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Synthesis Based on Cyclohexadienes: Part 10[1] Synthesis of 5,5-Dimethyl-7-methoxy-4-oxatricyclo[4.3.1.$0^{3,7}$]decan-2-ones.

Sadagopan Raghavan and G. S. R. Subba Rao*

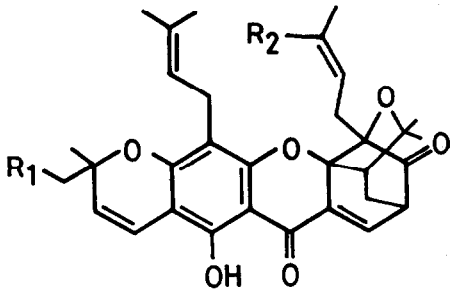
Department of Organic Chemistry,
Indian Institute of Science,
BANGALORE -560 012, India

(Key Words: Dihydroanisoles; Cycloadditions; Halocyclisation; Oxidative addition; Carbocation rearrangements; 4-Oxatricyclo[4.3.1.$0^{3,7}$]decan-2-ones)

ABSTRACT: *Synthesis of 5,5-dimethyl-7-methoxy-4-oxatricyclo[4,3,1,$0^{3,7}$]-decan-2-one* ***3a****, a novel heterocyclic ring system present in morellin* ***1****, and its 3-substituted derivatives* ***3b-e****, is described from the Diels-Alder adducts* ***7****, available from 1-methoxycyclohexa-1,4-dienes* ***4****. Two routes, which involved the halocyclisation and the oxidative addition, were investigated for the conversion of the adducts* ***7*** *into* ***3****. While the halocyclisation method resulted in mixtures, excellent yields of the target molecule were obtained by the second method. Solvolysis of the bromoether* ***9*** *resulted in a mixture of rearranged products* ***10****,* ***13****,* ***15*** *and* ***16****.*

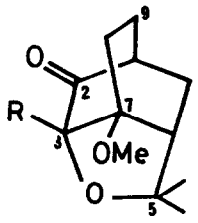
INTRODUCTION. The naturally occurring coloring matters, morellin[2] **1** and gambogic acid[3] **2** are the metabolites isolated from *Garcinia* species, and possess the oxatricyclo[4.3.1.$0^{3,7}$]decane ring system as shown in **3**. Although total synthesis of morellin has not been accomplished so far, synthesis of the heterocyclic bicyclo[2.2.2]octenone ring system has been reported[4,5] by using an intramolecular Diels-Alder strategy in the model systems. As part of our synthetic strategy towards morellin, we required an efficient method for the construction of the oxatricyclo[4.3.1.$0^{3,7}$]decanes. We now report a new strategy for the synthesis of 3-substituted-5,5-dimethyl-7-methoxy-4-oxatricyclo[4.3.1.$0^{3,7}$]decan-2-ones **3** from the readily available 1-methoxy-cyclohexa-1,4-dienes **4**.

RESULTS & DISCUSSION. Our approach to the synthesis of **3** is based on the preparation of the bicyclo[2.2.2]octene derivative, from 1-methoxy-



1 R_1 = H; R_2 = CHO

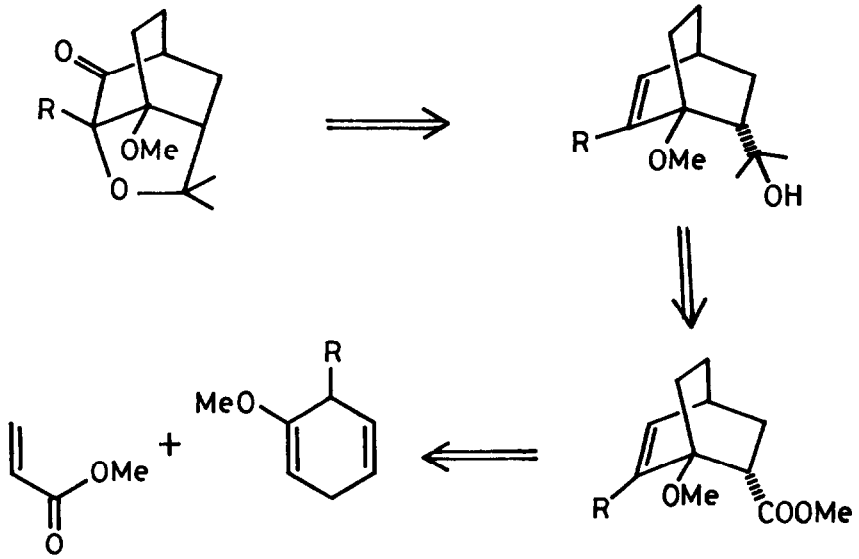
2 R_1 = $(CH_3)_2C{=}CHCH_2$; R_2 = COOH



3

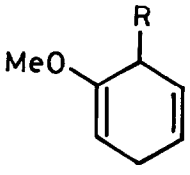
(a) R = H; (b) R = n-Butyl
(c) R = $(CH_3)_2C{=}CHCH_2$
(d) R = $(CH_3)_2C(OH)CH_2CH_2$
(e) R = $CH_3C(=CH_2)CH_2CH_2$

cyclohexa-1,4-diene with methyl acrylate, followed by an oxidative addition, leading to the tricyclic compound **3** as indicated in the retrosynthetic protocol indicated below.



1-Methoxycyclohexa-1,4-diene **4a**, obtained[6] by the Birch reduction of anisole, is conjugated[7] with potassium amide in liquid ammonia to the 1,3-

diene **6a** through the mesomeric anion **5**. Alkylation of the anion **5** *in situ* with alkyl halides afforded a (1:4) mixture of the 2-alkylated dienes **4b-c** and **6b-c**. Reaction of the diene mixture **4a** & **6a** with methyl acrylate in refluxing benzene afforded[8] the *endo* adduct **7**,(80%). Alternatively, the adduct **7a** can be prepared by heating diene **4a** with methyl acrylate in the presence of a catalytic amount of dichloromaleic anhydride[9] at 120°C for 48h. The *endo* and *exo* adducts resulting from the Diels-Alder reaction can be readily separated and identified from their ^{1}HNMR spectra. In particular, the vinylic protons appear upfield as a multiplet in the *endo* adduct while in the *exo* adduct they appear as a doublet in the downfield. Treatment of the adduct **7a** with excess of methylmagnesium iodide in dry ether afforded the alcohol **8a** which was reacted with N-bromosuccinimide in methylene chloride at -15°C, resulting in the bromoether **9a** (95%). The structure of **9a** is deduced from its ^{1}HNMR spectrum which showed resonances at δ, 4.21 as a doublet of a doublet for the C-2 proton and 4.27 as a doublet for the C-3 proton and was confirmed from its mass spectral analysis.



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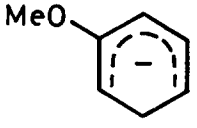

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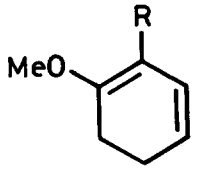

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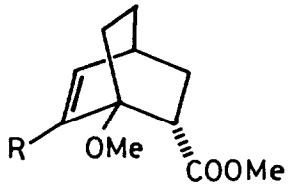

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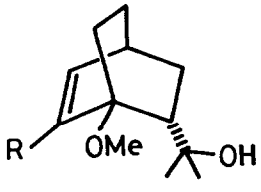

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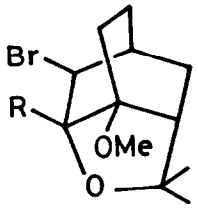
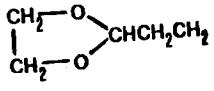
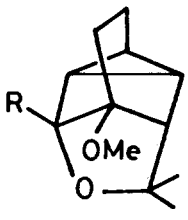


9

a) R = H; b) R = n-Butyl; c) R = 

Reaction of the bromoether **9a** with silver acetate in dry ether or tetrahydrofuran at varying temperatures did not yield the required acetate **12a**. Attempted S_N2 displacement of the bromide in **9a** by a hydroxide[10] or an azide [11] ion was not successful. Direct oxidation of the bromoether **9a** using dimethyl sulphoxide[12] or silver fluoroborate/dimethyl sulphoxide[13] or silver chromate/chromic anhydride[14] did not produce any of the desired product **3a**.

