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A STUDY OF THE OXYANION EFFECT IN REACTIONS OF 2-METHYL-2-PROPEN-1-OL.

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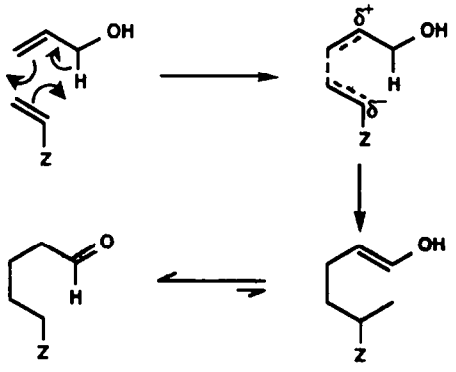
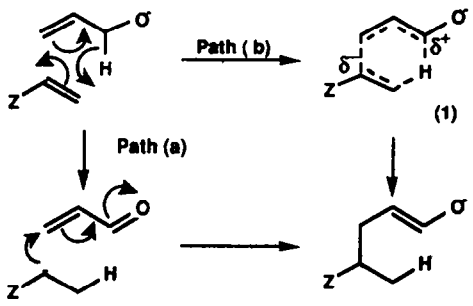
Abstract- Optimum conditions for the self reaction of the potassium alkoxide of 2-methyl-2-propen-1-ol to give 3,5,5,-trimethyltetrahydropyran-2-ol (7) have been developed. Evidence is presented to demonstrate that the key carbon carbon bond forming step in this reaction formally involves an unusual type of Ene reaction between 2-methylpropenal and the allylic alkoxide anion in which stepwise or highly asynchronous hydride transfer precedes carbon carbon bond formation. Under different reactions conditions the condensation of 2-methylpropenal with the potassium alkoxide of 2-methyl-2-propen-1-ol proceeds to give the bicyclic lactone, 6-*endo*-hydroxy-7-*exo*-(2-methyl allyloxymethyl)-3-oxa-1,5,7-trimethyl bicyclo[3,3,1]nonan-2-one (11) , the crystal structure of which is reported.

Considerable evidence is available[1] to demonstrate that the classical Alder Ene reaction, as illustrated for the known case of propenol with methyl acrylate,[2] (Scheme 1, Z= CO_2Me) involves a concerted but highly asynchronous transition state in which formation of the new carbon carbon bond by nucleophilic attack of the ene double bond on to the electron deficient enophile is well developed, prior to removal of an incipient "proton" from the ene component.



Scheme (1)

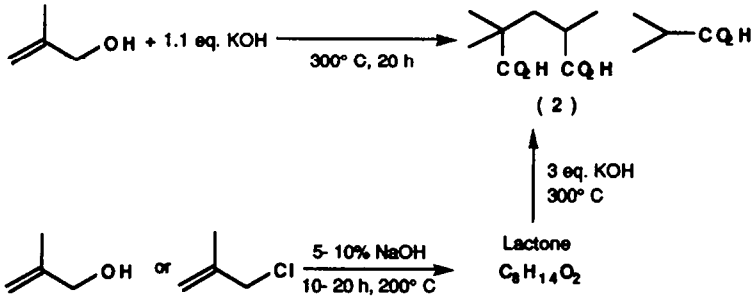
We envisaged however that an alternative process should exist whereby use of the derived allylic alkoxide *anion* in conjunction with an electron deficient enophile would lead to a reversal of the classical product regiochemistry (Scheme 2). Such a non-classical Ene reaction could therefore be considered, in stepwise terms (path a), as involving initial hydride transfer to the enophile followed by subsequent Michael addition of the resultant carbanion on to the derived α,β unsaturated carbonyl component.



Scheme (2)

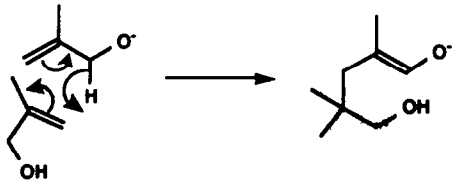
From a more concerted viewpoint, such a reaction could also be represented as an oxyanion assisted Ene reaction[1] in which the normal allylic assistance to carbon hydrogen bond breaking is reinforced by the presence of the alkoxide anion. Within the last decade, a variety of pericyclic processes including [3,3] and [1,3] sigmatropic rearrangements have benefited from the enormous rate enhancements induced by the α oxyanion effect.[3] Experimental observation and theoretical calculation[5] combine to demonstrate that the magnitude of this effect is considerable. Thus, the homolytic bond dissociation energy of the a C-H bond in "naked" methoxide anion is calculated to be some 19 kcal/mol lower than in methanol itself and a lowering of the activation energy by 16 kcal/mol relative to an analogous neutral process is not uncommon in the Oxy-Cope reaction. In similar fashion, the abnormal asynchronicity in the envisaged process shown (Scheme 2) should also be favoured by a lower activation energy. To the best of our knowledge Ene reactions in which carbon hydrogen bond breaking and making is more advanced than carbon carbon bond formation have not been discussed in the chemical literature. We now report in full detail[6], our search for a prototypical reaction which conforms to the above analysis.

Detailed examination of the literature revealed a German patent[7] of particular interest, which described the formation of 1,1,3-trimethylglutaric acid (2) by fusion of 2-methyl-2-propen-1-ol with potassium hydroxide in a rotating autoclave. Dimerically derived lactones whose structure was not rigorously assigned were also produced from either the alcohol or the corresponding chloride using aqueous sodium hydroxide. These reactions are summarised in Scheme 3.



Scheme (3)

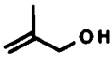
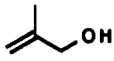
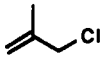
We were particularly intrigued by a possibility, not discussed by the author of the original paper[7], that the crucial carbon carbon bond formation in these reactions could result from an ene reaction of the type which we wish to propose (Scheme 4), and therefore set out to reproduce and examine this reaction in some detail.



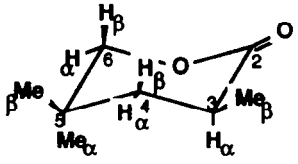
Scheme (4)

The results of this study are set out in Table 1 and clearly confirm the original observations concerning the formation of dimerically derived products.

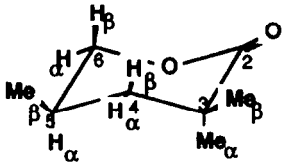
Table 1. Product Yields From Reactions with KOH or NaOH.

Substrate	Reaction Conditions	% Yield, 2-Methyl propanoic acid	% Yield, Trimethyl glutaric acid	%Yield Lactone
	1.1 eq Solid KOH, 300^0, 20h.	21	16	-
	1.1 eq 10% NaOH, 200^0, 20h.	3.8	4.4	6.4
	1.1 eq 10% NaOH, 200^0, 20h.	2.5	0.5	16.0

The structure of the isolated lactone fraction was of especial interest. Although homogeneous by analytical t.l.c., a careful g.l.c. examination revealed the existence of two compounds in a 6:1 ratio. This observation was fully confirmed by a detailed analysis of the 250 MHz spectra. Extensive decoupling experiments allowed all the coupling constants to be assigned (Table 2) and fully established the structures of the major and minor isomers as 3,5,5-trimethyl tetrahydropyran-2-one (3) and 3,3,5-trimethyl tetrahydropyran-2-one (4) respectively.



