed. These results strongly suggest that co-ordination is also important in the mechanism for fission of the second C-O bond.

The 2,8-dioxabicyclo[3.2.1]octane substrates were prepared from the sesquiterpene eremoacetal as described in the experimental. The cyclic ethers (**11**)-(**13**) were made from furan-3-carboxylic acid by the following route. The benzyloxy ketones (**16a**)-(**16c**) were synthesized by the method described[8] using alkyllithium reagents prepared in the presence of lithium furan-3-carboxylate. Successive reduction with $NaBH_4$ and then with lithium in ammonia at -78° gave the 1,4-diols (**14k**)-(**14m**) which readily cyclized to the ethers with p-toluenesulphonic acid in dichloromethane.

Formation of the acetals (**1e**) and (**1g**) from the ketones (**16a**) and (**16c**), followed by selective reduction with lithium in ammonia at -78° gave the alcohols (**1d**) and (**1f**) in good yields. Lithium aluminium hydride reduction of the acetal (**1h**), prepared from the β-keto ester (**16d**)[18] gave the alcohol (**1b**).

EXPERIMENTAL

IR spectra were recorded on Jasco IRA-1 and A-102 spectrometers. Mass spectra were recorded with an Hitachi Perkin Elmer RMU-7D or an AEI MS-30 instrument. GLC-MS were done with the AEI MS-30 spectrometer coupled to a Pye-Unicam 104 gas chromatograph. Analytical GLC was carried out on a Perkin-Elmer Sigma 3B instrument equipped with a flame ionisation detector coupled to a Perkin-Elmer M-2 printing integrator. The following columns were used:

A. 5% OV17 on Varaport (80/100), 4.5 m x 8 mm, glass,

B. 2% carbowax 20M on Varaport (30), 1.5 m x 8 mm, glass,

C. 5% carbowax 20M on Varaport (30), 1.5 m x 4 mm, glass.

N_2 was used as carrier gas at a flow rate of 40 ml/min for columns A and C and 25 ml/min for B.

^1H NMR spectra were recorded with JEOL HNM-PMX60 or Bruker WP80 DS spectrometers and ^{13}C NMR spectra with the Bruker WP80 DS instrument at 20.1 MHz. Chemical shifts are in p.p.m. downfield from TMS.

Preparative TLC plates were prepared from Merck Kieselgel G and HF254 (1:1). Flash chromatography was done using Merck Kieselgel 60 (230-400 mesh). Light petroleum refers to the fraction b.p. 60-70°. $MgSO_4$ was used as the drying agent. Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

General Reduction Details: Li wire (0.02% Na), stored under paraffin, was cut with a stainless steel spatula and washed with light petroleum. Li, in small pieces, was added to NH_3 under N_2. THF and ether were distilled from Na/benzophenone under N_2. NH_3 was purified in the following way: NH_3 (100 ml) was distilled from the cylinder into a flask containing Na (4 g) and anhydrous $FeCl_3$ (100 mg). After refluxing for 30 min the NH_3 was distilled under N_2. All reductions were carried out under a positive pressure of N_2 in a graduated, multi-necked Erlenmeyer flask fitted with an acetone/dry ice condenser and seals. Reagents were added with a syringe and stirring was done magnetically with a glass encased bar. Glassware was washed with aqueous Et_3N (1%), then with distilled H_2O and dried overnight at 130°. The assembled apparatus was flame dried and the joints sealed with Teflon tape.

A soln of the terpene derived substrate in THF was added over 5 min to a soln of Li in NH_3 (stirred for 15 min prior to the addition). The mixture was stirred and after the time indicated isoprene was added to remove the excess of Li. Solid NH_4Cl was added and the NH_3 allowed to evaporate. H_2O was added and the soln extracted with CH_2Cl_2 (4 times). The combined organic extracts were dried and evaporated under reduced pressure. The crude product was analysed by ^1H NMR and, where specified, the individual components were isolated by preparative TLC.

The GLC response ratios for the synthetic substrates and their reduction products were determined. A soln of the substrate and butyl nonyl ether (GLC standard) in THF was analyzed by GLC on the specified column. The reduction was then done for 10 min. Isoprene and NH_4Cl were added and the NH_3 allowed to evaporate (evaporation of NH_3 from several substrates and products showed insignificant volatility during the evaporation). H_2O was added and the mixture extracted with ether (4 times). The total ether extract was analyzed by GLC, then dried and evaporated. The products were identified by GLC retention time comparison with authentic samples and isolated where indicated. The individual components of the product mixture are quoted in the order of elution.

Reduction of Dihydroeremoacetal (2b)[11] A soln of (2b) (110 mg, 0.41 mmol) in THF (1 ml) was reduced with Li (40 mg, 5.76 mmol) in NH_3 (10 ml) for 3 h. Purification by preparative TLC (ether/light petroleum, 1:2) gave starting material (63%), oxepanes (3) and (4) (17%) and diol (5a) (7%). The products were identified by comparison with the authentic samples described below. A similar reduction, using (2b) (1.7 g) gave, in addition to recovered (2b) (1.1 g, 65%), the highest R_f product (2R,4R)-7-(furan-3'-yl)-4-methyl-2-(2"-methylpropyl)oxepan-4-ol (3) (116 mg, 6.8%), m.p. 67-68°. (Found: C, 71.7; H, 9.8. $C_{15}H_{24}O_3$ requires: C, 71.4; H, 9.6%). IR (Nujol) 3300, 1500, 1140, 1120, 1070, 1040, 1010, 940, 900, 870, 800, 780, 720 cm^{-1}. ^1H NMR δ ($CDCl_3$) 0.90 (6H, d, J=6.5 Hz), 1.26 (3H, s), 3.66 (1H, m), 4.26 (1H, dd, J=4.5, 9.0 Hz), 6.34 (1H, m), 7.35 (2H, m). m/z 252 (M), 234, 206, 193, 155, 151, 145, 133, 124, 110, 108, 97 (100), 95, 82, 81, 79, 71, 69, 55.

The lowest R_f product (2R,4R)-7-(furan-3'-yl)-4-methyl-2-(2"-methylpropyl)oxepan-4-ol (4) (160 mg, 9.4%), m.p. 46-47°. (Found: C, 71.7; H, 9.4. $C_{15}H_{24}O_3$ requires: C, 71.4; H, 9.6%) IR (Nujol) 3370, 3140, 1500, 1120, 1090, 1075, 1050, 1030, 1020, 910, 875, 730 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.75, 0.83 (each 3H, d, J=6.5 Hz), 1.37 (3H, s), 3.67 (1H, m), 4.7 (1H, dd, J=3.5, 9.5 Hz), 6.38 (1H, m), 7.35 (1H, m), 7.37 (1H, m). m/z 252 (M), 234, 206, 197, 191, 177, 151, 133, 127, 125, 124 (100), 110, 108, 97, 95, 81, 71, 69.