Since S_N2 displacement on the bromoether **9a** with nucleophiles failed, we investigated the solvolysis of **9a** under S_N1 reaction conditions. Thus, reaction of the bromoether **9a** with silver acetate in acetic acid in the presence of a catalytic amount of iodine at 90°C, resulted in the acetate **12a** (10%). In addition, two other products were formed which were separated by chromatography and identified as the tetracyclic compound **10a** (35%) and the rearranged acetate **14a** (10%). The structures of these compounds were deduced from their spectral and analytical data. The IR spectrum of **10a** showed absorptions at 1170 and 1080 cm^{-1} and its ^{1}HNMR spectrum had signals at δ, 1.35 as a singlet for the two methyl groups, a singlet at 3.21 for the methoxyl group and a doublet at 4.51(J=4.1Hz) for the proton on the carbon bearing the oxygen of the tetrahydrofuran ring besides signals due to -CH and $-CH_2$ protons. The alternative structure **11a** for the tetracyclic compound was excluded from its PMR analysis as it showed the presence of vicinal methylene groups and will be confirmed by X-ray study which is under progress. The IR spectrum of the acetate **12a** showed an absorption at 1730 cm^{-1} for the acetate group while its ^{1}H NMR spectrum had singlets at δ, 1.25, 1.41, 2.06 and 3.21 for the methyl, acetoxyl and the methoxyl groups; a doublet at 3.83(J=1.7Hz) and a doublet of a doublet at 4.84(J=4.1&1.7Hz) for the protons on the carbon bearing the oxygen of the tetrahydrofuran



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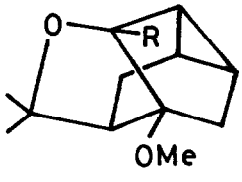

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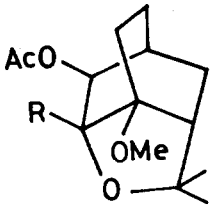

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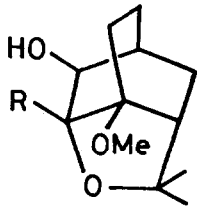
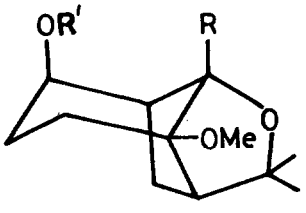
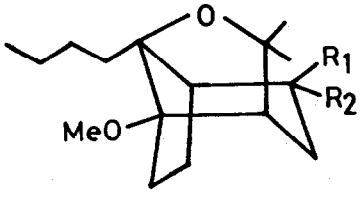


13

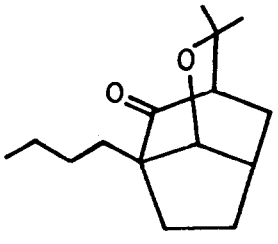
(a) R = H; (b) R = n-Butyl



14 (a) R = H; R' = Ac
(b) R = n-Bu; R'= H



15 (a) R_1 = H; R_2 = OH
(b) R_1 = R_2 = O



16

ring and the acetoxyl group respectively. The compound **14a** which is different from the acetate **12a** showed an absorption band at 1735cm^{-1} in its IR spectrum. The ^{1}H NMR spectrum had singlets at δ, 1.24, 1.3, 1.99 and 3.24 for the two methyls, acetoxyl and methoxyl protons besides signals at 4.32 and 4.78 as a doublet of doublets due to the protons on the carbon bearing the oxygen substituents. Solvolysis of **9a**, which resulted in the products **10a** or **11a**, **12a** and **14a**, can be explained by postulating[15] the nonclassical carbocations **17**,**18** and **19** as shown in the *scheme-1*. Hydrolysis of the acetate **12a** afforded the alcohol **13a**, which was oxidized with PCC in methylene chloride to the ketone **3a** in 85% yield from the acetate **12a**.

*SYNTHESIS OF 3-n-BUTYL-5,5-DIMETHYL-7-METHOXY-4-OXATRICYCLO[4.3.1.0^{3,7}]-DECAN-2-ONE **3b**.*

Synthesis of **3b** was undertaken as per the above sequence to establish the generality of the method. Reaction of the diene **4a** with potassium amide in liquid ammonia followed by quenching the resulting mesomeric anion **5** with 1-bromobutane afforded[16] a mixture of the dienes **4b** & **6b** in 85% yield. Refluxing this diene mixture with methyl acrylate at 90°C for 48h in the presence DCMA gave the *endo* adduct **7b** which was treated with excess of methylmagnesium iodide in dry ether affording the alcohol **8b**. Reaction of the alcohol **8b** with NBS in CH_2Cl_2 gave the bromoether **9b** in good yield.

The bromoether **9b**, upon reaction with silver acetate in acetic acid in the presence of a catalytic amount of iodine at 90°C for 2h gave a mixture of products from which the compound **10b** was isolated by chromatography in 40% yield. The structure of **10b** was assumed from its spectral data although the alternative structure **11b** could not be ruled out. The remaining product was hydrolysed with 10% aqueous methanolic KOH and the resulting alcohols were separated into the tricyclic alcohols (**13b**;10%), (**14b**;10%), (**15a**;10%) and the tricyclic ketone (**16**;20%). The structures of these compounds were deduced from their analytical and spectral data. The compound **16** showed an IR absorbtion at 1725 cm^{-1} typical of a keto group of the bicyclo[2.2.2]-octanone moiety. In addition, the absence of the methoxy resonance coupled with the presence of a signal due to the proton at C_2[δ,3.9(d,J=4Hz)] in the ^{1}H NMR spectrum established its structure. Further confirmation of the structures of **10b** and **16** by X-ray analysis is under progress. The tricyclic alcohol **13b**, on oxidation with PCC in CH_2Cl_2 afforded the desired tricyclic ketone **3b** in an overall yield of 9% from the adduct **7b**. The compound **3b** had an absorption band at 1725 cm^{-1} for the carbonyl group in its IR spectrum. The ^{1}H NMR spectrum showed resonances due to the methyl and methoxy protons at δ, 1.13, 1.36 and 3.27 respectively besides the CH and CH_2 protons.

PCC oxidation of **15a** gave the tricyclic ketone **15b**, the structure of which was deduced from its ^{1}H NMR spectrum, having signals at δ, 0.9, 1.22,

1.43 and 3.28 due to the methyl and methoxy protons respectively and confirmed[17] by its X-ray structural analysis. A perspective view of the molecule with the thermal ellipsoids at the 50% probability level is indicated in the *Fig 1*, shown below.