(3)

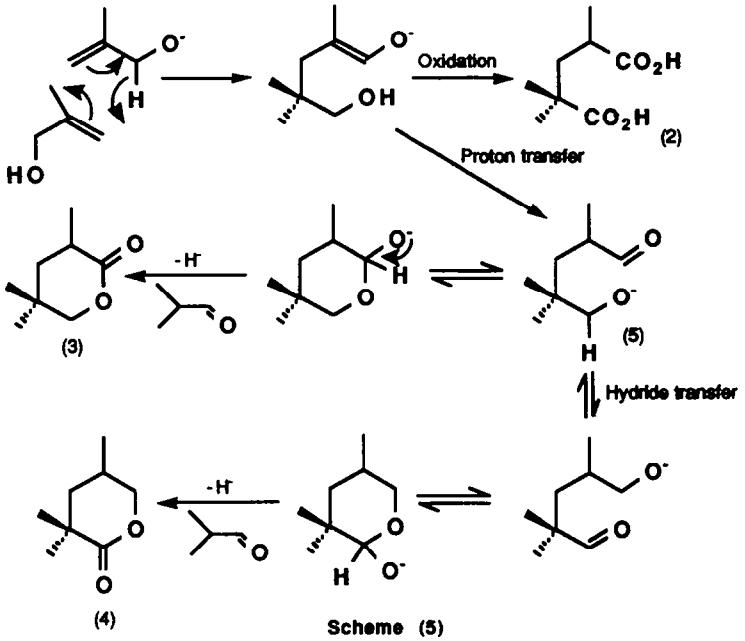


(4)

Table 2. ^{1}H NMR Parameters for (3) and (4).

(3)	(4)
1.04 (3H, s, 5-Me$_\beta$)	0.95 (3H, d, J 6.57 Hz, 5-Me)
1.08 (3H, s, 5-Me$_\alpha$)	1.29 (3H, s, 3-Me)
1.22 (3H, d, J 6.8 Hz, 3-Me)	1.31 (3H, s, 3-Me)
1.39 (1H, dd, J -12, 10 Hz,4-*H*$_\beta$)	1.49 (1H, dd, J -13.53, 12.6 Hz,4-*H*$_b$)
1.86 (1H, ddd, J -12,7.5,1.3 Hz,4-*H*$_a$)	1.73 (1H,m, J -13.53,3.5,2.8 Hz,4-*H*$_a$)
2.60 (1H, m, J 10, 7.5, 6.8 Hz,3-*H*)	2.20 (1H, m, J 12.6, 10.7, 6.574.92, 3.47 Hz, 5-*H*)
3.90 (1H, d, J -11.9 Hz, 6-*H*$_\beta$)	3.83 (1H, dd, J -10.9, 10.7 Hz, 6-*H*$_\beta$)
3.99 (1H, dd, J -11.9, 1.3 Hz,6-*H*$_a$)	4.30 (1H, m, J -10.9, 4.92, 2.8 Hz, 6-*H*$_a$)

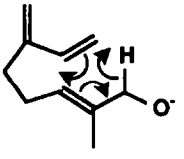
At this stage, it was therefore possible to rationalise the observed results (Scheme 5) in terms of a mechanism in which the desired ene reaction is followed either by oxidation to give the dicarboxylic acid (2) or by proton transfer and subsequent intermolecular hydride transfer to form the δ lactone (3). The formation of the minor regioisomeric δ lactone (4) may be explained by a subsequent intramolecular hydride transfer from the α carbon of the alkoxide (5) to the carbonyl carbon atom.



Scheme (5)

Wamhoff *et al* [8] have recently reported the first example of intramolecular hydride transfer in the case of acyclic ketols which are capable of forming γ lactols and the present case constitutes the first example of a similar situation for δ lactols with an aldehydic carbonyl carbon atom as the acceptor. With the results of the above study in hand, we then chose to avoid the intervention of hydroxide anion as a nucleophile in Cannizzaro type reactions, and hence to minimize the production of carboxylic acids as reaction products. Accordingly, the potassium alkoxide of 2-methyl-2-propen-1-ol, generated in diglyme (dimethoxy diethyl ether) using 1.1 equivalents of potassium hydride, was heated under reflux (162°C) for 15 hours. Protic work up then allowed isolation of a 10:1 mixture of the regioisomeric lactones (3) and (4) respectively in 15% yield, thus demonstrating that excessively high temperature and pressure was unnecessary.

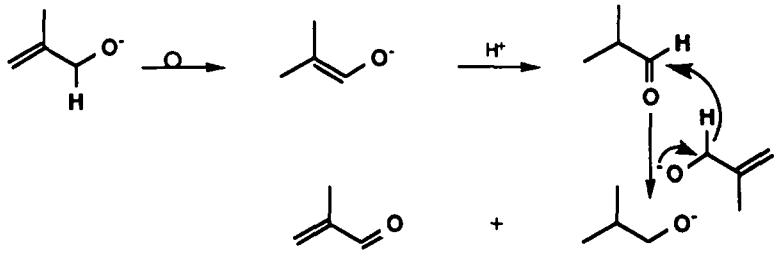
On the assumption (of Scheme 5) that the isolated carbon carbon double bond of 2-methyl-2-propen-1-ol was functioning as the enophilic component in this reaction, we then decided to attempt condensation of the potassium alkoxide of this alcohol with cyclohexene. However, even under extremely vigorous conditions, work up gave only the lactones (3) and (4) together with a hydrocarbon fraction whose mass spectrum suggested that cyclohexene had undergone no less than four consecutive ene reactions with itself. No crossed product was detected. Similarly, an attempted intramolecular variant of the reaction using myrcenol[9] (6) failed to provide any evidence for the formation of the desired cyclopentanoid product.



(6)

At this juncture, it was therefore necessary to re-examine the initial hypothesis. Clearly, the simple unactivated carbon carbon double bond is an unlikely partner for the allylic alkoxide anion. Moreover, the formation of lactones (3) and (4) as *oxidation* products under an inert atmosphere and essentially aprotic conditions is initially surprising and argues as an automatic corollary for the presence of a free carbonyl group (and not an enolate anion) as a hydride acceptor with

concomitant production of a reduced alkoxide anion. Accordingly, we set out to identify and quantify all possible intermediates and products in this reaction. A detailed g.l.c. examination of the reaction of 2-methyl-2-propen-1-ol with potassium hydride (1.1eq) in diglyme at 120°C proved to be most informative, and revealed the presence of 2-methylpropanal, 2-methylpropan-1-ol and 2-methylpropenal in the early stages of the reaction. The formation of the latter is most readily explained (Scheme 6) by a hydride transfer from the anion of methypropenol to a neutral molecule of methylpropanal with concomitant formation of the alkoxide anion of methylpropanol.



Scheme (6)

The required carbonyl group of methylpropanal may be derived by protonation of the corresponding enolate anion which is, in turn, formally produced by isomerisation of the allylic alkoxide anion. A simple experiment established that the most probable source of protons in the meliu is 2-methyl-2-propen-1-ol itself. Thus, measurement of the volume of hydrogen evolved during formation of the alkoxide of methylpropenol indicated incomplete oxyanion formation, even when a 10% molar excess of potassium hydride was employed. This is also a reflection of the difficulty in obtaining batches of potassium hydride of known and reproducible hydride concentration and activity. Further analysis of the g.l.c. traces also indicated that formation of lactones (3) and (4) was suppressed at the lower operating temperature of 125°C and that the major product at the end of the reaction was of significantly longer retention time. Chromatographic isolation of this fraction and careful re-examination using capillary g.l.c. revealed the presence of two overlapping bands. The complexity of the n.m.r. spectrum did not permit unambiguous assignments to be made at this stage, although the spectral evidence did suggest the products were alcohols. This was confirmed by bromine oxidation of this fraction, which cleanly afforded the previously characterised lactones (3) and (4). A crystalline *p*-nitrobenzoate was also prepared and shown by X-ray crystallography (Figure 1) to be a derivative of the lactol (8a). It is a significant warning that the determined structure proved in fact (*vide infra*) to be one of the minor components of the reaction.