The diol (4R,6R)-1-(furan-3'-yl)-4,8-dimethylnonane-4,6-diol (5a) (120 mg, 7%) was also obtained. IR (film) 3400, 1500, 1020, 870, 770 cm^{-1}. ^1H NMR δ (CCl_4) 0.93 (6H, d, J=7 Hz), 1.16 (3H, s), 2.44 (2H, m), 4.0 (1H, m), 4.4 (2H, br s, D_2O exch.), 6.28 (1H, m), 7.30 (1H, m), 7.37 (1H, m). m/z 254 (M), 236, 221, 219, 218, 179, 153, 152, 145, 137, 136, 135, 134, 127, 109, 95, 94 (100), 82, 81, 71, 69. It was further characterized as the acetonide (2,2-dimethoxypropane, acetone and TsOH), b.p. 100°/0.05 (block). (Found: C, 73.3; H, 10.0. $C_{18}H_{30}O_3$ requires: C, 73.4; H, 10.3%). IR (film) 1500, 1020, 960, 875, 780 cm^{-1}.

Reduction of Dihydroeremoacetal (2b) in the Presence of t-Butyl Alcohol. A soln of (2b) (500 mg, 2 mmol) and t-butyl alcohol (148 mg, 2 mmol) in THF (3.9 ml) was reduced with Li (85 mg, 12.25 mmol) in NH_3 (30 ml) for 3 h. Preparative TLC (ether/light petroleum, 1:2) gave starting material (330 mg, 66%) and a fraction containing oxepanes (3) and (4) and diol (5a) (121 mg, 24%; oxepane to diol ratio 7:3 by ^1H-NMR).

Competitive Reduction of Oxepanes (3) and (4). A soln of (3) (49 mg, 0.19 mmol) and (4) (50 mg, 0.20 mmol) in THF (1 ml) was reduced with Li (40 mg, 5.76 mmol) in NH_3 (10 ml) for 3 h. Preparative TLC (ether/light petroleum, 1:1) gave recovered oxepanes (3) (43 mg, 88%), (4) (40 mg, 80%) and diol (5a) (9.5 mg, 9%).

Reduction of Primary Alcohol (2d).[13] A soln of (2d) (200 mg, 0.89 mmol) in THF (2 ml) was reduced with Li (70 mg, 10.09 mmol) in NH_3 (20 ml) for 5.5 h. Preparative TLC (ether/methanol, 99:1) gave starting material (83 mg, 42%) and a fraction (3%) tentatively assigned as an oxepanol. ^1H NMR δ ($CDCl_3$) 1.16 (3H, s), 3.50 (2H, m), 4.00 (1H, m), 4.80 (1H, m), 6.30 (1H, m), 7.25 (2H, m). The lowest R_f fraction was (2S,4R)-7-(furan-3'-yl)-4-methylheptane-1,2,4-triol (5b) (83 mg, 41%). ^1H NMR δ ($CDCl_3$) 1.16 (3H, s), 1.62 (6H, m), 2.43 (2H, m), 3.50-4.00 (6H, m), 6.22 (1H, m), 7.16 (1H, m), 7.25 (1H, m). ^{13}C NMR δ ($CDCl_3$) 25.0 (t), 25.3 (t), 28.1 (q), 40.7 (t), 42.4 (t), 67.2 (t), 69.7 (d), 73.2 (s), 111.1 (d), 125.1 (s), 139.1 (d), 143.0 (d). The triol (5b) was further characterized as its diacetate, (2S,4R)-2-acetoxy-7-(furan-3'-yl)-4-hydroxy-4-methylheptyl acetate (5c). (HRMS Found: 312.1582. $C_{16}H_{24}O_6$ requires: 312.1572). IR (film) 3400, 2950, 1740, 1370, 1230, 875 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.20 (3H, s), 1.30-1.85 (6H, m), 2.03 (6H, s), 2.40 (2H, m), 4.10 (2H, m), 5.25 (1H, m), 6.20 (1H, m), 7.15 (1H, m), 7.25 (1H, m). ^{13}C-NMR δ ($CDCl_3$) 10.9 (q), 21.3 (q), 24.2 (t), 25.1 (t), 26.7 (q), 42.0 (t), 42.8 (t), 66.2 (t), 69.2 (d), 71.5 (s), 111.1 (d), 125.0 (s), 138.1 (d), 143.1 (d), 171.1 (s). m/z 312 (M), 294, 143, 135, 100, 95, 94 (100), 83, 43.

Preparation and Reduction of the Methoxymethyl Ether (2e). (i) To a stirred soln of the alcohol (2d) (520 mg, 2.36 mmol) in dry CH_2Cl_2 (5 ml) under N_2 at 0° were added ethyldiisopropylamine (3.1 g, 23.9 mmol) and chloromethyl methyl ether (4.4 g, 54.7 mmol). The soln was stirred at 10-15° for 24 h. CH_2Cl_2 (20 ml) was added and the soln was washed with water (4 x 15 ml), dried and evaporated under reduced pressure to yield (1R,3S,5R)-1-(furan-3'-yl)-3-(methoxymethyloxymethyl)-5-methyl-2,8-dioxabicyclo[3.2.1]octane (2e) (520 mg, 84%). (HRMS Found: 268.1308. $C_{14}H_{20}O_5$ requires: 268.1311). IR (film) 3125, 2910, 2860, 1600, 1500, 1370, 1340, 1145, 1030, 930, 870, 790 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.42 (3H, s), 1.50-2.40 (6H, m), 3.20 (3H, s), 3.54 (2H, m), 4.15 (1H, m), 4.58 (2H, s), 6.35 (1H, m), 7.20 (1H, m), 7.40 (1H, m). m/z 269, 268 (M), 193, 165, 147, 113, 95 (100), 45, 43, 41, 39.

(ii) The ether (2e) (400 mg, 1.49 mmol) in THF (3.5 ml) was reduced with Li (120 mg, 17.29 mmol) in NH_3 (35 ml) for 5.5 h. Preparative TLC (ether/light petroleum, 9:1) gave starting material (36 mg, 9%) and (2S,4R)-7-(furan-3'-yl)-1-(methoxymethyloxy)-4-methylheptane-2,4-diol (5d) (272 mg, 68%), b.p. 115°/0.001 mm (block). (Found: C, 62.0; H, 8.9. $C_{14}H_{24}O_5$ requires: C, 61.7; H, 8.9%). IR (film) 3400, 2960, 1500, 1460, 1440, 1370, 1140, 1100, 1030, 915, 870, 770 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.16 (3H, s), 1.65 (6H, m), 2.40 (2H, m), 3.30 (3H, s), 3.40 (2H, d), 3.95 (1H, m), 4.56 (2H, s), 6.20 (1H, m), 7.13 (1H, m), 7.23 (1H, m). ^{13}C NMR δ ($CDCl_3$) 24.9 (t), 25.1 (t), 28.0 (q), 40.3 (t), 42.5 (t), 111.0 (d), 124.9 (s), 138.9 (d), 142.8 (d). m/z 272 (M), 270, 254, 193, 179, 135, 95, 94, 83, 81, 45 (100), 42. A minor (1%) low R_f fraction, possibly an oxepanol, was present with δ ($CDCl_3$) 6.28 (1H, m), 7.28 (2H, m) for the furan protons.