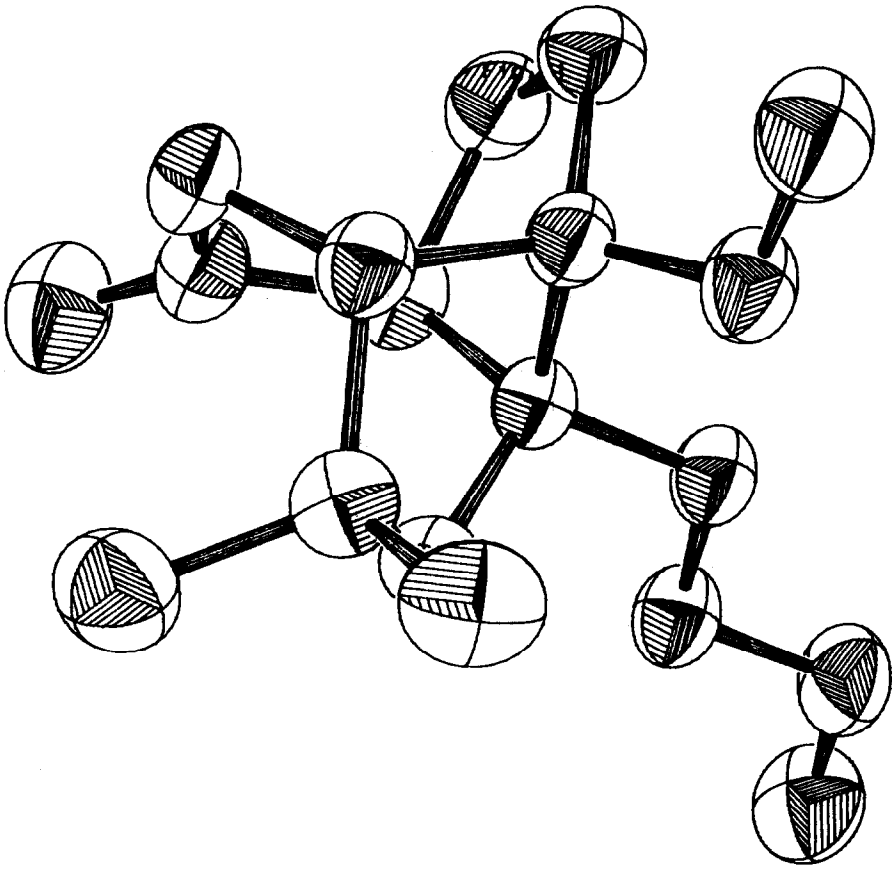
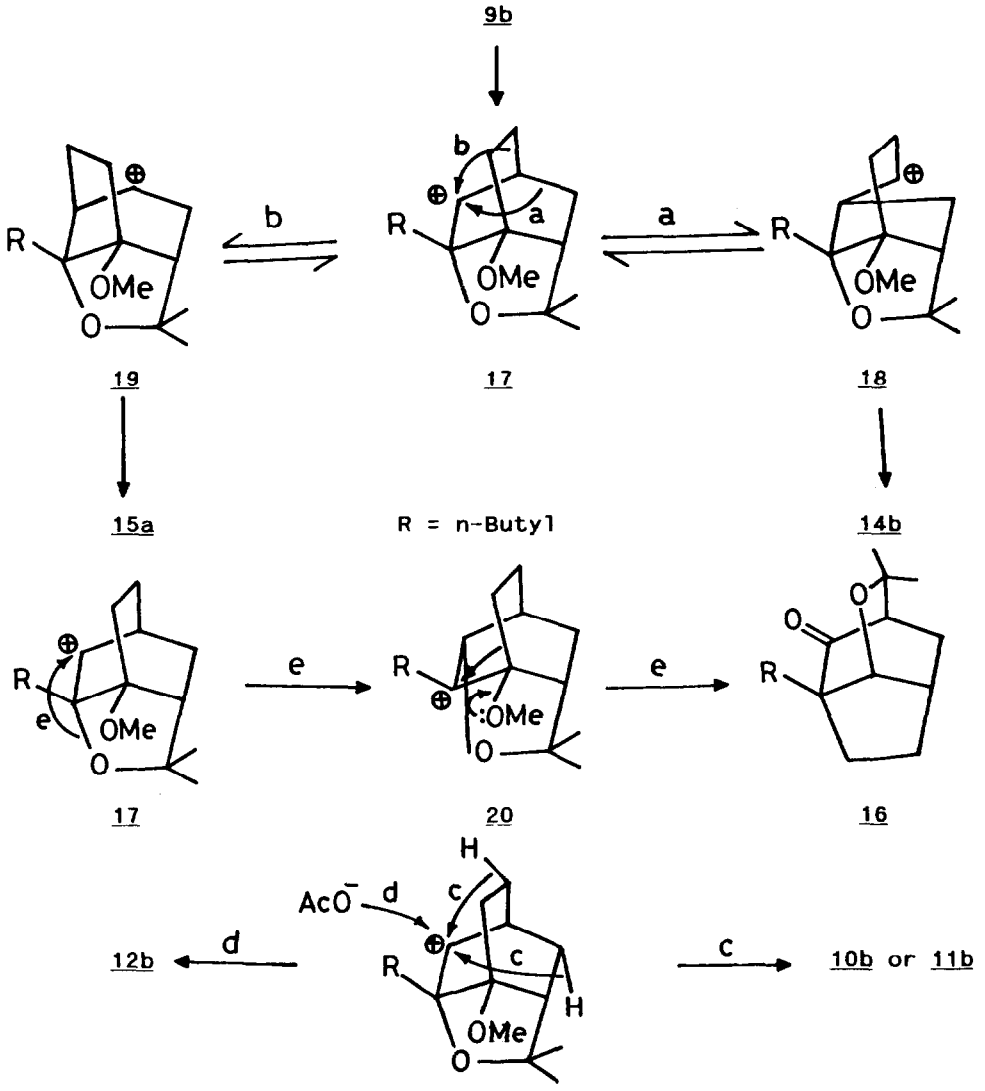


Fig 1

A probable mechanism for the formation of the products from the solvolysis of **9b** is depicted in *scheme 1* and involves the nonclassical carbocation **17** which is in equilibrium with its isomers **18** and **19** as indicated by *paths a & b*. The carbocation **19**, formed by the C_1-C_9 bond migration in **17**, yields the tricyclic compound **15a** while the carbocation **18**, resulting in the migration of the C_1-C_{10} bond in **17**, affords the compound **14b**. γ-Elimination of hydrogen from C_{10} or C_9 of the cation **17** as shown in *path c* results in the tetracyclicethers **10b** or **11b**. Direct quenching of the

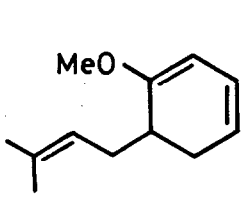
carbocation **17** leads to the product **12b** as indicated in *path d*. The ketone **16** is formed from the carbocation **17** as indicated in *path e* and involves a concerted migration of the C_3-O_4 & C_7-C_8 bonds which is triggered by the methoxy group as shown in the structure **20**.

Having achieved the synthesis of the tricyclic ketones **3a** and **3b**, the preparation of **3c**, a key subunit in morellins was undertaken.



Scheme 1

Alkylation of the mesomeric ion **5** with 3-methylbut-2-enyl bromide yielded a mixture of the alkylated dienes (**4c** & **21**) which on heating with methyl acrylate at 90°C in a sealed tube for 48h yielded only the adduct **22**. Since direct alkylation of **5** with prenyl bromide did not produce the required diene, alkylation was attempted with 2-(2-bromoethyl)-1,3-dioxolane[18], a masked aldehyde, which can be converted into the prenyl group when required. Alkylation of **5** with 2-(2-bromoethyl)-1,3-dioxolane gave a mixture which was subjected to Diels-Alder reaction with methyl acrylate resulting in the *endo* adduct **7c** in 20% yield. Addition of methylmagnesium iodide to **7c** afforded the alcohol **8c** which gave the bromo ether **9c** on treatment with NBS/CH_2Cl_2 . Solvolysis of **9c** did not yield any of the desired products.



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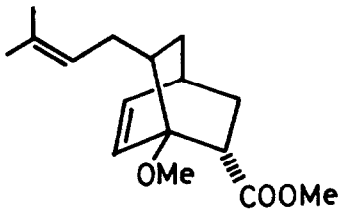

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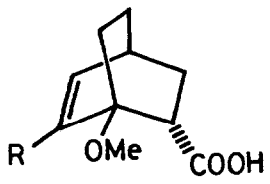

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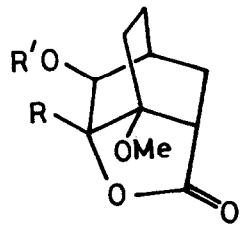

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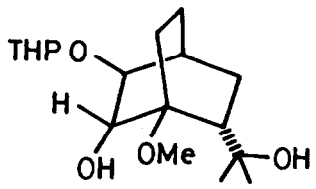
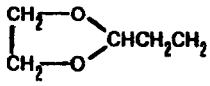


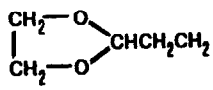
25

(a) R = H

(b) R = 

(a) R = R' = H

(b) R = H; R' = THP

(c) R' = H; R = 

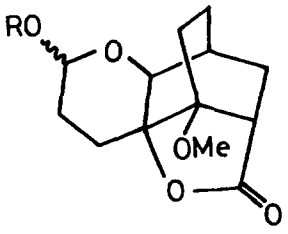
Since the halocyclisation route to the tricyclic ketone **3c** was unsuccessful, an alternative route was examined which involved the oxidative cyclisation of the adducts **23** using peracid.