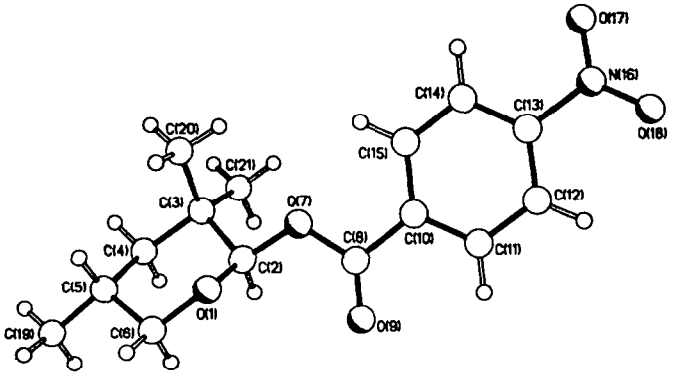


Figure 1. Molecular Structure of the *p*-Nitrobenzoate Derivative of 8a. Crystallographic numbering is shown.

With this knowledge in hand, it was then possible to determine the relative ratios of the four possible lactols (7a/7b) and (8a/8b) by the integration of distinguishable n.m.r. signals. These results are set out in Table 3, from which it is apparent that the isolated single crystal of *p*-nitrobenzoate ester actually corresponded to the *minor* rather than the major lactol isomer.

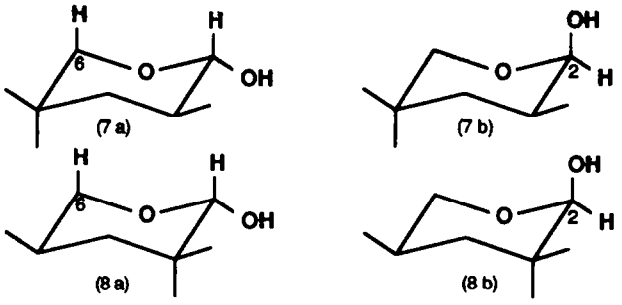


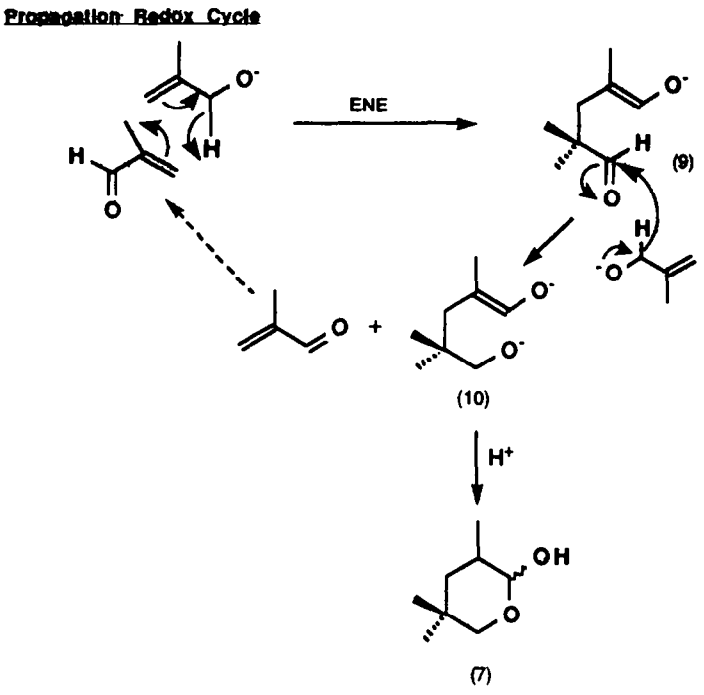
Table 3. Relative Ratios of the Lactols 7 and 8.

Isomer	Ring Hydrogen	δ,ppm	Relative ratio
(7a)	6-H_a	3.20	5.33
(7b)	2-H_b	4.96	2.33
(8a)	6-H_a	3.00	1.33
(8b)	2-H_b	4.60	1

These assignments of the lactol ring hydrogens were further confirmed by subsequently obtaining a regio-isomerically pure mixture of lactols (7a) and 7b) produced under optimised conditions (see part 11 of experimental section). The signals corresponding to 2, 3, 4, 5 and 6-H of both isomers were easily discerned, whereas a series of nOe experiments were required to assign the resonances due to the six methyl groups. The combined data demonstrated that the ratio of equilibrium concentrations 7a/7b was 2.28:1. It is therefore apparent that although the *trans* diequatorial isomer (7a) is expected to be considerably more stable on steric grounds, the stereoelectronic requirements of the anomeric effect[10] favour a significant concentration of the *cis* isomer (7b). From the results of the above investigation, it was now possible to propose a more satisfactory mechanism based on the operation of a redox cycle (Scheme 7) which is initiated by the production of a molecule of 2-methylpropenal as indicated in Scheme 6.

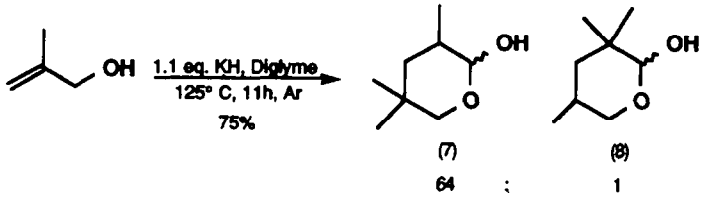
From the electronic standpoint, the use of electron deficient 2-methylpropenal as the active "enophile" or hydride acceptor is clearly much more acceptable. Subsequent intermolecular hydride transfer from the anion of 2-methylpropenol then occurs preferentially to the non-enolizable aldehyde in (9) to afford an intermediate dianion (10), with concomitant liberation of a further molecule of 2-methylpropenal as the chain carrier. Protonation on work up then leads to the observed lactols (7) as the major products of the reaction. The formation of the minor regioisomeric lactols (8) then requires *in situ* protonation of the dianion and intramolecular hydride shift of the resultant lactol alkoxide (5) as previously discussed (Scheme 5). Although a variety of alternative hydride transfers are possible, the net result is a redox stable system which allows propagation of the chain. The failure to observe lactone products at lower temperature is probably a reflection of the higher activation energy required to effect hydride transfer from the lactol alkoxide (5) as opposed to the anion of methylpropenol.

In practical terms, the above formulation also allowed us to define optimum experimental parameters for non-oxidative dimerisation, through variation of temperature, reaction time and potassium hydride concentration. Thus, formation of the potassium salt of 2-methyl-2-propen-1-ol using 1.1 equivalents of potassium hydride followed by heating in diglyme under argon at 125°C for 11h, afforded after protic work up a 73% yield of lactols (7) (Scheme 8). Careful g.l.c. analysis revealed that less than one percent of the regioisomeric lactols (8), or lactones (3) and (4) were formed under these



Scheme (7)

conditions. The concentration of potassium hydride used proved to be the most significant variable (Table 4) and several points are worthy of note from this data.



Scheme (8)

Table 4. Variation in Yield as a Function of Hydride Concentration.