Reduction of the Secondary Alcohol (7a). The alcohol (7a) (150 mg, 0.56 mmol) in THF (1 ml) was reduced with Li (40 mg, 5.76 mmol) in NH_3 (15 ml) for 3 h. Preparative TLC (ether) gave starting material (60 mg, 40%) and (3S,4S,6R)-9-(furan-3'-yl)-2,6-dimethylnonane-3,4,6-triol (8) (55 mg, 37%), b.p. 85°/0.001 mm (block). (Found: C, 67.0; H, 9.7. $C_{15}H_{26}O_4$ requires: C, 66.7; H, 9.7%). IR (film) 3400, 2980, 2940, 1510, 1475, 1030, 880 cm^{-1}. ^1H NMR δ ($CDCl_3$) 0.93, 0.96 (each 3H, d), 1.16 (3H, s), 1.56 (6H, m), 2.45 (2H, m), 2.65, 3.00, 3.50 (each 1H, br s, D_2O exch), 3.82 (2H, m), 6.15 (1H, m), 7.10 (1H, m), 7.20 (1H, m). ^{13}C NMR δ ($CDCl_3$) 17.0 (q), 19.6 (q), 25.0 (t), 28.3 (q), 29.8 (d), 39.9 (t), 42.7 (t), 69.3 (d), 73.2 (s), 79.5 (d), 110.9 (d), 124.8 (s), 138.8 (d), 142.8 (d). m/z 270 (M), 252, 197, 135, 95, 94 (100), 43. No furan proton resonances were present in a small low R_f fraction isolated.

Reduction of the Alcohol (9a). The inseparable mixture of the two alcohols (7c) and (9a) was made, the product acetylated and the acetates separated as described.[13] Acetate (7d), on reduction with $LiAlH_4$ in ether, gave (1R,1'R,3'S,5'R)-1-{1'-(furan-3"-yl)-5'-methyl-2',8'-dioxabicyclo[3.2.1]oct-3'-yl}ethan-1-ol (7c). ^1H NMR δ ($CDCl_3$) 1.16 (3H, d, J=6 Hz), 1.30 (3H, s), 1.50-2.30 (7H, m), 3.74 (2H, m), 6.32 (1H, m), 7.20 (1H, m), 7.32 (1H, m). Similarly, the acetate (9b) gave the epimer (9a). ^1H NMR δ ($CDCl_3$) 1.14 (3H, d, J=6 Hz), 1.30 (3H, s), 1.60-2.56 (7H, m), 3.68 (2H, m), 6.40 (1H, m), 7.25 (1H, m), 7.40 (1H, m).

The alcohol (9a) (50 mg, 0.21 mmol) in THF (1 ml) was reduced with Li (30 mg, 4.32 mmol) in NH_3 (10 ml) for 3 h. ^1H NMR of the crude product showed starting material and triol (10) in ratio of approx. 1:49. Preparative TLC (ether) gave (2R,3S,5R)-8-(furan-3'-yl)-5-methyloctane-2,3,5-triol (10a) (40 mg, 79%). IR (film) 3400, 2990, 2960, 1500, 1370, 1160, 1120, 870 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.14 (3H, d), 1.20 (3H, s), 1.60 (6H, br s), 2.40 (2H, m), 3.50-4.00 (5H, m, 3 x OH D_2O exch), 6.17 (1H, m), 7.15 (1H, m), 7.23 (1H, m). It was further characterized as the diacetate (10b), prepared with acetic anhydride and pyridine. (HRMS Found: 308.1620. $C_{17}H_{26}O_6$-H_2O requires 308.1623). IR (CCl_4) 3600, 3700, 2950, 2930, 2850, 1735, 1365, 1255, 1215, 1010, 905, 870 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.08 (3H, s), 1.11 (3H, d), 1.98 (6H, s), 2.32 (2H, m), 4.60-4.95 (2H, m), 6.12 (1H, m), 7.10 (2H, m).

Reduction of the Tertiary Alcohol (2f). The alcohol (**2f**) (100 mg, 0.38 mmol) in THF (1 ml) was reduced with Li (40 mg, 5.76 mmol) in NH_3 (10 ml) for 3 h. Preparative TLC (ether/light petroleum, 4:1) gave starting material (19 mg, 19%) and (4R,6R)-9-(furan-3'-yl)-2,6-dimethylnonane-2,4,6-triol (**5e**) (61 mg, 60%) as a viscous oil. (Found: C, 66.4; H, 9.6. $C_{15}H_{26}O_4$ requires: C, 66.6; H, 9.7%). IR (film) 3400, 1510, 1160, 1025, 875, 865, 785 cm^{-1}. ^1H NMR δ (CCl_4) 1.1, 1.2, 1.3 (each 3H, s), 2.4 (2H, m), 4.3-4.7 (4H, m, 3 x OH D_2O exch), 6.2 (1H, m), 7.2 (1H, m), 7.3 (1H, m). m/z 270 (M), 268, 252, 237, 234, 219, 216, 179, 178, 161, 153, 135, 134, 125, 95, 94 (100), 87, 85, 83, 82, 81, 79, 59.

Reduction of the Tertiary Alcohol (2g). A soln of the alcohol (**2g**) (100 mg, 0.40 mmol) in THF (1 ml) was reduced with Li (35 mg, 5.04 mmol) in NH_3 (10 ml) for 3 h. Preparative TLC (ether) gave starting material (18 mg, 18%) and (3S,5R)-8-(furan-3'-yl)-2,5-dimethyloctane-2,3,5-triol (**5f**) (63 mg, 62%), m.p. 79-82°, sublimed 75°/0.001 mm. (Found: C, 65.7; H, 9.7. $C_{14}H_{24}O_4$ requires: C, 65.6; H, 9.5%). IR ($CHCl_3$) 3650, 3400, 2925, 1600, 1495, 1455, 1370, 1150, 1100, 1015, 945, 895, 870 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.10, 1.13, 1.16 (each 3H, s), 1.35-1.60 (6H, m), 2.40 (2H, m), 3.60 (1H, t, J=6 Hz), 6.15 (1H, m), 7.10 (1H, m), 7.22 (1H, m). ^{13}C NMR δ ($CDCl_3$) 23.6 (q), 25.3 (t), 26.5 (q), 29.1 (q), 40.0 (t), 40.5 (t), 72.9 (d), 73.6 (s), 111.1 (d), 125.0 (s), 139.2 (s), 143.1 (s). m/z 256 (M), 238, 153, 152, 135, 129, 95, 94, 91, 82, 81, 71, 43 (100). A fraction (5%) with no furan proton resonances was also isolated.

Preparation of the Tetrahydrofuran Derivative (6a). The alcohol (**6b**)[11] (90 mg) was reduced with P_2-Ni[19] [prepared from nickel acetate (1 mmol)] in ethanol for 3 days. Isolation and preparative TLC (ether/hexane, 1:3) gave starting material (15 mg, 17%) and (2R,2'R,5'S)-1-[5'-(furan-3"-yl)-2'-methyltetrahydrofuran-2'-yl]-4-methylpentan-2-ol (**6a**) (70 mg, 77%), as a colourless oil, b.p. 110°/0.05 mm (block). (Found: C, 72.1; H, 9.1; HRMS 252.1729. $C_{15}H_{24}O_3$ requires: C, 71.4; H, 9.6%; 252.1725). IR (film) 3500, 3150, 1600, 1505, 1160, 1025, 920, 880, 785. ^1H NMR δ (CCl_4) 0.88 (6H, d, J=6 Hz), 1.23 (3H, s), 3.3 (1H, br s), 3.84 (1H, m), 4.80 (1H, t, J=6.8 Hz), 6.25 (1H, m), 7.22 (2H, m). m/z 252 (M), 234, 219, 177, 152, 151 (100), 135, 134, 133, 110, 107, 97, 95, 81, 79, 77, 69.