Hydrolysis of the ester **7a** with aqueous methanolic KOH gave the acid **23a** which afforded the hydroxy-lactone **24a**, with per-formic acid. The proximity of the carboxyl group to the double bond triggers[19] its participation during epoxidation resulting in the hydroxy-lactone. The tetrahydropyranyl ether **24b** of the hydroxy-lactone **24a**, on reaction with

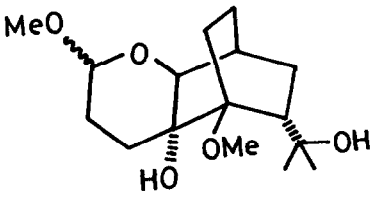
excess of methylmagnesium iodide afforded the diol **25** which was cyclodehydrated with PTS in benzene affording the hydroxy-ether **13a**, identical with the compound obtained by the halocyclisation route. PCC oxidation of **13a** gave the tricyclic ketone **3a** in 70% yield from the adduct **7a**.

SYNTHESIS OF 5,5-DIMETHYL-7-METHOXY-(3'-METHYL-2'-ENYL)-4-OXATRICYCLO-[4.3.1.$0^{3,7}$]DECAN-2-ONE **3c**.

Since the oxidative cyclisation route to the tricyclic ketone **3a** proved to be successful, synthesis of **3c** from the adduct **7c** was next examined. Hydrolysis of the ester **7c** with aqueous methanolic KOH gave the acid **23b** which afforded the hydroxylactone **24c** with m-chloroperbenzoic acid. Reaction of the tetrahydropyranyl ether of **24c** with excess of methylmagnesium iodide was unsuccessful. However hydrolysis of **24c** with pyridinium *para*-toluenesulphonate[20] in aqueous acetone afforded the lactone **26a**, which readily yielded a methyl ether **26b** with PTS in methanol. Reaction of **26b** with excess of methyl lithium yielded the diol **27** which was cyclodehydrated with PTS in benzene to the ether **28a**. Hydrolysis of **28a** with pyridinium *p*-toluenesulphonate in aqueous acetone afforded the hemiacetal **28b** which was oxidised with PCC to the δ-lactone **29** having the characteristic IR absorption at 1740 cm^{-1}. Reaction of **29** with excess methylmagnesium iodide resulted in the tricyclic diol **30** which was smoothly oxidized to the tricyclic compound **3d** having the IR bands at 3440,1730 cm^{-1}.



26
(a) R = H
(b) R = Me



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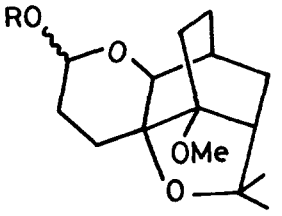
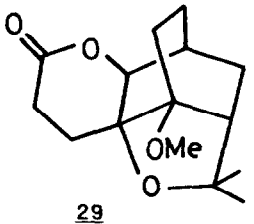
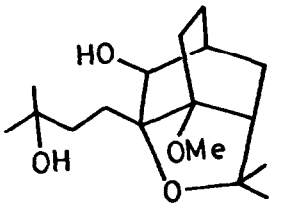


28
(a) R = Me
(b) R = H



29



30

Dehydration of **3d** with phosphoryl chloride and pyridine in the presence of catalytic amount of DMAP yielded a mixture of olefins **3c** and **3e** which could not be separated. However this mixture was readily isomerised with rhodium chloride[21] in isopropanol to give exclusively the tricyclic ketone **3c** (64% from **3d**) in an overall yield of 38% from **7c** having the IR absorption band at 1730 cm^{-1} for the carbonyl group. The ^{1}HNMR spectrum had signals at δ 1.33, 1.36, 1.67, 1.74 and 3.26 due to the methyl and methoxy groups besides the olefinic proton at 5.05 in addition to the CH and CH_2 protons.

In conclusion, a new and efficient method for the synthesis of 5,5-dimethyl-7-methoxy-4-oxatricyclo[4.3.1.$0^{3,7}$]decan-2-ones, a moiety present in the naturally occurring complex xanthone, morellin **1**, has been achieved.

EXPERIMENTAL

M.p.s and b.p.s are uncorrected. IR spectra were recorded as liquid films or nujol mulls on a Perkin-Elmer model 781 spectrometer. ^{1}H NMR spectra were recorded on a Varian T-60 & JEOL FX-90Q spectrometers in $CDCl_3$ unless otherwise stated. Chemical shifts are reported in ppm using TMS as internal standard. J values are given in Hz. Low and high resolution mass spectra were recorded on a JEOL MS-DX-303 with a built in direct inlet system. Microanalysis were carried out using a Carlo Erba 1106 instrument. Analytical TLC was performed on glass plates coated with Acme silica gel G (containing 13% calcium sulphate as the binder). Acme silica gel (60-120) was used for column chromatography. Work-up procedure involved dilution of the reaction mixture with water, extraction with ether, washing of the organic extract with water, brine and water followed by drying (Na_2SO_4) and evaporation of the solvent under reduced pressure. The residue was purified by chromatography on silica gel and the product was eluted with hexane containing ethyl acetate (5%).

1-Methoxycyclohexa-1,4-diene **4a**.-Sodium(9.2g,400 mmol) was added in portions to a stirred solution of anisole(10.8g,100 mmol) and ethanol (27g,600 mmol) in dry ammonia (300ml). After 30 min, excess sodium was destroyed by adding solid NH_4Cl. Ammonia was allowed to evaporate, water was added and extracted with hexane (3X100ml). Removal of the solvent gave 1-methoxycyclohexa-1,4-diene, **4a**(10.45g,95%);ν_{max}/cm^{-1}1690,1660;δ_H 2.7(m,4H, CH_2),3.46(s,3H,OMe),4.46(bs,1H,olefinic),5.66(s,2H,olefinic).

6-endoCarbomethoxy-1-methoxybicyclo[2.2.2]oct-2-ene **7a**.- 1-Methoxycyclohexa-1,4-diene, **4a** (5g,45 mmol), methyl acrylate(5ml), hydroquinone(10mg) and DCMA(10mg) were heated together in a sealed tube at 120° for 48 h. After cooling, excess of the methyl acrylate was removed under reduced pressure and the residue was worked up to afford the pure endo adduct **7a** (7.13g,80%);(Found:C,67.2;H,8.0;$C_{11}H_{16}O_3$ requires C,67.3 and H,8.2%);ν_{max}/cm^{-1} 1730,1210,1175;δ_H 1.42-2.02(m,6H),2.6(m,1H,bridge-head proton),2.9(dd,J=9& 5.8,1H,CHCOOMe),3.36(s,3H,OMe),3.64(s,3H,COOMe),6.26(m,2H,olefin);
HRMS: Found 196.1077;$C_{11}H_{16}O_3$ requires 196.1099.

6-endo-(1-Hydroxy-1-methylethyl)-1-methoxybicyclo[2.2.2.]oct-2-ene **8a**.- To a solution of methylmagnesium iodide in dry ether(50ml), prepared from Mg turnings(3.04g,123 mmol) was added dropwise with stirring, the adduct **7a** (7g,36 mmol) in ether(25ml) and the mixture was stirred for 12 h. The reaction mixture was cooled and worked up to give the alcohol **8a** (6.65g, 95%) as a viscous liquid,(Found:C,73.0;H,10.5;$C_{12}H_{20}O_2$ requires C,73.4 and H,10.3%);ν_{max}/cm^{-1} 3500,1105; δ_H 0.93(s,6H,2Me),1.38-2.0(m,7H),2.39(m,1H, bridgehead proton),3.34(s,3H,OMe),4.79(bs,1H,OH),6.13(m,2H,olefin).
HRMS:Found 196.1458;$C_{12}H_{20}O_2$ requires 196.1463.