Entry	KH,eq	Time,h	% Lactols (7) and (8)	% Lactones (3) and (4)	Total Yield,%
1	0.1	41	22	78	16.0
2	0.9	14	68	32	68.7
3	1.1	11	98	2	75.1

Thus, carbon-carbon bond formation can still occur even at relatively low alkoxide anion concentration. Under these conditions however, higher concentrations of free methylpropanal are necessarily present, and since this may act as a hydride acceptor, higher concentrations of lactones relative to lactols are formed. At higher alkoxide anion concentrations methylpropanal is present as its enolate anion and consequently cannot function as an oxidant. At this stage, although the crucial carbon-carbon bond forming reaction may be regarded either as a concerted but highly asynchronous ene reaction involving 2-methylpropenal and the anion of methylpropenol, or as a stepwise hydride transfer to give 2-methylpropenal and methylpropanal enolate followed by Michael addition, all evidence indicated that 2-methylpropenal must be considered as the

enophilic hydride acceptor. It was therefore of considerable interest to examine the direct use of 2-methylpropenal in the reaction mixture in conjunction with the allylic alkoxide anion. Accordingly, an equimolar mixture of the allylic alcohol and the α,β unsaturated aldehyde was added to potassium hydride in tetrahydrofuran at room temperature. Under these conditions, although 2-methylpropenal was entirely consumed within three hours, no traces of lactols or lactones were detected, and work up afforded a white crystalline solid (24% yield based on 2-methylpropenal). Mass spectroscopy and microanalytical data served to establish the tetramerically derived molecular formula $C_{16}H_{26}O_4$ whilst infrared spectra exhibited both hydroxyl (3511cm^{-1}) and carbonyl absorption (1721cm^{-1}). X-ray analysis (Figure 2)[11] revealed the structure (Figure 2) to be the bicyclic hydroxy lactone (**11**) (Scheme 9).

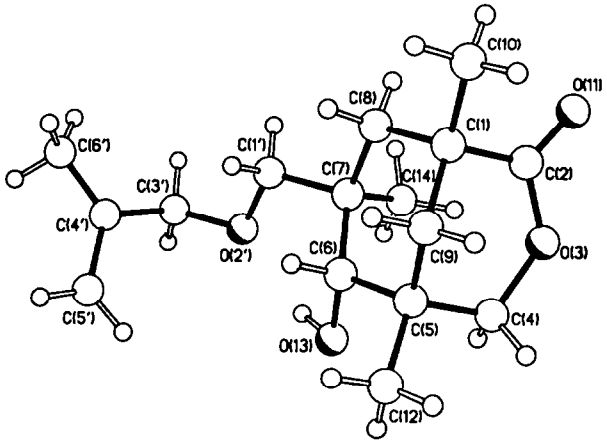
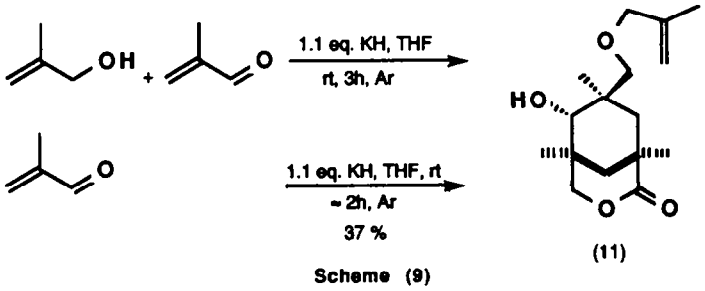
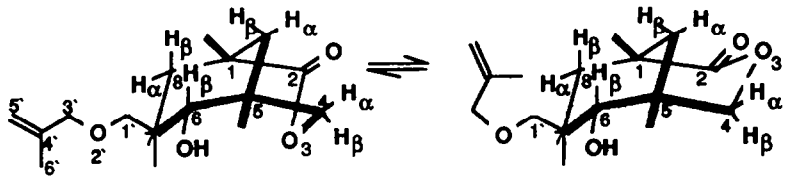


Figure 2. Molecular Structure of 11. Crystallographic numbering is shown.



Scheme (9)

A series of ^{1}H nuclear Overhauser n.m.r. experiments (Table 5) not only allowed a complete proton assignment but also indicated that the lactone ring exists partially in the boat form (**11b**).



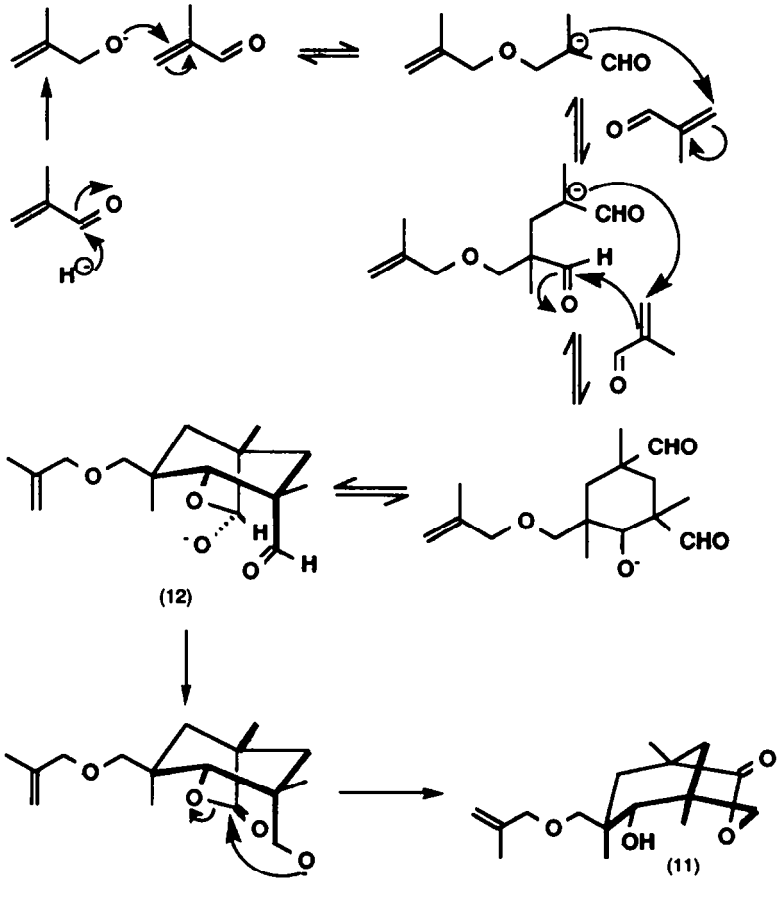
11a **11b**

Table 5. Nuclear Overhauser Assignments for 11.

δ,ppm	Enhanced signals	Assignment
1.07	3.5 (6-H), 3.87 (4-H_α)	5-Me
1.11	1.7 (8-H_β), 3.1 (1`- CH_2), 3.24 (OH), 4.65 (4-H_β)	7-Me
1.18	1.68 (8H_α), 1.8 (9-H_β)	1-Me

From these results and inspection of models, it can be seen that the enhancement of 4-Hα and 4-Hβ by irradiation of the 5-Me and 7-Me signals respectively can only be achieved if the lactone ring exists in a chair boat equilibrium. This is further confirmed by the observation of long range W coupling between 9-Hβ and 4-Hβ.

The formation of the bicyclic hydroxy lactone (11) may be rationalised (Scheme 10) by involving three consecutive Michael addition reaction featuring one molecule of methylpropenoxide and three subsequent molecules of 2-methylpropenal. Intramolecular aldolisation to give a six membered ring di-aldehyde may then be followed by an alkoxide mediated Cannizzaro reaction whose regiospecificity can be determined by intramolecular hydride transfer from the favoured cyclic γ-lactol alkoxide anion (12). Translactonisation may then occur to give the observed product (11). The above reaction is therefore an example of a one pot multicomponent annulation[12] sequence in which five new bonds, four stereocentres, and two six membered rings are formed.