Competitive Reduction of the Tetrahydrofuran (6a) and the Oxepane (3). A mixture of (**6a**) (52 mg) and (**3**) (52 mg) in THF (12 ml) was reduced with Li (20 mg) in NH_3 (70 ml) for 1 h. Preparative TLC (ether/hexane, 4:1) gave the tetrahydrofuran (**6a**) (3 mg, 6%), the oxepane (**3**) (45 mg, 90% recovery) and the diol (**5a**) (50 mg).

Reduction of the Tetrahydrofuran (11). A soln of (**11**) (105 mg, 0.76 mmol) and butyl nonyl ether (60 mg) in THF (3 ml) was analysed by GLC (Column A, 120-200° at 5°/min). The soln was added over 1 min to Li (90 mg, 12.97 mmol) in NH_3 (40 ml) and the reduction was terminated after a further 14 min. GLC on the crude ether extract showed starting material (< 1%) and alcohol (**14a**) (93%). Preparative TLC (ether/light petroleum, 1:1) gave 4-(furan-3'-yl)butan-1-ol (**14a**) (94 mg, 90%), b.p. 35°/0.002 mm (block). (Found: C, 68.6; H, 8.6. $C_8H_{12}O_2$ requires C, 68.6; H, 8.6%). IR (film) 3400, 2970, 2890, 1505, 1160, 1065, 1030, 880 cm^{-1}. ^1H NMR δ (CCl_4) 1.30-1.80 (4H, m), 2.37 (2H, m), 3.64 (1H, D_2O exch), 3.8 (2H, m), 6.10 (1H, m), 7.03 (1H, m), 7.16 (1H, m). m/z 140 (M), 95 (100), 94, 82, 81, 69, 53, 41.

Reduction of Tetrahydropyran (12). A soln of the tetrahydropyran (**12**) (150 mg, 0.99 mmol) and butyl nonyl ether (71 mg) in THF (3.9 ml) was submitted to GLC analysis (Column B, 75° (isothermal 5 min) - 150° at 6°/min). The above soln was added over 1 min to a stirred soln of Li (120 mg, 17.3 mmol) in NH_3 (50 ml). The reduction was terminated after a further 14 min and the crude ether extract was submitted to GLC analysis (Column B, 75° (isothermal 5 min) - 150° at 6°/min). The GLC data revealed starting material (76%) and alcohol (**14b**) (18%). Preparative TLC (ether/light petroleum, 1:3) gave starting material (97 mg, 65%) and 5-(furan-3'-yl)pentan-1-ol (**14b**) (26 mg, 17%), b.p. 45°/0.002 mm (block). (Found: C, 70.5; H, 8.8; HRMS 154.0933. $C_9H_{14}O_2$ requires: C, 70.1; H, 9.2%; 154.0994). IR (film) 3350, 2925, 2850, 1505, 1460, 1380, 1160, 1065, 1025, 870, 780 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.20-1.90 (7H, m), 2.36 (2H, m), 3.51 (2H, t J=6 Hz), 6.11 (1H, m), 7.05 (1H, m), 7.17 (1H, m). m/z 154 (M), 95, 94, 82, 81 (100), 69, 67, 53, 40, 38, 31.

Reduction of Oxepane (13). A soln of the oxepane (**13**) (125 mg, 0.75 mmol) and butyl nonyl ether (62 mg) in THF (3 ml) was submitted to GLC analysis (Column B, 75° (isothermal 4 min) - 150° at 6°/min). The above soln was added over 1 min to a stirred soln of Li (92 mg, 13.3 mmol) in NH_3 (40 ml). The reduction was terminated after a further 14 min and the crude ether extract was submitted to GLC analysis (Column B, 75° (isothermal 4 min) - 150° at 6°/min). The GLC revealed starting material (85%) and alcohol (**14C**) (13%). Preparative TLC (ether/light petroleum, 1:3) gave starting material (93 mg, 74%) and 6-(furan-3'-yl)-hexan-1-ol (**14C**) (17 mg, 13%), b.p. 45°/0.008 mm (block). (Found: C, 71.7; H, 9.4. $C_{10}H_{16}O_2$ requires: C, 71.4; H, 9.6%). IR (film) 3350, 2925, 2820, 1500, 1460, 1380, 1160, 1020, 870, 775 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.15-1.65 (8H, m), 1.85 (1H, br s, OH), 2.32 (2H, m), 3.50 (2H, t, J=6 Hz), 6.12 (1H, m), 7.05 (1H, m), 7.20 (1H, m). m/z 168 (M), 95, 94, 82 (100), 81, 67, 53, 41, 39, 31.

Competitive Reduction of Compounds (11) - (13). A soln of (11), (12) and (13) (170 mg) and butyl nonyl ether in THF (4 ml) was analysed by GLC (Column A, 100-200° at 6°/min). The four components were observed in a ratio of 1.02:1.3:1.3:1, respectively. The soln was added over 1 min to a stirred soln of Li (105 mg, 15.1 mmol) in NH_3 (50 ml). The reduction was terminated after a further 11 min and the crude ether extract was submitted to GLC analysis (Column B, 75° (isothermal 4 min) - 150° at 6°/min and Column A for the detection of (11) only, 100-200° at 6°/min). GLC revealed (11) (< 1%), (12) (88%), (13) (87%) and the corresponding cleavage products (14a) (98%), (14b) (10%) and (14c) (8%), respectively.

Competitive Reduction of Tetrahydropyran (12) and Methyl Ether (14d). A soln of the tetrahydropyran (12) (13.5 mg, 0.10 mmol), methyl ether (14d) (18 mg, 0.08 mmol) and butyl nonyl ether (8.8 mg) in THF (0.5 ml) was submitted to GLC analysis (Column B, 75° (isothermal 5 min) - 200° at 6°/min). The soln was added over 0.5 min to a stirred soln of Li (20 mg, 2.88 mmol) in NH_3 (10 ml). The reduction was terminated after a further 16.5 min and the crude ether extract was analysed by GLC (Column B, 75° (isothermal 5 min) - 200° at 6°/min). GLC revealed (12) (68%), (14d) (78%) and the corresponding cleavage products (14b) (30%) and (14n) (15%), respectively.

Reduction of Acetal Alcohol (1b). (i) A soln of the alcohol (1b) (58.5 mg, 0.32 mmol) and butyl nonyl ether (16.5 mg) in THF (0.75 ml) was submitted to GLC analysis (Column B, 75° (isothermal 3 min) - 190° at 6°/min). The above soln was added over 1 min to a stirred soln of Li (22 mg, 3.17 mmol) in NH_3 (10 ml). The reduction was terminated after a further 14 min and the crude ether extract was analysed by GLC (Column B, 75° (isothermal 3 min) - 190° at 6°/min). The GLC data revealed alcohol (14e) (55%), 2,5-dihydrofuran (15a) (10%), starting material (1b) (3%) and diol (14f) (13%). GLC-MS data (Column C, 160° (isothermal 5 min) - 230° at 5°/min) on component (15a) showed m/z 128 (M).

