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Rearrangement in *endo* Annulated Bicyclo[2.2.2]Octenone Framework: A New Route to Functionalized Tricyclo[5.3.1.$0^{2,6}$] Ring System and *cis:syn:cis* Tricyclopentanoids

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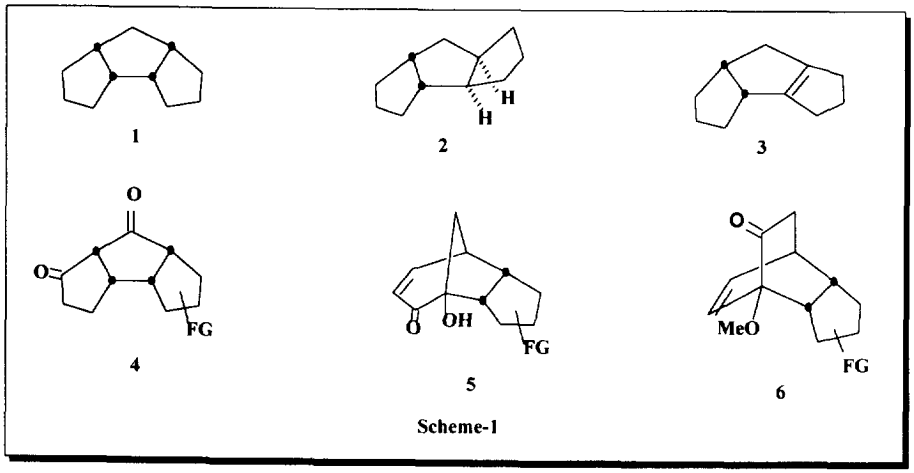
Abstract: Synthesis of 1-hydroxy[5.3.1.$0^{2,6}$]undecadienones **15-18** from annulated bicyclo[2.2.2]octenones **10-14** *via* carbocationic rearrangement has been described and a new route to *cis:syn:cis* tricyclopentanoids **25**, **26** from **15**, **18** reported.

Tricyclopentanoids having *cis:syn:cis* geometry such as **1** are versatile intermediates for the synthesis of a variety of novel polyhedra such as peristylane, dodecahedrane and other related systems.[1-3] Recently *cis:syn:cis* tricyclopentanoids have also been employed as preorganized unit in the synthesis of molecular clefts and related hosts.[4] While a large number of methods have been developed for the synthesis of the thermodynamically more stable *cis:anti:cis* fused tricyclopentanoids **2**,[5] only a few methods are available for the less stable *cis:syn:cis* isomer of type **1**.[6] This is due to the fact that classical methods of cyclopentane annulation are not suitable for *cis:syn:cis* triquinane synthesis and generally indirect sequences such as hydrogenation of tricyclic systems **3** are employed for this purpose.[7]

In connection with a synthetic endeavour towards polyquinane based hosts we desired a synthesis of functionalized *cis:syn:cis* tricyclopentanoids of type **4**(scheme-1) from readily available starting precursors. In this context it was envisaged that the *cis:syn:cis* triquinane of type **4** would be readily available from the *endo* tricyclic keto alcohol **5** which is endowed with requisite stereochemical and functional features for its elaboration to **4.** It was further thought that the key intermediate **5** having annulated bicyclo[3.2.1] framework should be amenable through a regioselective carbocationic