Scheme (10)

It is also of interest to note that the same product (11) was also produced in a "blank" experiment in which 2-methylpropenal itself was reacted with potassium hydride. The caveat that potassium hydride may occasionally function as a nucleophile for an α,β-unsaturated aldehyde accordingly follows.

The predominant reaction pathway between 2-methylpropenal and potassium methylpropenoxide at room temperature is therefore initiated by a classical series of Michael addition and aldolisation steps. At higher temperature however such processes are inherently reversible and are therefore overcome by the ene reaction to form lactols (7). The foregoing discussion has therefore demonstrated the possibility of forming a new carbon carbon bond by an ene type process involving hydride transfer together with, or closely followed by 1,4 addition. Moreover, the necessity for use of an electron deficient enophile together with the consequential reversal of regioselectivity have been observed. Work is currently in hand to examine the synthetic potential of such reactions in the intramolecular mode[13,14] where problems of enophile polymerisation may be controlled.

Experimental.

Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. Infra red spectra were recorded on Perkin Elmer 298 and 983G grating Infra red spectrophotometers using a thin film or as a solution in dichloromethane . ^1H NMR were recorded at 60 MHz on a Varian EM-360A, at 90 MHz on a Jeol FX 90Q, and at 250 MHz on a Bruker WM-250, and are quoted for solutions in $CDCl_3$ with tetramethyl silane as an internal standard. Mass spectra were determined with a VG micromass 7070P instrument. Elemental microanalyses were performed in the Imperial College Chemistry Department microanalytical laboratory. Analytical thin layer chromatography was performed on precoated glass-packed plates (Merck Kieselgel 60 F_{254}) and preparative chromatography was conducted under low pressure using MN Kieselgel 60 (230-400 mesh). Silica gel refers to the Kieselgel. Petrol refers to light petroleum ether with b.p. 40-60°C unless otherwise stated, and was redistilled from phosphorus pentoxide before use. Diethyl ether, 1,2-dimethoxyethane and tetrahydrofuran were dried by refluxing over sodium/benzophenone and distilled before use. Diglyme was dried by refluxing over sodium and distilled before use. Dichloromethane was dried by refluxing over phosphorus pentaoxide and distilled before use. Dimethyl sulphoxide was dried by prolonged storage over 4Å molecular sieves followed by distillation under reduced pressure onto 4 Å molecular sieves. Benzene and toluene were dried over sodium wire and acetonitrile dried over calcium hydride and all were distilled before use. Pyridine, di-isopropylamine and triethylamine were distilled from calcium hydride and stored over potassium hydroxide pellets. All other solvents and reagents were purified by standard techniques. Solutions were dried over anhydrous magnesium sulphate and evaporated with a rotary evaporator followed by static evaporation with an oil pump. All experiments employing potassium or sodium hydrides were performed in a three-necked flask fitted with a magnetic bar, septum, blue silica gel tube bearing an argon inlet and a condenser (if refluxed), bearing a gas exit. The flask was flame dried and flushed with argon before use.

1. Reaction of 2-methyl-2-propen-1-ol with potassium hydroxide[7]. Isolation of 1,1,3-trimethyl glutaric acid (2)...A mixture of 2-methyl-2-propen-1-ol (20.0 g, 0.277 mol) and solid potassium hydroxide (17.12 g, 0.305 mol) was placed in a stainless steel bomb of 100 ml capacity and fused in a rotating autoclave at 300° C for 20 h. After dilution with water (50 ml) and acidification with dilute hydrochloric acid, the aqueous phase was extracted with dichloromethane (4 x 50 ml). The organic phase was dried over ($MgSO_4$) and concentrated under reduced pressure to afford a crude mixture (8.7 g) as a yellow oil. Chromatography of a 1.0 g sample over silica gel (gradient elution, 20% ethyl acetate-cyclohexane Æ 100% ethyl acetate) afforded 1,1,3-trimethyl glutaric acid (2) (0.44, 16%) as white crystals, m.p. 95-96° C ; (found: C, 54.19; H, 8.14, calc. $C_8H_{14}O_4$ C, 55.16 ; H, 8.10%) ; ν_{max} (CH_2Cl_2) 3320-2890 (OH), 1707 (CO) cm^{-1} ; δ_H (250 MHz) 1.19 (3H, d, J 6.94 Hz, CH_3CH), 1.24 (3H, s, Me), 1.27 (3H, s, Me), 1.34 (1H, dd, J -14.1 and 2.9 Hz, CH_bCHCH_3), 2.3 (1H, dd, J -14.1 and 11.9 Hz, CH_aCHCH_3), 2.67 (1H, m, J 6.94, 2.9 and 11.9 Hz, CH_2CHCH_3) and 12.15 (2H, s, CO_2H) ; δ_C (250 MHz) 184, 183 (2C, CO_2H) , 45 (CH_2), 41 ($C(Me_2)$ CO_2H), 36 (CH-), 28, 22, and 18 (3Me) ; m/z, 129 (M^+- CO_2H), 88 ($(Me_2C{=}C(OH)_2)^+$, 83 (M^+-$2CO_2H$) and 70 $(Me_2C{=}C{=}O)^+$. Isobutyric acid (0.589 g, 21%) was also isolated as a colourless oil, ν_{max} (film) 3550-2890 (OH), 1707 (CO) cm^{-1}, δ_H (60 MHz), 1.2 (6H, d, J 8Hz, Me_2), 2.55 (1H, m, $CHCMe_2$) and 12.1 (1H, s, COOH), identical with an authentic sample.

The solid residue produced by evaporation of the aqueous layer was suspended in methanol (130 ml), slow addition of acetyl chloride (6ml) gave a solution of hydrogen chloride in methanol for Fischer esterification and the reaction mixture was refluxed for 48h. Filtration of the esterification reaction, concentration under reduced pressure and column chromatography (silica gel, 20% Ethyl acetate-cyclohexane) afforded dimethyl methylsuccinate (73) (0.4g, 1%) as a colourless oil, ν_{max} (film) 2983, 1735 ; δ_H (60 MHz) 1.25 (3H, d, J 7 Hz, CH_3), 2.3-3.3 (3H, m, $CH_3.CHCH_2$); m / z 129 (M^+- OMe), 101 (M^+- CO_2Me), 87, 69, 59.