Preparative TLC (ether/light petroleum, 4:1) gave 2,5-dihydrofuran (15a) (5 mg, 8%). (HRMS Found: 128.0838. $C_7H_{12}O_2$ requires: 128.0837). ^1H NMR δ ($CDCl_3$) 1.10 (1H, s, D_2O exch), 1.50 (2H, m), 2.15 (2H, m), 3.60 (2H, t, J=5 Hz), 4.50 (4H, br s), 5.50 (1H, br s). ^{13}C NMR δ ($CDCl_3$) 23.7 (t), 30.9 (t), 62.7 (t), 76.3 (t), 119.6 (d). (15a) was not further investigated.

(ii) In a larger scale reaction a soln of the alcohol (1b) (300 mg, 1.63 mmol) in THF (4.8 ml) was added dropwise over 5 min to a stirred soln of Li (115 mg, 16.57 mmol) in NH_3 (50 ml). The reduction was terminated after a further 13 min. Preparative TLC (ether/light petroleum, 4:1) of the crude material (210 mg) gave starting material (7 mg, 2%) and 3-(furan-3'-yl)-propan-1-ol (14e) (113 mg, 55%), b.p. 45°/0.5 mm (block). (Found: C, 66.1; H, 8.0; HRMS: 126.0632. $C_7H_{10}O_2$ requires: C, 66.6; H, 8.0%; 126.0681). IR (film) 3360, 2960, 2890, 1500, 1150, 1050, 1020, 870 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.80 (2H, m), 2.45 (2H, t, J=7 Hz), 3.06 (1H, s, D_2O exch), 3.52 (2H, t, J=6Hz), 6.10 (1H, m), 7.05 (1H, m), 7.16 (1H, m). m/z 126 (M), 82, 81, 44 (100), 40, 34, 32.

The low R_f fraction was 3-(furan-3'-yl)-3-(2"-hydroxyethoxy)propan-1-ol (14f) (59 mg, 19%), b.p. 80°/0.002 mm (block). (Found: C, 57.7; H, 7.2; HRMS: 186.0893. $C_9H_{14}O_4$ requires: C, 58.0; H, 7.6%; 186.0892). IR (film) 3400, 2960, 2880, 1500, 1150, 1100, 1050, 1020, 870 cm^{-1}. ^1H NMR δ ($CDCl_3$) 2.02 (2H, m), 3.40-3.90 (8H, m, 2 x OH, D_2O exch), 4.50 (1H, dd, J=5, 7 Hz), 6.30 (1H, m), 7.26 (2H, m). m/z 186 (M), 141, 122, 97, 95 (100), 94, 66, 65, 43, 41.

Reduction of Acetal Alcohol (1d). (i) A soln of the alcohol (1d) (56.5 mg, 0.29 mmol) and butyl nonyl ether (11.2 mg) in THF (0.75 ml) was analysed by GLC (Column B, 75° (isothermal 3 min) - 190° at 6°/min). The above soln was added over 1 min to a stirred soln of Li (24 mg, 3.46 mmol) in NH_3 (10 ml). The reduction was terminated after a further 14 min and the crude ether extract was submitted to GLC analysis (Column B, 75° (isothermal 3 min) - 190° at 6°/min). The GLC data revealed alcohol (14g) (48%), 2,5-dihydrofuran (15b) (5%), starting material (28%) and diol (14h) (10%). GLC-MS data (Column C, 160° (isothermal 5 min) - 230° at 5°/min) on component (15b) showed m/z 142 (M).

(ii) (14g) and (14h) were isolated from a larger scale reaction. The alcohol (1d) (200 mg, 1.01 mmol) in THF (3 ml) was added dropwise over 5 min to a stirred soln of Li (70 mg, 10.09 mmol) in NH_3 (30 ml). The reduction was terminated after a further 13 min. Preparative TLC (ether/light petroleum, 4:1) gave starting material (68 mg, 34%) and 4-(furan-3'-yl)butan-1-ol (14g) (59 mg, 42%), identical with the sample obtained from the Li in NH_3 reduction of tetrahydrofuran (11).

The low R_f fraction was 4-(furan-3'-yl)-4-(2"-hydroxyethoxy)butan-1-ol (14h) (30 mg, 15%), b.p. 85°/0.002 mm (block). (Found: C, 58.7; H, 8.2. $C_{10}H_{16}O_4 \frac{1}{4}H_2O$ requires: C, 58.7; H, 8.1%; HRMS: 200.1060. $C_{10}H_{16}O_4$ requires: 200.1049). IR (film) 3400, 2960, 2890, 1500, 1150, 1100, 1055, 1020, 870 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.40-1.90 (4H, m), 2.76 (2H, br s, D_2O exch), 3.30-3.77 (6H, m), 4.30 (1H, t, J=7 Hz), 6.29 (1H, m), 7.30 (2H, m). m/z 200 (M), 155, 141, 97 (100), 95, 79, 77, 45, 44, 39, 32.

Competitive Reduction of Acetal Alcohols (1b) and (1d). A soln of (1b) (53.7 mg, 0.29 mmol), (1d) (52 mg, 0.26 mmol) and butyl nonyl ether (13.9 mg) in THF (1.5 ml) was analysed by GLC (Column B, 75° (isothermal 3 min) -190° at 6°/min). The above soln was added over 1 min to a stirred soln of Li (40 mg, 5.76 mmol) in NH_3 (20 ml). The reduction was terminated after a further 14 min and the crude ether extract was submitted to GLC analysis (Column B, 75° (isothermal 3 min) -190° at 6°/min). The GLC data showed alcohol (14e) (52%), 2,5-dihydrofuran (15a) (18%), starting material (1b) (3%) and diol (14f) (12%) for (1b) and alcohol (14g) (50%), 2,5-dihydrofuran (15b) (2%), starting material (1d) (33%) and diol (14h) (12%) for (1d).

Competitive Reduction of (1b) and (1f). A mixture of (1b) and (1f) (160 mg) and butyl nonyl ether in THF (2.2 ml) was submitted to GLC analysis (Column B, 75° (isothermal 4 min) -200° at 6°/min). The three components were observed in a ratio of 5.34:5.89:1, respectively. The soln was added over 1 min to a stirred soln of Li (80 mg, 11.53 mmol) in NH_3 (30 ml). The reduction was terminated after a further 14 min and the crude ether extract was analysed by GLC (Column B, 75° (isothermal 4 min) -200° at 6°/min). The GLC data showed alcohol (14e) (38%), 2,5-dihydrofuran (15a) (18%), starting material (1b) (2%) and diol (14f) (16%) for (1b) and alcohol (14i) (41%), starting material (1f) (43%), diol (14j) (13%) for (1f). Alcohol (14i) and diol (14j) are characterized below.

Reduction of Benzyloxy Acetal (1e). A soln of benzyloxy acetal (1e) (84 mg, 0.30 mmol) and butyl nonyl ether (22 mg) in THF (0.75 ml) was submitted to GLC analysis (Column B, 75° (isothermal 3 min) -190° at 6°/min). The above soln was added over 1 min to a stirred soln of Li (20 mg, 2.88 mmol) in NH_3 (10 ml). The reduction was terminated after a further 14 min and the crude ether extract was submitted to GLC analysis (Column B, 75° (isothermal 3 min) -190° at 6°/min). The GLC data revealed alcohol (14g) (41%), bibenzyl, parent alcohol (1d) (43%) and diol (14h) (1%).