Scheme-1

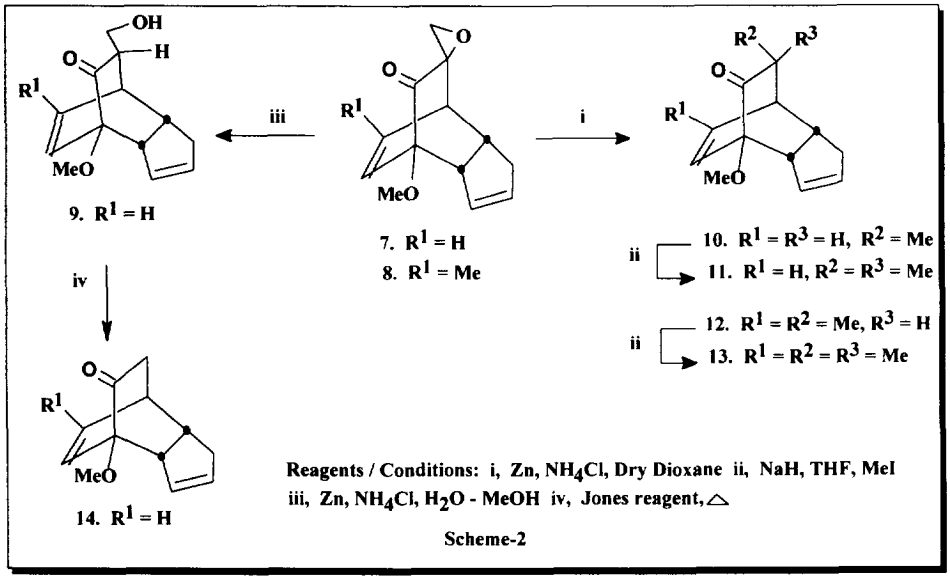
rearrangement of the readily available precursors of type **6**, especially since such type of rearrangements are known to occur in simple bicyclic systems.[8] It may be mentioned here that there are no direct routes even to the bicyclo[5.3.1.$0^{2,6}$] ring systems of type **5**, though this ring system represents the carbocyclic core of gymnomitrol, an important class of naturally occurring sesquiterpene.[9]

In this paper we wish to describe a facile rearrangement of *endo* tricyclic systems **10-14** to **15-18** respectively and a new route to *cis:syn:cis* tricyclopentanoids **25** and **26**. The requisite ketones **10-14** were prepared from the readily available keto epoxides **7, 8** following a procedure developed in our laboratory[10](scheme-2).

The keto epoxide **7** was reduced with zinc in dry dioxane containing ammonium chloride to give the monomethyl ketone **10** as a *syn:anti* mixture (300 MHz, ^{1}H NMR) in good yield. The ketone **10** was alkylated with methyl iodide in the presence of sodium hydride in tetrahydrofuran to give dimethyl analogue **11**. Similar transformations on keto epoxide **8** gave the corresponding analogues **12** and **13**, respectively. The parent system **14** was obtained *via* reduction of **7** with zinc in methanol-water followed by oxidation of the resulting β-keto alcohol to β-keto acid and subsequent decarboxylation(scheme-2). The structures of all the compounds **10-14** were clearly revealed through their high field(300 MHz) ^{1}H NMR, ^{13}C NMR and other analytical data.

In order to explore the acid catalysed rearrangement of annulated bicyclo[2.2.2]octenones, we first treated the compound **11** with *p*-toluenesulfonic acid in refluxing benzene following a procedure by

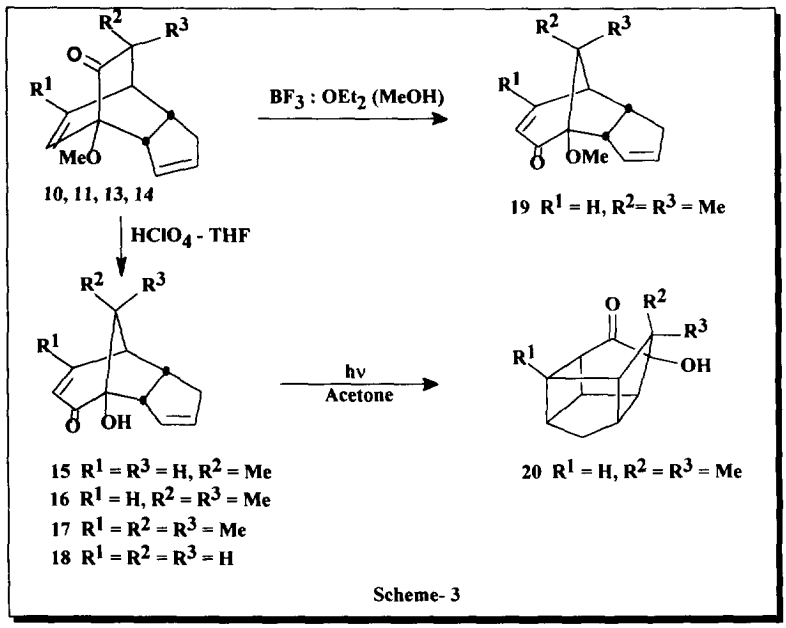
Rogers and co-workers.[8] However it gave a complex mixture of products. The treatment of ketone **11** with $BF_3.OEt_2$ in dry methanol at -50°C though furnished the rearranged product **19**, the rearrangement was slow and incomplete.[11] Soon after this observation we discovered that perchloric acid(70%) in tetrahydrofuran is the most suitable reagent for the above rearrangement. Thus a brief treatment of the