2. Reaction of 2-methyl-2-propen-1-ol with aqueous sodium hydroxide[7]···A mixture of 2-methyl-2-propen-1-ol (10 g, 0.139 mol) and 10% aqueous sodium hydroxide (6.1g, 0.153 mol) was heated at 200° C for 20h in a stainless steel autoclave. After dilution with water (50ml) and, acidification with dilute hydrochloric acid, the aqueous layer was extracted with dichloromethane (4 x 50ml). Drying ($MgSO_4$) and concentration under reduced pressure afforded 2.64 g of crude mixture, which was initially purified by acid/base extraction. Then the mixture was dissolved in diethyl ether (100 ml), and thoroughly extracted with saturated sodium bicarbonate solution (2 x 30ml) . The ether layer was washed with water (50ml), brine (50ml), and dried over magnesium sulphate. Concentration under reduced pressure followed by silica gel chromatography (5% ethyl acetate- cyclohexane) afforded a 6:1 mixture of lactones (3) and (4) (by G.C), homogeneous by t.l.c., (0.63 g,6.4%), as a very pale yellow oil. Lactone, 3,5,5-trimethyl-tetrahydropyran-2-one (3). Bp_{760} = 232-4°C, ν_{max} (film), 2965, 1735 (lactone C=O), 1458, 1381, 1161, 1091 cm^{-1} ; δ_H (250 MHz) 1.04 (3H, s, 5-Me_b), 1.08 (3H, s, 5-Me_a), 1.22 (3H, d, J 6.8 Hz, 3-Me), 1.39 (1H, dd, J -12 and 10 Hz, 4-H_a), 1.86 (1H, ddd, J -12, 7.5 and 1.3 Hz,4-H_b), 2.6 (1H, m, J 10, 7.5 and 6.8 Hz, 2-*H*), 3.91(1H, d,J -11.9 Hz, 6-H_a) and 3.99 (1H,dd, J -11.9 and 1.3 Hz, 6-H_b). δ_C(250 MHz) 16.36 , 24.68 , 27.09 , 30.39 , 32.12, 41.97, 74.5 and 174.9 ; m/z, 143 $(M+H)^+$, 113 (M^+-CH_2O+H), 70 (M^+-CH_2O - *i*-Pr). 3,3,5-Trimethyl-tetrahydropyran-2-one (4) δ_H (250 MHz) 0.95 (3H, d, J 6.57 Hz, 5-Me), 1.29 (3H, s, 3-Me), 1.31 (3H, s, 3-Me), 1.49 (1H, d, J -13.53 and 12.6 Hz, 4-H_a), 1.73 (1H, m, J -13.53, 3.47 and 2.8 Hz, 4-H_b), 2.2 (1H, m, from decoupling, J 12.6, 10.7, 6.57, 4.92 and 3.47 Hz, 5-*H*), 3.83 (1H, dd, J -10.9 and 10.7 Hz, 6-H_a) and 4.3 (1H,m, J -10.9, 4.92 and 2.8 Hz, 6-H_b) ; δ_C (250 MHz) 16.25, 25.80, 28.04, 28.15, 30.40, 43.84, 75.50 and 174.67. The aqueous layer was acidified with 10% aqueous hydrochloric acid (30 ml) and thoroughly extracted with dichloromethane (5 x 20 ml). The combined dichloromethane extracts were washed with brine (20 ml). Drying ($MgSO_4$) and concentration under reduced pressure followed by chromatography (gradient elution, 50% ethyl acetate-cyclohexane and 1% acetic acid Æ 100% ethyl acetate) afforded isobutyric acid (0.46 g, 3.8%) and 1,1,3-trimethyl glutaric acid (2) (0.53g, 4.4%) whose spectral properties were identical with those described above.

3. Reaction of 2-Methyl chloropropene with aqueous sodium hydroxide[7]···A mixture of methyl chloropropene (9.055g, 0.1 mol) and 10% aqueous sodium hydroxide (4.4 g, 0.11 mol) was heated at 200° C for 20 h in stainless steel autoclave. After dilution with water (30 ml) the aqueous layer was extracted with diethyl ether (3 x 50 ml). The combined ethereal extract was dried over potassium carbonate and solvent evaporated under reduced pressure. Chromatography over silica gel (5% ethyl acetate- petrol 30-40°) afforded lactones (3) and (4) (1.09 g, 15.4%). The aqueous layer was acidified with 10% aqueous hydrochloric acid and extracted with benzene (4 x 50 ml). Drying over potassium carbonate (to separate the acidic products from the lactones) and concentration under reduced pressure followed by chromatography (15% ethyl acetate- petrol 30-40° C) afforded lactones (3) and (4) (30 mg, 0.4%) and isobutyric acid (85 mg, 1%) . Re-extraction of the aqueous layer with dichloromethane (3x40) followed by drying the combined dichloromethane layers (K_2CO_3) and concentration under reduced pressure afforded 1,1,3-trimethyl glutaric acid (2) (33 mg, 0.4%). The aqueous layer was reacidified with 10% hydrochloric acid and brought to constant extraction by dichloromethane (100 ml) in soxhlet apparatus for 6 days. The dichloromethane layer was washed once with brine (30 ml) and dried ($MgSO_4$). Concentration under reduced pressure followed by chromatography (15% ethyl acetate - petrol 30-40°C) afforded an additional quantity of the lactones (17 mg, 0.24%) and isobutyric acid (135 mg, 1.5%). Total yields of isolated lactones (3) and (4) (1.137 g, 16%), isobutyric acid (0.22 g, 2.5%) and 1,1,3-trimethyl glutaric acid (2) (33 mg, 0.4%), identical with the previously described samples).

4. Attempted dimerization of 2-methyl-2-propen-1-ol...A solution of 2-methyl-2-propen-1-ol (1.44 g, 0.02 mol) in dry diglyme (10 ml) was heated at 125°C for 20hr. After dilution with water (20 ml) the organic layer was extracted with diethyl ether (4 x 30 ml). The combined ether layers were washed with water and dried ($MgSO_4$). Concentration under reduced pressure afforded only starting material. No trace of lactol or lactone product was detected in this reaction by analytical t.l.c.

5. Reaction of 2-methyl-2-propen-1-ol with potassium hydride in diglyme... A three necked flask fitted with a magnetic bar, septum, a blue silica gel tube bearing an argon inlet and a condenser bearing a gas exit was flamed and flushed with argon. Potassium hydride (6.30 g, 0.055 mol, 35% dispersion in oil) was placed in the flask, washed with dry THF (3 x 30 ml) and suspended in 25 ml of dry diglyme. The allylic alcohol (3.61 g, 0.05 mol) was then added *via* a syringe over a 15 min. period. The resulting slightly yellow solution was stirred at room temperature for 1 h then refluxed for 19 h , and the dark brown suspension was allowed to cool to room temperature. After dilution with water (20 ml) and acidification with 10% aqueous hydrochloric acid, the aqueous layer was thoroughly extracted with dichloromethane (4 x50 ml).The combined organic extracts were then dried ($MgSO_4$) and concentrated under reduced pressure. Diglyme was finally removed by distillation using a vigreux column at 162° C. Chromatography of the residue (10% ethyl acetate - petrol 60-80°C) afforded the previously described lactones (3) and (4) (10:1, gc) (0.53 g, 15%) as a slightly yellow oil, and a colourless liquid (0.03 g, 0.8%) which was latter identified as an epimeric mixture of the corresponding lactols (7) and (8) (*vide infra*).

6. Attempted Ene reaction between cyclohexene and 2-methyl-2-propen-1-ol at elevated temperature... A mixture of 2-methyl-2-propen-1-ol (5.05 g, 0.07 mol), cyclohexene (57.51 g, 0.7 mol) and solid potassium hydroxide (4.32 g, 0.077 mol) was fused in a rotating autoclave at 300° C for 20 h. After dilution with water (200 ml) the aqueous layer was extracted with diethyl ether (4 x 75 ml). The combined ether layers were washed with brine (75 ml), dried ($MgSO_4$) and concentrated under reduced pressure . Chromatography (100% cyclohexane) afforded a hydrocarbon mixture (15.51 g, 27%) as a colourless oil, ν_{max} (film) 3020, 2923, 2851, 1448, 1349, 707 cm^{-1}; δ_H (250 MHz) 0.97-2.1 (br, m, cyclohexane protons) and 5.63 (2H, d, J 14.5 Hz) ; m/z 410 (M^+), 328 ($M^+ - C_6H_{10}$), 246 ($M^+ - (C_6H_{10})_2$), 164 ($M^+ - (C_6H_{10})_3$), 163, 81 $(C_6H_9)^+$. After acidification of the aqueous layer with 10% hydrochloric acid, the aqueous layer was extracted with dichloromethane (4 x 50 ml). Drying ($MgSO_4$) and concentration under reduced pressure followed by chromatography (gradient elution 30% ethyl acetate - cyclohexane Æ 100% ethyl acetate) afforded isobutyric acid (2.95 g, 58.5%) and 1,1,3-trimethyl glutaric acid (0.984 g, 16.6%) (2) identical in all respects with previously described samples .