Reduction of Benzyloxy Acetal (1g). A soln of benzyloxy acetal (1g) (220 mg, 0.70 mmol) and butyl nonyl ether (55 mg) in THF (1.75 ml) was submitted to GLC analysis (Column B, 75° (isothermal 3 min) -220° at 6°/min). The above soln was added over 1 min to a stirred soln of Li (55 mg, 7.93 mmol) in NH_3 (20 ml). The reduction was terminated after a further 14 min and the crude ether extract was submitted to GLC analysis (Column B, 75° (isothermal 3 min) -220° at 6°/min). The GLC data revealed alcohol (14i) (29%), bibenzyl, parent alcohol (1f) (54%) and diol (14j) (16%). Preparative TLC (ether/light petroleum, 4:1) gave alcohols (14i) (37 mg, 31%) and (1f) (79 mg, 50%) (identical with authentic samples above) and a low R_f fraction, 6-(furan-3'-yl)-6-(2"-hydroxyethoxy)hexan-1-ol (14j) (26 mg, 16%). (HRMS Found: 228.1357. $C_{12}H_{20}O_4$ requires: 228.1362). IR (film) 3400, 2940, 2860, 1505, 1460, 1160, 1110, 1060, 1020, 910, 870 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.25-1.85 (8H, m), 2.00 (2H, br s, D_2O exch), 3.30-3.70 (6H, m), 4.25 (1H, t, J=6 Hz), 6.30 (1H, m), 7.31 (2H, m).

Competitive Reduction of Benzyloxy Acetals (1b) and (1g). A soln of (1b) (40.5 mg, 0.15 mmol), (1g) (37 mg, 0.12 mmol) and butyl nonyl ether (15 mg) in THF (0.75 ml) was submitted to GLC analysis (Column B, 75° (isothermal 4 min) -220° at 6°/min). The soln was added over 1 min to a stirred soln of Li (23 mg, 3.31 mmol) in NH_3 (10 ml). The reduction was terminated after a further 14 min and the crude ether extract was submitted to GLC analysis (Column B, 75° (isothermal 4 min) -220° at 6°/min). The GLC showed alcohol (14e) (70%), parent alcohol (1b) (4%) and diol (14f) (12%) for (1b) and alcohol (14i) (29%), parent alcohol (1f) (49%) and diol (14j) (17%) for (1g). Bibenzyl was also evident by GLC.

Reduction of Alcohol (14o) to 1-(Furan-3'-yl)-butane-1,4-diol (14k). Alcohol (14o) (2.13 g, 8.66 mmol) in dry THF (25 ml) was added to a stirred soln of liquid NH_3 (300 ml, distilled) and Li (1 g) at -78°. The blue soln was stirred at -78° for 30 min, isoprene was then added to discharge the blue colour and the NH_3 was allowed to evaporate. H_2O (20 ml) was added and the mixture was extracted with CH_2Cl_2 (5 times), dried and evaporated under reduced pressure to yield a pale yellow oil. Flash chromatography (ether/light petroleum, 1:1 to 1:0) gave 1-(furan-3'-yl)-butane-1,4-diol (14k) (1.15 g, 85%). (HRMS Found: 156.0784. $C_8H_{12}O_3$ requires: 156.0786). IR (film) 2350, 2925, 2850, 1500, 1155, 1040, 1020, 870 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.75 (4H, m), 3.30 (2H, br, D_2O exch), 3.58 (2H, m), 4.60 (1H, m), 6.30 (1H, m), 7.26 (2H, m). m/z 156 (M), 138, 110, 97 (100), 69, 41, 39. This sample was used without further purification.

Cyclization of Diol (14k) to Tetrahydrofuran (11). Diol (14k) (1.12 g, 7.18 mmol), p-toluene sulfonic acid (80 mg) in CH_2Cl_2 (250 ml) containing 4Å sieves, was stirred at 0° under N_2 for 2 h. The soln was stirred at 25° for a further 24 h, washed with $NaHCO_3$ (10% aqueous, 50 ml), dried and evaporated under reduced pressure to yield 3-(tetrahydrofuran-2'-yl)furan (11) (975 mg, 98%), b.p. 92-96°/22 mm (block). (Found: C, 69.8; H, 7.5. $C_8H_{10}O_2$ requires C, 69.6; H, 7.3%). IR (film) 2975, 2860, 1600, 1500, 1155, 1050, 1020, 875 cm^{-1}. ^1H NMR δ ($CDCl_3$) 2.00 (4H, m), 3.95 (2H, m), 4.85 (1H, m), 6.40 (1H, m), 7.38 (2H, m). ^{13}C NMR δ ($CDCl_3$) 26.0 (t), 32.8 (t), 68.1 (t), 73.7 (d), 109.1 (d), 127.5 (s), 139.4 (d), 143.5 (d).

Preparation of 5-Benzyloxy-1-(furan-3'-yl)pentan-1-one (16b). The reaction was done using furan-3-carboxylic acid (4.48 g, 40 mmol), MeLi (40 mmol), 1-benzyloxy-4-chlorobutane [prepared from 4-benzyloxybutanol[20] with Ph_3P and CCl_4[21] in 86% yield, b.p. 78-80°/0.5 mm (lit.[22] 75°/0.7mm)] (9.9 g, 50 mmol) and Li alloy (2% Na, 750 mg) by the literature method.[8] After 1 h at -45° and 8 h at -30° to -20°, isolation gave a yellow oil. Chromatography on alumina (ether/light petroleum, 1:1 to 1:0) gave 5-benzyloxy-1-(furan-3'-yl)pentan-1-one (16b) (2.85g, 27.6%), b.p. 88-90°/0.005 mm (block). (Found: C, 74.5; H, 7.2. $C_{16}H_{18}O_3$ requires: C, 74.4: H, 7.0%). IR (film) 3120, 3050, 3020, 2925, 2850, 2750, 1675, 1600, 1560, 1505, 1450, 1150, 1100, 870, 735, 700 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.72 (4H, m), 2.75 (2H, m), 3.48 (2H, m), 4.48 (2H, s), 6.75 (1H, m), 7.35 (5H, s), 7.39 (1H, m), 8.00 (1H, m). m/z 258 (M), 215, 167, 152, 123, 95 (100), 91.

Reduction of Ketone (16b) to Alcohol (14p). Ketone (16b) (2.5 g, 9.69 mmol) was reduced with $NaBH_4$ (200 mg) in CH_3OH (50 ml). Workup as before gave 5-benzyloxy-1-(furan-3'-yl)pentan-1-ol (14p) (2.5 g, 99%). (HRMS Found: 260.1414. $C_{16}H_{20}O_3$ requires: 260.1412). IR (film) 3400, 3075, 3050, 3025, 2925, 2850, 1600, 1500, 1450, 1360, 1155, 1100, 1020, 870, 730, 700 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.60-1.90, 7H, 1 x OH, D_2O exch), 3.45 (2H, m), 4.42 (2H, s), 4.60 (1H, m), 6.34 (1H, m), 7.25 (7H, s). m/z 260 (M), 188, 151, 97 (100), 92, 91. This product was used directly to prepare (141).