2-Bromo-5,5-dimethyl-7-methoxy-4-oxatricyclo[4.3.1.$0^{3,7}$]decane **9a**.-A freshly recrystallised sample of N-bromosuccinimide(6.49g,36 mmol) was added to a stirred solution of the alcohol **8a** (6.5g,33 mmol) in dry CH_2Cl_2 (40ml), maintained at ice-salt temperature. After 6 h, additional CH_2Cl_2 was added and the organic layer was worked up to give the bromoether **9a** (8.69g, 95%) as a crystalline solid, m.p 84°C;(Found:C,52.3;H,6.9;$C_{12}H_{19}BrO_2$ requires C,52.1 and H,7.1%);ν_{max}/cm^{-1}1105,1040,725;δ_H 1.26(s,3H,Me),1.41(s,3H,Me), 1.82-2.2(m,8H),3.21(s,3H,OMe),4.21(dd,J=3.6&1.7,1H,CHBr),4.27(d,J=1.7,1H, HC-O); HRMS: Found 274.0565, $C_{12}H_{19}O_2Br$ requires 274.0569.

Solvolysis of the bromoether **9a**.-To the bromoether **9a** (4.25g,15.4 mmol) in glacial acetic acid(25ml) was added silver acetate(4.6g,27.6 mmol) and iodine(50mg) and the mixture heated at 90° for 12 h. The reaction mixture was filtered to remove the salts, diluted with water and extracted with benzene. The organic layer was worked-up to afford a mixture which was separated by chromatography into the following three compounds.

5,5-dimethyl-7-methoxy-4-oxatetracyclo[4.4.0.$0^{2,10}$.$0^{3,7}$]decane **10a**.-(1.05g, 35%);(Found:C,73.9;H,9.4;$C_{12}H_{18}O_2$ requires C,74.2 and H,9.3%);ν_{max}/cm^{-1}1170, 1080;δ_H1.35(s,6H,2Me),1.8-2.86(m,8H),3.21(s,3H,OMe),4.51(d,J=4.1,1H,HC-O); HRMS: Found 194.1318, $C_{12}H_{18}O_2$ requires 194.1307.

2-Acetoxy-5,5-dimethyl-7-methoxy-4-oxatricyclo[4.3.1.$0^{3,7}$]decane **12a**.-(391mg, 10%);(Found:C,66.2;H,8.5;$C_{14}H_{22}O_4$ requires C,66.1 and H,8.7%);ν_{max}/cm^{-1} 1730, 1235;δ_H 1.25(s,3H,Me),1.33-2.36(m,8H),1.41(s,3H,Me),2.06(s,3H,OCOMe),3.21(s, 3H,OMe),3.83(d,J=1.7,1H,CHOR),4.84(dd,J=4.1& 1.7,1H, CHOCOMe);
HRMS: Found 254.1518, $C_{14}H_{22}O_4$ requires 254.1518.

10-Acetoxy-4,4-dimethyl-7-methoxy-5-oxatricyclo[4.4.0.$0^{3,7}$]decane **14a**.-(391mg, 10%);(Found:C,65.9;H,8.8;$C_{14}H_{22}O_4$ requires C,66.1 and H,8.7%); ν_{max}/cm^{-1}1735,1250;δ_H 1.2-2.9(m,8H),1.24(s,3H,Me),1.30(s,3H,Me),1.99(s,3H, COMe),3.24(s,3H,OMe),4.32(dd,J=6.6&1.7,1H,HC-O),4.78(dd,J=11&6.6,1H,CHO COMe);HRMS:Found 254.1512, $C_{14}H_{22}O_4$ requires 254.1518.

5,5-Dimethyl-2-hydroxy-7-methoxy-4-oxatricyclo[4.3.1.$0^{3,7}$]decane **13a**.- The acetate **12a** (375mg,1.48 mmol) in methanol(2.5ml) and aqueous NaOH(0.5g in 2.5ml) and stirred at r.t. for 24 h. Methanol was distilled at reduced pressure and the residue worked up to give the alcohol **13a** (280mg,90%); (Found C,68.1;H,9.4;$C_{12}H_{20}O_3$ requires C, 67.9 and H,9.4%); ν_{max}/cm^{-1}3400,1045; δ_H1.16(s,3H,Me),1.2-2(m,8H),1.33(s,3H,Me),2.52(bs,1H,OH),3.13(s,3H,OMe),3.69 (d,J=1.7,1H,HC-O),3.84(dd,J=4.1&1.7,1H,CHOH).
HRMS: Found 212.1406, $C_{12}H_{20}O_3$ requires 212.1412.

5,5-Dimethyl-7-methoxy-4-oxatricyclo[4.3.1.$0^{3,7}$]decan-2-one **3a**.-To a solution of the alcohol **13a** (250mg,1.18 mmol) in CH_2Cl_2(1ml) was added pyridinium-chlorochromate(381mg,1.77mmol) and stirred for 30 min. The reaction mixture was filtered through a neutral alumina column and the solvent distilled to afford the ketone **3a** (224mg,95%).(Found: C,68.6; H, 8.6;$C_{12}H_{18}O_3$ requires C,68.7 and H,8.8%);ν_{max}/cm^{-1}1720,1060;δ_H 1.17(s,3H,Me),1.45(s,3H,Me),1.53-2.37(m,8H),3.26(s,3H,OMe),3.94(d,J=1.7,1H,HC-O).
HRMS: Found 210.1274 $C_{12}H_{18}O_3$ requires 210.1256.
6-n-Butyl-1-methoxycyclohexa-1,4-diene **4b**.- To a stirred solution of potassamide, prepared from potassium(2.15g,50 mmol), in liquid ammonia (150ml),1-methoxycyclohexa-1,4-diene **3a** (5.5g,50 mmol) was added and the resulting red solution was stirred for 20 min. 1-Bromobutane(13.7g,100 mmol) was then added to the mixture as rapidly as the exothermic reaction would allow and the mixture was stirred for 30 min. The Reaction mixture was worked-up to yield the diene **4b**;ν_{max}/cm^{-1}1690,1660,1610.
2-n-Butyl-6-endo carbomethoxy-1-methoxybicyclo[2.2.2]oct-2-ene **7b**.- The diene **4b**, methyl acrylate (6ml), hydroquinone (10mg) and DCMA (10mg) was heated in a sealed tube at 90° for 48 h. Excess of methyl acrylate was removed under reduced pressure and the residue on work-up yielded the adduct **7b** (9.45g,75%) as a liquid; (Found C,71.3;H,9.6;$C_{15}H_{24}O_3$ requires C, 71.4 and H,9.5%);ν_{max}/cm^{-1}1735,1210; δ_H 0.89(t,3H,CH_2Me),1.08-2.24(m,12H), 2.48(m,1H,bridgehead proton),3.05(dd,J=9&5.8,1H,CHCOOMe),3.35(s,3H,OMe), 3.61(s,3H,COOMe),5.84(dt,J=7&2,1H,olefin).
HRMS: Found 252.1724, $C_{15}H_{24}O_3$ requires 252.1725.
2-n-Butyl-6-endo-(1-hydroxy-1-methylethyl)-1-methoxybicyclo[2.2.2]oct-2-ene **8b**.- The adduct **7b** (6.3g,25 mmol) in dry ether (18ml) was added slowly to a cooled solution of methylmagnesium iodide in dry ether, prepared from Mg (1.82g,74.8 mmol) and methyl iodide and stirred for 12 h at r.t. The reaction mixture, on usual work-up, afforded **8b** (5.98g,95%) as a colorless liquid;(Found:C,71.6;H,9.5;$C_{16}H_{28}O_2$ requires C,71.4 and H,9.5%);ν_{max}/cm^{-1} 3500,1120; δ_H 0.98(s,3H,Me),1.03(s,3H,Me),1.03(t,3H,CH_2Me),1.15-2.44(m,13H), 3.4(s,3H,OMe),5.77(d,J=7,1H,olefin).
HRMS: Found 252.2083, $C_{16}H_{28}O_3$ requires 252.2089.
2-Bromo-3-n-butyl-5,5-dimethyl-7-methoxy-4-oxatricyclo[4.3.1.$0^{3,7}$]decane **9b**.- A mixture of the alcohol **8b** (5g,19.8 mmol) and N-bromosuccinimide (3.85g,21.6 mmol)in CH_2Cl_2(30ml) were stirred at -5°C for 6 h. Excess CH_2Cl_2 was added and the organic layer was worked up resulting in the bromo-ether **9b** (6.5g,100%) as a colorless liquid, (Found C,57.8; H,8.0, $C_{16}H_{27}O_2Br$ requires C,58.0 and H,8.2%); ν_{max}/cm^{-1} 1110,750;δ_H 0.91(t,3H,CH_2Me),1.25(s, 3H,Me),1.33(s,3H,Me),1.43-2.3(m,14H),3.17(s,3H,OMe),4.47(dd,J=3.3&1.7,1H, CHBr). m/z 330 and 332.
3-n-Butyl-5,5-dimethyl-7-methoxy-4-oxatetracyclo[4.4.0.$0^{2,10}$.$0^{3,7}$]decane **10b**.- A mixture of the bromoether **9b** (6g,18.1 mmol), silver acetate (5.44g, 32.6 mmol), iodine(50mg),in glacial acetic acid(27ml) was heated at 90° for 2h. The reaction mixture was worked up by extraction with benzene. Removal of the solvent from the organic extract yielded a crude mixture of products