7. G.l.c. examination of the reaction of 2-methyl-2-propen-1-ol with potassium hydride... To a stirred suspension of potassium hydride (6.30 g, 0.055 mol, 35% dispersion in oil, prewashed with sodium dried ether (3 x 40 ml)) in dry diglyme (30 ml) at room temperature under argon was added a solution of the alcohol (3.605 g, 0.05 mol) in diglyme (6 ml). The resulting yellow suspension was stirred at room temperature for 90 min. and then heated at 115-130° C for 22 h. One ml aliquots of the reaction mixture were periodically withdrawn and worked up by acidification with dilute hydrochloric acid and extraction with ether (2 ml). The ether layer was then filtered through a small column of magnesium sulphate. G.l.c. examination using a 1500 carbowax column and a temperature gradient program [50°C (6 min) —Æ165° C (4 min)], allowed the detection of the following compounds by comparison with authentic samples : isobutyraldehyde [R_t = 1.0 min.], 2-methylpropenal [R_t = 1.8 min.], isobutyl alcohol [R_t = 6.5 min.], 2-methyl-2-propen-1-ol [R_t = 9.8 min.], an unknown material [R_t = 14.5 min.] and the lactones [(3) and (4), R_t = 15.5 and 15.9 min. respectively, with 1 : 9 ratio. The reaction mixture was worked up by dilution with water (30 ml), acidification with aqueous hydrochloric acid and extraction with ether (4 x 50 ml) . Drying over ($MgSO_4$), concentration under reduced pressure and removal of diglyme by distillation at 162°C, led to a residue, which on chromatography (30% ethyl acetate - cyclohexane) afforded the lactones (3) and (4) (0.166 g, 4.7%) and an epimeric mixture of 3,5,5-trimethyl-tetrahydropyran-2-ol (7) and 3,3,5,-trimethyl-tetrahydropyran-2-ol (8) (homogeneous by t.l.c) (1.493 g, 41.5%) as a colourless oil. (Found; C, 66.94; H, 11.31, $C_8H_{16}O_2$ requires C, 66.63 ; H, 11.18%) ; ν_{max} (film) 3391, 2952, 2869, 1364, 1072, 992 cm^{-1}; m/z 144 (M^+), 127 (M^+ - OH), 109 (M^+ - OH, -H_2O), 98, 69, 56, 43 . The ^1H NMR spectra could not be completely resolved at this stage.

8. Bromine oxidation of the regioisomeric mixture of lactols (3) and (4)... A cold solution (0°C) of barium benzoate dihydrate (1.869, 4.9 mmol) in water (53ml) was added to the lactols (7) and (8) (0.5 g, 3.5 mmol) at 0°C. Bromine (0.666 g, 4.2mmol) was added dropwise to the stirred solution. The mixture was stirred at 0°C for 30 min and at room temperature for 36 h, after which the excess bromine was removed by a stream of argon. The reaction mixture was quenched with 5N sulphuric acid (1.90 ml) and treated with decolourizing carbon (0.33g). After filtration, the filtrate was extracted with diethyl ether (4 x 40 ml). The combined ether layers were washed with saturated sodium bicarbonate (3 x 30 ml). Drying ($MgSO_4$) followed by concentration under reduced pressure afforded the lactones (3) and (4) (64 :1 by g.l.c.) (0.32 g, 64%), whose spectral and chromatographic properties were identical with previously described samples.

9. Measurment of the volume of hydrogen...A three-necked flask fitted with a magnetic bar subo-seal, a gas exit tube and a blue silica gel tube bearing an argon inlet was flame dried and flushed with argon . Potassium hydride (0.126 g , 1.1 mmol , 35% dispersion in oil) was placed in the flask and washed with THF (3 x 10 ml) in THF(5 ml) at room temperature under argon. The argon flow was stopped and the gas exit was replaced by one end of a double ended needle with the other end connected to a 50 ml burette to measure the volume of hydrogen evolved on addition of methyl allyl alcohol. The alcohol (72 mg, 1 mmol) was then added dropwise to the stirred suspension of potassium hydride. The resulting mixture was stirred for 2 h and the volume of hydrogen was measured as 17.5 ml compared with the calculated 22.54 ml for monoanion formation. No change in the gas volume was observed on stirring overnight.

10. Variation of potassium hydride concentration...To a stirred suspension of potassium hydride (35% dispersion in oil, prewashed with dry ether (4 x 30 ml)) in diglyme (20 ml) at room temperature under argon, was added a solution of the alcohol (2.16g, 0.03 mol) in diglyme (5 ml) dropwise in 45 min. The resulting yellow suspension was stirred at room temperature for 1h before heating at 125° for 11-41hr. After dilution with water (30 ml) and acidification with dilute hydrochloric acid, the aqueous layer was extracted with ether (4 x 40 ml). The combined ether layers were washed with water (5x50 ml), dried over magnesium sulphate and concentrated under reduced pressure to afford the expected products (Table 4)

11. Optimization of the reaction conditions for lactol (7) formation...To a stirred suspension of potassium hydride (3.78 g, 0.033 mol, 35% dispersion in oil, pre-washed with dry ether (4 x 30 ml)) in diglyme (20 ml) at room temperature under argon, was added a solution of 2-methylpropenol (2.1 g, 0.03 mol) in diglyme (5 ml) dropwise in 45 min. The resulting yellow solution was stirred at room temperature for 1h and then heated at 125° C for 11 hr. Work up as before afforded lactones (3) and (4) (28 mg, 1.5%) (9:1, homogeneous by t.l.c.) as a colourless oil and 3,3,5-trimethyl-tetrahydropyran-2-ol (7) and 3,5,5-trimethyl-tetrahydropyran-2-ol (8) (1.333g, 73.6%) (g.l.c, 1:64; homogeneous by t.l.c) as a colourless oil. Compound (7) exists as a stereoisomeric (at the epimeric centre) mixture of (7a) and (7b) (5:2 from NMR integration, homogeneous by t.l.c.), (Found; C, 66.94 ; H, 11.31, $C_8H_{16}O_2$ requires C, 66.63; H, 11.18%); ν_{max} (film) 3391, 2952, 2869, 1364, 1072, 992 cm^{-1}; δ_H (250 MHz) 0.76 [3H, s, 5-Me_a (7a) isomer], 0.77 [3H, s, 5-Me_a , (7 b)], 0.84 [3H, d, J 7.3 Hz, 3-Me, (7b) isomer], 0.86 [3H, d, J 6.6 Hz, 3-Me (7a)], 0.98 [3H, s, 5-Me_b (7b)], 1.02 [3H, s, 5-Me_b (7a)], 1.36-1.46 (4H, m, 4-H_2 of both isomers), 1.64 [1H, m, 3-*H* (7a)], 1.90 (1H, m, 3-*H*(7b)], 3.01 (1H, dd, J -10.9, 2.49 Hz, 6-H_b (7b)], 3.20 (1H, d, J -11.26 Hz, 6-H_a (7a)], 3.43 (1H, dd, J -11.26, 3.05 Hz and 6-H_b (7a)], 3.66 (1H, d, J -10.9 Hz, 6-H_a (7b)], 4.17 (1H, d, J 8.5 Hz, 2-H_a (7a)] and 4.97 (1H, d, J 3.43 Hz, 2-H_b (7a)]; δ_C (250 MHz) for (7a), 16.78 (3-Me), 24.25 (5-Me_a), 26.62 (5-Me_b), 31 (CMe_2), 34 ($CHCH_3$), 45.2 (CCH_2CHMe), 76.2 (CH_2-O) and 102.2 (*C*HOH). For (7b) isomer, 16.78 (3-Me), 24 (5-Me_a), 27.39 (3-Me_b), 30.48 (*C*HMe), 30.8 (CMe_2), 39.3 (CH_2CHMe), 68.53 (CH_2-O) and 94.1 (O-*C*H-OH) ; m/z 144 (M^+), 127 (M^+ - OH), 109 (M^+ - OH, - H_2O), 98, 69, 56, 43 .