Reduction of Alcohol (14p) to give Diol (141). Alcohol (14p) (2.45 g, 9.42 mmol) was reduced with distilled liquid NH_3 (400 ml), Li (1 g) and dry THF (50 ml) at -78° for 1 h. Workup as above and flash chromatography (ether/light petroleum, 1:1 to 1:0) gave 1-(furan-3'-yl)pentane-1,5-diol (141) (1.12 g, 70%). IR (film) 3350, 2940, 2855, 1500, 1160, 1060, 1020, 875 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.38-1.88 (6H, m), 3.15 (2H, D_2O exch), 3.63 (2H, m), 4.60 (1H, t, J=5 Hz), 6.35 (1H, m), 7.35 (2H, m). m/z 170 (M), 151, 97 (100), 95. This diol (141) (1.10 g) was cyclized directly in CH_2Cl_2 (250 ml) containing TsOH (100 mg) and 4Å sieves with stirring under N_2 for 6 h at 0° and then 12 h and 20°. Isolation gave 2-(furan-3'-yl)tetrahydropyran (12) (895 mg, 91%), b.p. 130-133°/20 mm (block). (Found: C, 70.9; H, 8.1. $C_9H_{12}O_2$ requires: C, 71.0; H, 8.0%). IR (film) 3140, 2930, 2850, 1600, 1505, 1440, 1270, 1205, 1160, 1090, 905, 875, 790, 760 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.38-1.85 (6H, m), 3.55 (1H, m), 4.05 (1H, m), 4.25 (1H, m), 6.38 (1H, m), 7.36 (2H, m). m/z 152 (M), 151, 95 (100).

Preparation of 6-Benzyloxy-1-(furan-3'-yl)hexan-1-one (16c). The reaction was done using furan-3-carboxylic acid (4.48 g, 40 mmol), MeLi (40 mmol), 1-benzyloxy-5-chloropentane [prepared from 5-benzyloxypentanol[20] with Ph_3P and CCl_4[21] in 73% yield, b.p. 67-69°/0.005 mm (lit.[22] 86°/0.1 mm)] (10.5 g, 49.5 mmol) and Li alloy (2% Na, 750 mg) by literature method.[8] After 3.5 h at 30° to 40° and 12 h at 20°, workup gave a yellow oil. Chromatography on alumina (ether/light petroleum, 2:3 to 1:0) gave 1-benzyloxypentane (6 g) [^1H NMR δ ($CDCl_3$) 1.88 (3H, br t), 1.10-1.80 (6H, m), 3.40 (2H, br t), 4.30 (2H, s), 7.20 (5H, s)] and 6-benzyloxy-1-(furan-3'-yl)hexan-1-one (16c) (2.85 g, 26.2%), b.p. 130-133°/0.006 mm (block). (Found: C, 75.0; H, 7.3. $C_{17}H_{20}O_3$ requires: C, 75.0; H, 7.4%). IR (film) 3110, 3050, 3010, 2920, 2840, 1675, 1560, 1510, 1450, 1150, 1100, 870, 735, 695 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.50-1.85 (6H, m), 2.72 (2H, br t), 3.48 (2H, br t), 4.48 (2H, s), 6.70 (1H, m), 7.26 (5H, s), 7.36 (1H, m), 7.95 (1H, m). m/z 272 (M), 222, 186, 95 (100), 91, 65, 39.

Reduction of Ketone (16c) to Alcohol (14). Ketone (16c) (2.5 g, 9.19 mmol) was reduced with $NaBH_4$ (250 mg) in MeOH (50 ml). Workup gave 6-benzyloxy-1-(furan-3'-yl)hexan-1-ol (14) (2.5 g, 99%). HRMS Found: 274.1565. $C_{17}H_{22}O_3$ requires: 274.1569). IR (film) 3400, 3090, 3060, 3030, 2940, 2850, 1600, 1505, 1495, 1450, 1365, 1160, 1100, 1025, 875, 795, 740, 700 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.18-1.85 (9H, m, 1 x OH, D_2O exch), 3.40 (2H, br t), 4.42 (2H, s), 4.50 (1H, m), 6.26 (1H, m), 7.20 (7H, s). m/z 274 (M), 183, 165, 97 (100), 92, 91, 41.

Reduction of Alcohol (14q) to Diol (14m). Alcohol (14q) (2.48 g, 9.05 mmol) was reduced with distilled liquid NH_3 (400 ml) and Li (1.5 g) at -78° for 1 h. Isolation and preparative TLC (ether) gave 1-(furan-3'-yl)-hexane-1,6-diol (14m) (1.35 g, 81%). (HRMS Found: 184.1098. $C_{10}H_{16}O_3$ requires: 184.1099). IR (film) 3350, 2940, 2850, 1505, 1160, 1055, 1025, 910, 875 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.35-1.85 (8H, m), 2.65 (2H, D_2O exch), 3.59 (2H, br t), 4.62 (1H, t, J=6 Hz) H1; 6.37 (1H, m), 7.33 (2H, m). m/z 184 (M), 167, 97 (100), 95, 81, 41.

Cyclization of Diol (14m) to Oxepane (13). Diol (14m) (1.2 g, 6.52 mmol) in CH_2Cl_2 (250 ml) containing TsOH (100 mg) and 4Å sieves was stirred under N_2 for 5 h at 0° and then at 15° for 36 h. Isolation and preparative TLC (ether/light petroleum, 1:9) gave 2-(furan-3'-yl)oxepane (13) (685 mg, 63%), b.p. 135°/18 mm (block). (Found: C, 72.3; H, 8.5. $C_{10}H_{14}O_2$ requires: C, 72.3; H, 8.5%). IR (film) 3140, 2945, 2850, 1600, 1505, 1165, 1120, 1040, 1025, 880 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.40-1.85 (8H, m), 3.62 (2H, m), 4.50 (1H, m), 6.35 (1H, m), 7.34 (2H, m). m/z 166 (M), 97, 96, 95 (100).

Preparation of 3,3-Ethylenedioxy-3-(furan-3'-yl)propan-1-ol (1b). The β-keto ester (16d) was prepared[18] from monoethyl malonate and furan-3-carbonyl chloride. A mixture of β-keto ester (16d) (3 g), ethylene glycol (8.91 g) and TsOH (120 mg) in 1,2-dichloroethane (60 ml) was heated under reflux for 15 h under N_2 in a system equipped with a modified Dean and Stark apparatus in which the solvent passed through a short column of 4Å sieves before returning to the

reaction flask. After cooling to 20°, Et_3N (0.75 ml) was added, the mixture poured into NH_4OH (10% aqueous, 50 ml), the layers separated, and the aqueous phase extracted with CH_2Cl_2 (3 times). After drying and evaporation a mixture (3.38 g) (19:1, by ^1H NMR) of ethyl 3,3-ethylenedioxy-3-(furan-3'-yl)-propanoate (**1h**) and starting material was isolated. Because this mixture was difficult to purify it was reduced directly with $LiAlH_4$ (600 mg) at 25° for 2 h in ether. Workup gave a yellow oil which on flash chromatography (ether/light petroleum, 1:1) gave 3,3-ethylenedioxy-3-(furan-3'-yl)propan-1-ol (**1i**) (2.16 g, 71.2%), b.p. 50-52°/0.01 mm (block). (Found: C, 58.8; H, 6.7. $C_9H_{12}O_4$ requires C, 58.7; H, 6.6%). IR (film) 3440, 3160, 2980, 2920, 1590, 1500, 1050, 1030, 945, 870 cm^{-1}. ^1H NMR δ ($CDCl_3$) 2.10 (2H, t, J=5.5 Hz), 2.30 (1H, s, D_2O exch), 3.62 (2H, t, J=5.5 Hz), 3.95 (4H, m), 6.31 (1H, m), 7.36 (2H, m). m/z 184 (M), 166, 154, 139 (100), 95.