Scheme-2

compound **11** with perchloric acid(70%) gave the rearranged product **16** in excellent yield(86%)(scheme-3). The structure of the product **16** was deduced as follows. The IR spectrum of **16** showed strong absorption bands at 1690 and 3350 cm^{-1} corresponding to α,β-unsaturated carbonyl and hydroxyl groups respectively. Its high field ^1H NMR(300 MHz) displayed resonances at δ 7.1(dd, J_1=9Hz and J_2=6Hz, 1H), 6.1(d, J=6Hz, 1H) characteristic of β and α protons of α,β-enone moiety.[12] The signal for other olefinic protons were observed at δ 5.6 and 5.55 as multiplets. Furthermore a signal was observed at δ 4.0(br s) for OH proton. The methyl group showed resonances at δ 0.85(s, 3H) and 1.2(s, 3H) corresponding to *syn* and *anti* methyl groups. Other resonances for methine and methylene protons appeared at δ 3.5(m, 1H), 3.35(complex m, 1H), 2.7(t, J=6Hz, 1H), 2.42(dd of part of AB system, J_{AB}=15Hz, J_2=6Hz, J_3=3Hz, 1H, CH_2 proton) and 2.0(m of AB, J_{AB}=15Hz, 1H, CH_2 proton). The lack of signal for methoxy group in the ^1H NMR spectrum and other spectral features described above, coupled with mechanistic considerations[8] suggested the structure **16** for the rearranged product which was also supported from its ^{13}C NMR spectrum. Thus the ^{13}C spectrum of **16** showed a signal at δ 202.97

for a conjugated carbonyl carbon and signals at δ 153.39, 132.37, 130.28, 128.10 for four olefinic carbon atoms.[13] The two quaternary carbons C-O and C-C- appeared at δ 90.47, 53.89 respectively, among other signals for methine, methylene and methyl carbons. The *endo* structure of the rearranged product **16** was proved through its facile intramolecular $\pi^2s+\pi^2s$ photoreaction to the novel trishomocubane derivative **20**(scheme-3).

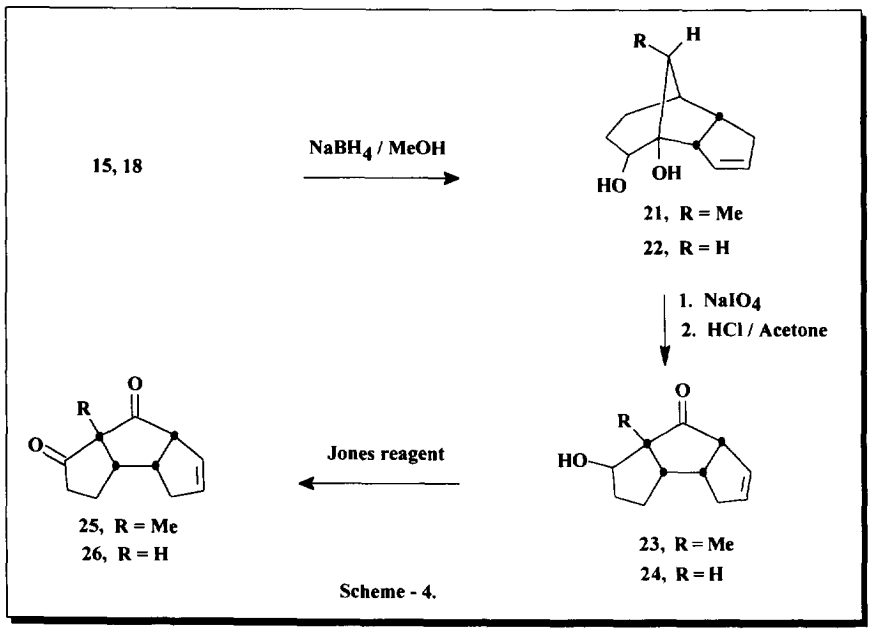


Scheme- 3

Following the above observation, we also treated other ketones **10, 13** and **14** with perchloric acid in tetrahydrofuran which gave the corresponding rearranged products **15**, **17** and **18** respectively in good yields(85%). The structures of enones **15**, **17** and **18** were also clearly revealed through their spectral and analytical data.