from which the tetracyclic compound **10b** (1.81g,40%) was obtained by chromatography as a colorless liquid, (Found: C,76.5,H,10.5,$C_{16}H_{26}O_2$ requires C, 76.8 and H, 10.4%); ν_{max}/cm^{-1} 1160,1030; δ_H 0.92(t,3H,$(CH_2)_3$Me),1.24(s,3H, Me), 1.29(s,3H,Me),1.4-2.3(m,14H),3.16(s,3H,OMe); HRMS: Found 250.1944, $C_{16}H_{26}O_2$ requires 250.1933.

Further elution with hexane-ethyl acetate(4:1) yielded a mixture which could not be separated and was subjected to hydrolysis.

The crude mixture(2.81g) in methanol(10ml) was treated with an aqueous NaOH (2g in 10ml) and stirred at r.t. for 24h. Methanol was distilled, and the residue was extracted with ether (3X50ml). Removal of the solvent yielded a product which was chromatographed over silica gel. Elution with hexane-ethylacetate (22:3) afforded the following compounds.

3-n-Butyl-9,9-dimethyl-8-oxatricyclo[4.3.1.$0^{3,7}$]decan-2-one **16**.- (715mg), (20%) as a colorless liquid;(Found:C,76.1;H,10.3;$C_{15}H_{24}O_2$ requires C,76.2 and H,10.2%); ν_{max}/cm^{-1} 1725,1240; δ_H 0.92(t,3H,CH_2Me),1.16(s,3H,Me),1.28(s,3H,Me), 1.38-2.47(m,14H),3.9(d,J=4,1H,CHOR).

HRMS: Found 236.1768, $C_{15}H_{24}O_2$ requires 236.1776.

7-n-Butyl-5,5-dimethyl-2-hydroxy-8-methoxy-6-oxatricyclo[5.3.$0^{1,7}$.$0^{4,8}$]decane **15a**.- (405mg,10%) as a colorless liquid;(Found:C,71.8;H,10.3;$C_{16}H_{28}O_3$ requires C,71.6 and H,10.5%); ν_{max}/cm^{-1} 3520,1120;δ_H 0.92(t,3H,CH_2Me),1.4-2.4 (m,14H),1.52(s,6H,2Me),3.17(s,3H,OMe),3.58(d,J=6,1H,CHOH).

HRMS: Found 268.2007, $C_{16}H_{28}O_3$ requires 268.2039.

3-n-Butyl-5,5-dimethyl-2-hydroxy-7-methoxy-4-oxatricyclo[4.3.1.$0^{3,7}$]decane **13b**.- (405mg,10%);(Found:C,71.5;H,10.2;$C_{16}H_{28}O_3$ requires C,71.6 and H,10.5%); ν_{max}/cm^{-1} 3450,1110;δ_H 0.89(t,3H,CH_2Me),1.21(s,3H,Me),1.25-2.43(m,14H),1.33 (s,3H,Me),3.14(s,3H,OMe),3.95(d,J=4.1,1H,CHOH).

HRMS: Found 268.2005, $C_{16}H_{28}O_3$ requires 268.2039.

6-n-Butyl-4,4-dimethyl-10-hydroxy-7-methoxy-5-oxatricyclo[4.4.0.$0^{3,7}$]decane **14b**.-(405mg,10%);(Found:C,71.5;H,10.3;$C_{16}H_{28}O_3$ requires C,71.6 and H,10.5%); ν_{max}/cm^{-1} 3400,1115;δ_H 0.90(t,3H,CH_2Me),1.22(s,3H,Me),1.27(s,3H,Me),1.38-2.4 (m,14H),3.26(s,3H,OMe),3.87(dd,J=11&6.6,1H,CHOH).

HRMS: Found 268.2018; $C_{16}H_{28}O_3$ requires 268.2039.

3-n-Butyl-5,5-dimethyl-7-methoxy-4-oxatricyclo[4.3.1.$0^{3,7}$]decan-2-one **3b**.- PCC(300mg,1.4 mmol) was added to the alcohol **13b** (250mg,0.93 mmol) in CH_2Cl_2 (1ml) and stirred at r.t. for 30 minutes. The reaction mixture was filtered through a neutral alumina column to be rid of the chromium salts and the residue was worked to afford the ketone **3b** (235mg,95%);(Found:C,71.9;H,9.8; $C_{16}H_{26}O_3$ requires C,72.2 and H,9.8%); ν_{max}/cm^{-1} 1725,1105;δ_H 0.89 (t,3H,CH_2Me), 1.13(s,3H,Me),1.23-2.57(m,14H),1.36(s,3H,Me),3.27(s,3H,OMe).

HRMS: Found 266.1892;$C_{16}H_{26}O_3$ requires 266.1884.

7-n-Butyl-5,5-dimethyl-8-methoxy-6-oxatricyclo[5.3.$0^{1,7}$.$0^{4,8}$]decan-2-one **15b**.- To a solution of the alcohol **15a** (250mg,0.93 mmol) in CH_2Cl_2(1ml) was added PCC(300mg,1.4 mmol) and stirred at r.t.for 30 min. The reaction mixture was passed through a neutral alumina column and the solvent distilled to afford the ketone **15b** (235mg,95%) as a crystalline solid, m.p 92°C;(Found:C,72.3; H,9.7;$C_{16}H_{26}O_3$ requires C,72.2 and H,9.8%); ν_{max}/cm^{-1} 1720,1080;δ_H 0.90 (t,3H,

CH_2Me),1.22(s,3H,Me),1.3-2.73(m,14H),1.43(s,3H,Me),3.28(s,3H,OMe). HRMS: Found 266.1889;$C_{16}H_{26}O_3$ requires 266.1884.

2-(3,3-Ethylenedioxypropyl)-6-endo carbomethoxy-1-methoxybicyclo [2.2.2]-oct-2-ene **7c**.- To a solution of potassamide, prepared from potassium(2.15g, 55 mmol), in liquid ammonia(150ml), 1-methoxycyclohexa-1,4-diene **4a** (5.5g, 50 mmol) was added and the mixture stirred for 20 min. The resulting red solution was treated with 2-(2-bromoethyl)-1,3-dioxolane(18g,100 mmol). The reaction mixture was worked up to yield the diene **4c** which was directly used in the next step. ν_{max}/cm^{-1} 1690, 1660,1610.

A mixture of the above diene **4c**, methyl acrylate(6ml), hydroquinone (10mg) and DCMA(10mg) was heated at 135° for 48 h. Excess of the methyl acrylate was distilled at reduced pressure and the residue was worked up affording the adduct **7c** (2.96g,20%) as a colorless liquid;(Found:C,64.7; H,8.1;$C_{16}H_{24}O_5$ requires C,64.9 and H,8.1%); ν_{max}/cm^{-1} 1730,1180; δ_H 1.06-2.44 (m,10H),2.98(dd,J=9&5.8,1H,CHCOOMe),3.26(s,3H,OMe),3.53(s,3H,COOMe),3.81 (m,4H,OCH_2CH_2O),4.80(t,J=4.8,1H,OCHO),5.81(d,J=7,1H,olefine).
HRMS: Found 296.1635, $C_{16}H_{24}O_5$ requires 296.1624.