Preparation of 4,4-Ethylenedioxy-4-(furan-3'-yl)butan-1-ol (**1d**). (i) The acetal (**1e**) was prepared from ketone (**16a**) (3.5 g, 14.3 mmol), ethylene glycol (8.8 g) and TsOH (120 mg) in 1,2-dichloroethane (60 ml) by the method above. Workup after 15 h reflux gave a brown mobile oil. The residue was purified by flash chromatography (ether/light petroleum, 1:4) to afford 2-(3'-benzyloxypropyl)-2-(furan-3"-yl)-1,3-dioxolane (**1e**) (3.78 g, 92%), b.p. 77-80°/0.005 mm (block). (Found: C, 71.1; H, 7.2. $C_{17}H_{20}O_4$ requires: C, 70.8; H, 7.0%). IR (film) 3150, 3090, 3060, 3040, 2960, 2900, 1595, 1500, 1450, 1150, 1100, 1140, 1020, 870, 795, 725, 680 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.50-2.00 (4H, m), 3.40 (2H, t, J=6 Hz), 3.86 (4H, m), 4.47 (2H, s), 6.38 (1H, m), 7.35 (5H, s), 7.40 (2H, m). m/z 288 (M), 158, 139 (100), 95, 91.

(ii) Acetal (**1e**) (3.2 g, 11.1 mmol) in dry THF (40 ml) was added to a stirred solution of Li (850 mg) in distilled NH_3 (400 ml) at -78° for 30 min. Isolation and flash chromatography CH_2Cl_2/MeOH, 99:1) gave 4,4-ethylenedioxy-4-(furan-3'-yl)butan-1-ol (**1d**) (1.88 g, 85%), b.p. 60°/0.002 (block). (Found: C, 60.7; H, 7.1. $C_{10}H_{14}O_4$ requires: C, 60.6; H, 7.1%). IR (film) 3400, 2960, 2910, 1500, 1185, 1150, 1040, 875 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.37-2.01 (4H, m), 2.20 (1H, s, D_2O exch), 3.51 (2H, t, J=5.5 Hz), 3.84 (4H, m), 6.21 (1H, m), 7.22 (2H, m). m/z 198 (M), 181, 167, 154, 137, 95 (100).

Preparation of 6,6-Ethylenedioxy-6-(furan-3'-yl)hexan-1-ol (**1f**). (i) The acetal (**1g**) was prepared from ketone (**16c**) (1.0 g, 3.68 mmol), ethylene glycol (4 ml) and TsOH (100 mg) in 1,2-dichloroethane (50 ml) as described above. Flash chromatography (ether/light petroleum, 1:4) gave 2-(5'-benzyloxypentyl)-2-(furan-3"-yl)-1,3-dioxolane (**1g**) (1.03 g, 89%), b.p. 125°/0.005 mm (block). (Found: C, 72.5; H, 7.4. $C_{19}H_{24}O_4$ requires: C, 72.2; H, 7.7%). IR (film) 3150, 3075, 3050, 2960, 2875, 1595, 1510, 1455, 1370, 1190, 1160, 1100, 1050, 1030, 875, 800, 735, 700 cm^{-1}. ^1H NMR δ (CCl_4) 1.23-2.00 (8H, m), 3.30 (2H, t, J=5 Hz), 3.75 (4H, m), 4.35 (2H, s), 6.15 (1H, m), 7.15 (5H, s), 7.20 (2H, m). m/z 316 (M), 139 (100), 95, 91, 63, 38.

(ii) Acetal (**1g**) (200 mg, 0.64 mmol) in THF (3 ml) was reduced with Li (60 mg) in NH_3 (30 ml) at -78° for 30 min as previously described. Preparative TLC (ether/light petroleum, 8:1) gave 6,6-ethylenedioxy-6-(furan-3'-yl)hexan-1-ol (**1f**) (110 mg, 76%), b.p. 65-68°/0.001 mm (block). (Found: C, 63.7; H, 8.0. $C_{12}H_{18}O_4$ requires: C, 63.7; H, 7.7%). IR (film) 3400, 3150, 2950, 2900, 1595, 1505, 1190, 1160, 1070, 1050, 1020, 945, 870, 800, 730 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.20-2.00 (8H, m), 2.20 (1H, s, D_2O exch), 3.60 (2H, t, J=5 Hz), 3.85 (4H, m), 6.23 (1H, m), 7.28 (2H, m). m/z 226 (M), 139 (100), 110, 95.

Preparation of 2-(2'-Benzyloxyethyl)-2-(furan-3"-yl)-1,3-dioxolane (**1c**). The alcohol (**1b**) (200 mg) in DMF (0.5 ml) and THF (1 ml) was added to a suspension of NaH (50 mg, washed with light petroleum) over 45 min. Benzyl bromide (204 mg, 1.19 mmol) was added and the soln was stirred for 18 h at 15°. H_2O (5 ml) was added and the mixture was extracted with ether (4 x 10 ml). The organic phase was dried, evaporated under reduced pressure and chromatographed by preparative TLC to yield 2-(2'-benzyloxyethyl)-2-(furan-3"-yl)-1,3-dioxolane (**1c**). (209 mg, 64%), b.p. 65-70°/0.005 mm (block). (HRMS Found: 274.1211. $C_{16}H_{18}O_4$ requires: 274.1205). IR (film) 3130, 3050, 3025, 2950, 2875, 1590, 1500, 1450, 1365, 1180, 1155, 1100, 1045, 870, 800, 735, 695 cm^{-1}. ^1H NMR δ (CCl_4) 2.16 (2H, t, J=7 Hz), 3.45 (2H, t, J=7 Hz), 3.80 (4H, m), 4.32 (2H, s), 3.16 (1H, m), 7.10 (5H, s), 7.16 (2H, m). m/z 274 (M), 158, 139 (100), 95, 91.

Preparation of the Tertiary Alcohols (**2f**) and (**2g**). (i) Eremoacetal (**2a**) (0.25 g) was added to a yellow suspension prepared by addition of $Hg(OAc)_2$ (0.32 g) to H_2O (5 ml) and THF (5 ml). After stirring for 10 min, $NaBH_4$ (0.1 g) in NaOH solution (3M, 5 ml) was added and the mixture stirred for 2 h. After extraction with CH_2Cl_2 (4 x 10 ml) workup gave (1R,3'S,5'R)-1-{1'-(furan-3"-yl)-5'-methyl-2',8'-dioxabicyclo[3.2.1]oct-3'-yl}-2-methylpropan-2-ol (**2f**) (0.28 g, 99%), b.p. 135°/0.05 mm (block). (Found: C, 67.8; H, 8.3. $C_{15}H_{22}O_4$ requires: C, 67.6; H, 8.3%). IR (film) 3500, 1610, 1510, 1160, 935, 880, 795 cm^{-1}. ^1H NMR δ (CCl_4) 1.17, 1.22 (each 3H, s), 1.33 (3H, s), 2.8 (1H, br s, D_2O exch), 4.27 (1H, m), 6.43 (1H, m), 7.37 (1H, m), 7.46 (1H, m). m/z 266 (M), 207, 193, 95 (100), 70, 59.

(ii) The tertiary alcohol (**2g**) was prepared from eremoacetal as described.[23]

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