12. Combined reaction of 2-methylpropenal and 2-methyl-2-propen-1-ol with potassium hydride. Preparation of 6-endo-hydroxy-7-exo-(2-methyl allyloxy methyl)-3-oxa-1,5,7-trimethyl bicyclo [3,3,1] nonan-2-one (11)...To a stirred suspension of potassium hydride (1.26 g, 0.011 mol, 35% dispersion in oil, prewashed with dry THF (3 x 30ml)), in THF (5 ml) at room temperature under argon, was added a mixture of 2-methyl-2-propen-1-ol (0.72 g, 0.01 mol) and 2-methylpropenal (91) (0.7 g, 0.01 mol) in THF (20 ml) dropwise over 20 min. The resulting orange homogeneous solution was stirred at room temperature for 3 h. After cautious dilution with water (15 ml), the aqueous layer was extracted with ether (4 x 50 ml). Drying ($MgSO_4$) and concentration under reduced pressure followed by chromatography (25% ethyl acetate-cyclohexane) afforded 6-*endo*-hydroxy-7-*exo*-(2-methyl allyloxy methyl)-3-oxa-1,5,7-trimethyl bicyclo[3,3,1] nonan-2-one (**11**) (0.164 g, 24%) as white crystals mp. 94° C, (R_f 0.27, 50% diethylether - petrol); (found; C, 68.12 ; H, 9.38 ; $C_{16}H_{26}O_4$ requires C, 68.06 ; H, 9.26%); ν_{max} (DCM) 3511, 3020, 2959, 2929, 2856, 1721, 1653, 1605, 1471, 1458, 1380, 1161, 1105, 1034, 990 cm^{-1}; δ_H (250 MHz) 1.07 (3H, s, 5-Me), 1.11 (3H, s, 7-Me), 1.18 (3H, s, 1-Me), 1.22 (1H, d, J -13.6 Hz, 8-H_β), 1.38 (1H, dd, J -13.18 and 2.13 Hz, 9-H_α), 1.68 (1H, dd, J -13.6 and 2.13 Hz, 8-H_α), 1.70 (3H, s, 6'-Me), 1.80 (1H, dd, J -13.18 and 2.76 Hz, 9-H_β), 3.11 (2H, dd, J -8.25 Hz, 1`-$CH_2$ ), 3.24 ( 1H, s, CHO*H*), 3.50 ( 1H,s, 6-C*H* OH), 3.87 ( 1H, d, J -12.38 Hz, 4-$H_\alpha$ ), 3.90 ( 2H, s, 3`-CH_2), 4.65 (1H, dd,J -12.38 and 2.58 Hz, 4-H_β), 4.89 (2H, vwt, 5`-CH_2), m/z 282 (M^+), 227 (M^+ - CH_2=CHCHMe$_2$), 195, 181, 151, 123, 109, 95, 55, 43 .

13. Action of potassium hydride on 2-methylpropenal...To a stirred suspension of potassium hydride (1.26g, 1.1 mmol, 35% dispersion in oil, prewashed with dry THF (4 x 30 ml)) in THF (15 ml) at room temperature under argon was added a solution of 2-methylpropenal (0.7g; 1 mmol) in THF (5 ml) dropwise over 10 min. After 3h at room temperature the reaction mixture was quenched by dropwise addition of water (2 ml). The solution was diluted with diethyl ether (25 ml) and washed with water (10 ml). The aqueous layer was neutralized with dilute aqueous hydrochloric acid (15%) and extracted with ether (5 x 25 ml). The combined organic extracts were washed with brine (40 ml) and dried over ($MgSO_4$). Concentration and chromatography on silica gel (1:1 diethyl ether-cyclohexane) afforded 6-*endo*-hydroxy-7-*exo*-(2-methyl allyloxymethyl)-3-oxa-1,5,7-trimethyl-bicyclo[3.3.1] nonan-2-one (11) (0.26 g, 37%) as a white solid, mp. 94° C, which is a mixture of three stereoisomers (R_f 0.27, 50% diethyl ether - petrol); (found; C, 68.12 ; H, 9.38 ; $C_{16}H_{26}O_4$ requires C, 68.06 ; H, 9.26%).

14. Crystal Data...Compound (11) $C_{16}H_{26}O_4$, M = 282.4, orthorhombic, a = 9.724(3), b = 12.431(3), c = 26.179(7)Å, U = 3164Å^3, μ (Cu-K_α) = 6 cm^{-1}, λ = 1.54178Å, space group *Pbca*, Z = 8, D_c = 1.19 g cm^{-3}, $F(000)$ = 1232. Approximate crystal dimensions 0.15 x 0.10 x 0.02 mm. The *p*-nitrobenzoate derivative of (8a), $C_{15}H_{19}O_5$, M = 293.3, triclinic, a = 7.015(4), b = 8.341(5), c = 14.744(10)Å, α = 80.34(5)°, β = 87.37(5)°, γ = 64.37(4)°, U = 766Å^3, μ(Cu-K_α) = 8 cm^{-1}, λ = 1.54178Å, space group $P1$, Z = 2, D_c = 1.28 g cm^{-1}, $F(000)$ = 312. Approximate crystal dimensions 0.10 x 0.10 x 0.01 mm.

Data collection and Processing. Compound (11), 2124 independent measured reflections (θ ≤ 58°), 1061 observed [$|F_0| > 3\sigma(|F_0|)$], *p*-nitrobenzoate of (8a), 2060 independent measured reflections (θ ≤ 58°), 1323 observed [$|F_0| > 3\sigma(|F_0|)$]. All data measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromator) using ω scans.

Structure Analysis and Refinement. Both structures were solved by direct methods and the non-hydrogen atoms in each were refined anisotropically. In (11) the hydrogen atom on O(13) was located from a ΔF map, idealised (O-H = 0.96Å) and refined isotropically. All other hydrogen atom positions in both structures were idealised (C-H = 0.96Å), assigned isotropic thermal paramters [$U(H) = 1.2U_{eq}(C)$] and allowed to ride on their parent carbon atoms. All the methyl groups were refined as rigid bodies. Refinement was by block-cascade full-matrix least-squares and converged to give for (11) R = 0.094, R_ω = 0.097 ($\omega^{-1} = \sigma^2(F) + 0.00120\,F^2$) and for the *p*-nitrobenzoate of (8a), R = 0.068, R_ω = 0.065 ($\omega^{-1} = \sigma^2(F) + 0.00137\,F^2$). Computations were carried out using the SHELXTL program system[11]. Fractional atomic coordinates, tables of bond lengths and angles and isotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

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