6-endo-Carboxy-1-methoxybicyclo[2.2.2]oct-2-ene **23a**.- To a solution of the adduct **7a** (1g,5.1 mmol) in methanol(2ml), was added an aqueous solution of KOH (500mg in 3ml) and refluxed for 6h. The solvent was removed and the reaction mixture was worked up to give the crude acid **23a** (836mg,90%) as a gum. ν_{max}/cm^{-1}1705,1235;δH(DMSO-d_6),1.33-1.83(m,6H),2.52(m,1H,bridgehead-H), 2.79(dd,J=9&6,1H,CHCOOH),3.3(s,3H,OMe),6.13(m,2H,olefins). This was used in the next step without purification.

10-Hydroxy-7-methoxy-5-oxatricyclo[4.3.1.$0^{3,7}$]decan-4-one **24a**.- H_2O_2 (750mg, 100 vol) was added to the acid **23a** (810mg,4.45 mmol) in 85% formic acid (2ml) and the mixture stirred at 60°C for 1h during which time it became homogeneous. The reaction mixture was worked up with ethyl acetate. Removal of the solvent from the dried extract followed by usual work-up furnished the hydroxy-lactone **24a** (775mg, 88%); m.p 93°C;(Found:C,60.4;H,7.1;$C_{10}H_{14}O_4$ requires C,60.6 and H,7.2%); ν_{max}/cm^{-1} 1780,1100; δ_H 1.26-2.49(m,7H),3.17(s, 3H,OMe),4.03(dd,J=4.1&1.7,1H,CHOH),4.25(d,J=1.7,1H,CHOR).
HRMS: Found 198.0890; $C_{10}H_{14}O_4$ requires 198.0890

*7-Methoxy-5-oxa-10-tetrahydropyranyloxytricyclo[4.3.1.$0^{3,7}$]decan-4-one***24b**.- A mixture of the hydroxy-lactone **24a** (760mg,3.84 mmol), dihydropyran(483mg, 5.75 mmol) and PTS(20mg) in CH_2Cl_2(10ml) was stirred at r.t. for 1h. Excess CH_2Cl_2 was added and the organic layer was worked up to afford the lactone **24b** (1.03g,95%) as a mixture of epimers,m.p 71°C;(Found:C,63.9;H,7.6; $C_{15}H_{22}O_5$ requires C,63.8 and H,7.9%); ν_{max}/cm^{-1} 1780,1105; δ_H 1.55-2.16(m,7H),2.45,2.55 (2bs,1H,CHCOO),3.22(2s,3H,OMe),3.98(dd,J=4.1&1.7,1H,CHOTHP),4.24 and 4.54 (2d,1.7,1H,CHOCOR),4.65 and 4.74(2bs,1H,OCHO).
HRMS: Found 282.1479,$C_{15}H_{22}O_5$ requires 282.1467.

2-endo Hydroxy-6-endo(1-hydroxy-1-methylethyl)-3-exo tetrahydropyranyloxy-1-methoxybicyclo[2.2.2]octane **25**.- To a solution of MeMgI in dry ether (10ml),[prepared from Mg turnings (302mg,12.9 mmol)] was added a solution of the lactone **24b** (1g,3.55 mmol) in dry ether(5ml) and stirred for 12h.

The reaction mixture was cooled, the complex destroyed by careful addition of a saturated solution of NH_4Cl and extracted with ether. The organic layer was worked up to yield the product **25** (1.05g,95%), m.p 165°C;(Found:C,64.6; H,9.6; $C_{17}H_{30}O_5$ reqires C,65.0 and H,9.6%); ν_{max}/cm^{-1} 3300,3220,1100; δ_H 1.06(s, 3H,Me),1.38(s,3H,Me),1.41-1.85(m,14H),3.13(2s,3H,OMe),3.26-3.89(m,6H), 4.50 (bs,1H,OCHO). The mass spectrum showed the molecular ion at m/z,230 due to the loss of the dihydropyran ring [M^+-84].

5,5-Dimethyl-2-hydroxy-7-methoxy-4-oxatricyclo[4.3.1.$0^{3,7}$]decane **13a**.-To a solution of the compound **25** (500mg,1.59 mmol) in dry benzene(3ml) was added PTS(20mg) and stirred at r.t. for 1h. The reaction mixture was diluted with benzene and worked up to afford a crude product which upon purification over silica gel and elution with hexane-ethyl acetate(17:3) afforded the alcohol **13a** (338mg,98%), identical with the sample obtained from the hydrolysis of the acetate **12a**.

6-endo Carboxy-2-(3,3-ethylenedioxypropyl)-1-methoxybicyclo[2.2.2]oct-2-ene **23b**.- To a solution of the adduct **7c** (500mg,1.69 mmol) in methanol(2ml) was added an aqueous solution of KOH(500mg in 3ml) and refluxed for 6h. The solvent was distilled from the reaction mixture, the residue was dissolved in water and extracted with ether to remove impurities. The aqueous layer was acidified and extracted with ethyl acetate(3x50 mmol). Removal of the solvent from the dried extract gave the acid **23b** (428mg,90%) as a gum which resisted crystallisation and was directly used in the next reaction. ν_{max}/cm^{-1} 1700; δ_H 3.4(s,3H,OMe),3.83(m,4H,OCH_2CH_2O),4.85(t,J=4.8,1H,OCHO), 5.86(d,J=7, 1H,olefin),9.42(bs,1H,COOH).

6-(3,3-Ethylenedioxypropyl)-10-hydroxy-5-oxa-7-methoxy-tricyclo[4.3.1.$0^{3,7}$] decan-4-one **24c**.- The acid **23b** (410mg,1.45 mmol) in CH_2Cl_2(4ml) was treated with m-chloroperbenzoic acid(376mg.,2.18 mmol) and stirred at r.t. for 6 h. The reaction mixture was diluted with CH_2Cl_2 and the organic layer was worked up to afford the lactone **24c** (411mg,95%) as a viscous liquid. ν_{max}/cm^{-1} 3480,1780,1100; δ_H1.4-2.44(m,11H),2.74(bs,2H,OH,CHCOO),3.18(s,3H,OMe),3.70 (m,4H,OCH_2CH_2O),4.0(d,J=4.1,1H,CHOH),4.91(t,6.4,1H,OCHO).

HRMS:Found 298.1411; $C_{15}H_{22}O_6$ requires 298.1416.

3,8-Dioxa-4-hydroxy-11-methoxytetracyclo[8.3.1.$0^{2,7}$.$0^{7,11}$]tetradecan-9-one **26a**.- A solution of the compound **24c** (400mg,1.34 mmol) in acetone(3ml) containing PPTS(10mg) was refluxed overnight. The solvent was removed under reduced pressure, diluted with ether and worked up to yield a crude product mixture which on purification by column chromatography over silica gel and elution with hexane-ethyl acetate(4:1) afforded an epimeric mixture of the hemiacetal **26a** (324mg,95%) as a viscous liquid. ν_{max}/cm^{-1} 3400,1780,1050; δ_H 1.44-2.57(m,11H),2.81(m,1H,CHCOO),3.21,3.27(2s,3H,OMe),4.09(d,J=4.1,1H,HC-O),4.31 and 5.3(s&t,J=6.63,1H,OCHO).

HRMS:Found 254.1142; $C_{13}H_{18}O_5$ requires 254.1153.

4,11-Dimethoxy-3,8-dioxatetracyclo[8.3.1.$0^{2,7}$.$0^{7,11}$]tetradecan-9-one **26b**.-A solution of the hemiacetal-lactone **26a** (310mg,1.22 mmol) in CH_2Cl_2(3ml) containing methanol(.5ml) and PTS(10mg) was stirred at r.t.for 4h. The solution was diluted with CH_2Cl_2 and the organic layer was worked up to

afford the compound **26b** (310mg,95%) as a solid, recrystallised from ether m.p 78°C;(Found:C,62.8;H,7.4,$C_{14}H_{20}O_5$ requires C,62.7 and H,7.5%);ν_{max}/cm^{-1} 1780,1045;δ_H 1.19-2.36(m,11H),2.71(d,J=7.6,1H,CHCOO),3.13(s,3H,OMe),3.28(s, 3H,OMe),3.87(d,J=4.1),4.71(t,J=7,1H,OCHO).
HRMS:Found 268.1306;$C_{14}H_{20}O_5$ requires 268.1311.

3,8-Dimethoxy-7-hydroxy-9-(1-hydroxy-1-methylethyl)tricyclo[6.2.2.$0^{2,7}$]-undecane **27**.- To a solution of MeLi in dry ether(5ml), prepared from lithium(26mg,3.75 mmol), was added the solution of the acetal **26b** (250mg, 0.93 mmol) in dry ether(3ml) under nitrogen. The reaction mixture was stirred at r.t. for 6 h. It was cooled and the complex destroyed by the carefull addition of a sat. solution of NH_4Cl. The organic layer was worked up to afford a crude product which on chromatography yielded the diol **27** (270mg, 85%) as a solid, crystallised from methanol,m.p 146°C;(Found C,63.8; H,9.5;$C_{16}H_{28}O_5$ requires C,64.0 and H,9.3%);ν_{max}/cm^{-1} 3280,1130;δ_H 1.59-2.07(m, 12H),1.13(s,3H,Me),1.43(s,3H,Me),3.2(s,3H,OMe),3.33(s,3H,OMe),3.77(bs,1H) 4.8(dd,J=7.7&4.1,1H,OCHO); HRMS:Found 300.1929;$C_{16}H_{28}O_5$ requires 300.1936.

4,11-Dimethoxy-9,9-dimethyl-3,8-dioxatetracyclo[8.3.1.$0^{2,7}$.$0^{7,11}$]tetradecane **28a**.- To a solution of the diol **27** (250mg,0.83 mmol) in dry benzene(2ml) was added PTS(10mg) and stirred at r.t. for 1h. The solution was diluted with benzene and the organic layer was worked up to afford the compound **28a** (223mg,95%), crystallised from methanol,m.p 87°C;(Found:C,68.2;H,9.0; $C_{16}H_{26}O_4$ requires C,68.1 and H,9.2%);ν_{max}/cm^{-1}1100,1030;δ_H 1.6-2.3(m,12H),1.25(s,3H, Me),1.35(s,3H,Me),3.14(s,3H,OMe),3.35(s,3H,OMe),3.84(d,J=4.1,1H,HC-O), 4.74 (t,J=6.7,1H,OCHO);HRMS:Found 282.1828;$C_{16}H_{26}O_4$ requires 282.1831.

9,9-Dimethyl-3,8-dioxa-4-hydroxy-11-methoxytetracyclo[8.3.1.$0^{2,7}$.$0^{7,11}$]-tetradecane **28b**.- A solution of the compound **28a** (210mg,0.74 mmol) in wet acetone(2ml) containing PPTS(5mg) was refluxed for 6 h. The solvent was distilled, diluted with ether and worked-up to yield a crude product which was purified by chromatography to afford the compound **28b** (189mg,95%) as a crystalline solid,m.p 135°C;ν_{max}/cm^{-1} 3600,1100;δ_H 1.23(s,3H,Me),1.35(s,3H, Me),1.5-2.3(m,13H),3.13(s,3H,OMe),3.98(d,J=4,1H,HC-O),5.25(t,J=7,1H,OCHO). HRMS:Found 268.1683;$C_{15}H_{24}O_4$ requires 268.1674.

9,9-Dimethyl-3,8-dioxa-11-methoxytetracyclo[8.3.1.$0^{2,7}$.$0^{7,11}$]tetra-decan-4-one **29**.- To a solution of the hemiacetal **28b** (175mg,0.65 mmol) in CH_2Cl_2(2ml), was added PCC (211mg,0.98 mmol) and let stir at r.t. for 30 minutes. The reaction mixture was diluted with CH_2Cl_2 and filtered through a neutral alumina column to get rid of the chromium salts. Removal of the solvent gave the lactone **29** (165mg,95%) which slowly solidified. This was crystal-lised from methanol,m.p 118°C;ν_{max}/cm^{-1} 1740,1050;δ_H 1.25(s,3H,Me),1.36(s,3H, Me),1.5-2.64(m,12H),3.14(s,3H,OMe),4.36(dd,J=4.1&1.7,1H,HCO).
HRMS:Found 266.1537 $C_{15}H_{22}O_4$ requires 266.1518.

5,5-Dimethyl-2-hydroxyl-3-(3-hydroxyl-3-methylbutyl)-7-methoxy-4-oxatri-cyclo [4.3.1.$0^{3,7}$]decane **30**.- To a cold solution of MeMgI in dry ether(3ml), prepared from Mg turnings(46mg,1.96 mmol), was added the lactone **29** (150mg) in dry ether(2ml) and stirred over-night. The reaction mixture was cooled and a sat. solution of NH_4Cl added carefully to destroy the complex. The

reaction mixture was extracted with ether and worked up to yield the crude product which was purified by chromatography resulting in the diol **30** (169mg,95%) as a crystalline solid, m.p 200°C(dec); ν_{max}/cm^{-1} 3380,1100; δ_H 1.23(s,9H,3Me), 1.3(s,3H,Me),1.48-2.26(m,12H),2.81(bs,2H,2OH),3.13 (s,3H, OMe),3.96(d,J=4.1,1H,CHOH). HRMS:Found 298.2152; $C_{17}H_{30}O_4$ requires 298.2144.

5,5-Dimethyl-3-(3-hydroxyl-3-methylbutyl)-7-methoxy-4-oxatricyclo-[4.3.1.$0^{3,7}$]decan-2-one **3d**.- To a solution of the diol **30** (140mg, 0.47 mmol) in CH_2Cl_2(1ml), PCC(152mg, 0.71 mmol) was added and stirred at r.t. for 30 min. It was diluted with CH_2Cl_2 and filtered through a neutral alumina column. Distillation of the solvent gave the keto-alcohol **3d** (132mg,95%) as a liquid. ν_{max}/cm^{-1} 3440,1730,1090; δ_H 1.13(s,3H,Me),1.22(s,3H,Me),1.38(s,3H, Me),1.45(s,3H,Me),1.56-2.54(m,12H),3.13(s,3H,OMe),3.23(s,1H,OH). HRMS:Found 296.1997; $C_{17}H_{28}O_4$ requires 296.1988.

5,5-Dimethyl-7-methoxy-3-(3-methylbut-2-enyl)-4-oxatricyclo[4.3.1.$0^{3,7}$]decan-2-one **3c**.-To a solution of the keto-alcohol **3d** (50mg,0.17 mmol) in pyridine (0.5ml) containing DMAP(5mg), a few drops of freshly distilled $POCl_3$ was added and stirred at r.t. for 12 h. The solvent was removed under reduced pressure and the residue was extracted with ether. Usual work-up followed by chromatography afforded a mixture of **3c** and **3e** (38mg,80%).

The above mixture(5mg) in i-PrOH(1ml),and $RhCl_3$(1mg) was heated at 85°C for 10 min. Removal of the solvent at reduced pressure followed by purification by chromatography afforded the pure tricyclic ketone **3c** (4mg,80%) as a colorless liquid.(Found:C,73.2;H,9.5; $C_{17}H_{26}O_3$ requires C,73.4 and H,9.4%); ν_{max}/cm^{-1} 1730,1230; δ_H 1.13(s,3H,Me),1.36(s,3H,Me),1.6-2.71(m, 10H),1.67(s, 3H,Me),1.74(s,3H,Me),3.26(s,3H,OMe),5.05(t,J=7,1H,olefin). HRMS:Found 278.1881; $C_{17}H_{26}O_3$ requires 278.1882.

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