Towards synthesis of *cis:syn:cis* tricyclopentanoids the enone **15** was reduced with sodium borohydride[14] at -10°C to give the diol **21** whose ^{1}H NMR(270 MHz) clearly revealed that borohydride had reduced both the enone double bond as well as the carbonyl group. The diol **21** was cleaved with sodium metaperiodate and the resulting keto aldehyde was immediately subjected to aldol condensation with HCl in acetone[15] to give two stereoisomers of keto alcohol **23** which were oxidized with Jones' reagent[16] to give the dione **25**(scheme-4). The structure of the dione was established through spectral and analytical data. Thus the IR spectrum of **25** showed strong absorption bands at 1758, 1712 cm^{-1} for cyclopentanone carbonyls. Its ^{1}H NMR(300 MHz) exhibited signals at δ 5.82(complex m, 2H) and

3.68(m of d, J=8Hz, 1H) for olefinic protons and the proton at allylic ring junction respectively. It further showed signals at δ 3.26 (d of dd, J_1=16Hz, J_2=8Hz and J_3=2Hz, 1H), 2.8-2.62(cluster of m, 2H), 2.52(d with structure, J=16Hz, 1H), 2.36-2.2(several m, 3H). The ^{13}C NMR showed characteristic resonances at δ 212.8 and 212.0 for the carbonyl groups in addition to signals at δ 133.6, 128.5 for olefinic carbons. The other eight carbons appeared at δ 66.7(quaternary carbon), 59.0, 49.0, 37.2, 36.2, 34.6, 21.2 and 18.5(for methine, methylene and methyl carbons). Similarly the parent tricyclopentanoid **26**(scheme-4) was synthesised from **18** following the above mentioned sequence. The structure of the ene dione **26** is fully consistent with its spectral data.



Scheme - 4.

In summary we have described a facile route to 1-hydroxytricyclo [5.2.2.$0^{2,6}$]undecadienones via rearrangement of the appropriate annulated bicyclo[2.2.2]octenones and demonstrated the synthetic potential of the above rearrangement towards linearly fused *cis:syn:cis* tricyclopentanoids.

EXPERIMENTAL :

General remarks: IR spectra were recorded on Perkin-Elmer 681 and Nicolet FT-IR instrument Impact 400. UV spectra were recorded on Shimadzu 260 instrument. ^{1}H NMR(300 MHz) and ^{13}C NMR(75 MHZ) were recorded on Varian VXR 300 instrument. ^{1}H NMR(500 MHz) and ^{13}C NMR(125 MHz) were recorded on GE omega NMR instrument. All the samples were dilute solutions in $CDCl_3$ with $SiMe_4$ as internal standard. Elemental analyses were performed on a CEST 1106 instrument. Mass

spectra were recorded on HP GCD 1800A mass spectrometer. Melting points were determined on a Veego apparatus of Buchi type and are uncorrected. All organic extracts were dried on anhydrous sodium sulfate. Reactions were monitored with thin layer chromatography and spots were visualized with iodine vapour.

The epoxy ketones **7, 8** and the compounds **10-13** were prepared following a procedure developed in our laboratory.[10]

8-Hydroxymethyl-1-methoxytricyclo[5.2.2.$0^{2,6}$]undeca-3,10-dien-9-one (9):

To a suspension of zinc(20g) in methanol(60ml) and water(15ml), was added NH_4Cl(4g) and **7**(4.0g, 0.018mol) and the reaction mixture was stirred at room temperature(~30°C) for 4h. Zinc was filtered off on a celite bed and methanol was removed under reduced pressure. Water(20ml) was added to the residue and extracted with CH_2Cl_2(4x20ml). The organic extract was washed with brine and dried. Removal of the solvent and chromatography on silica gel gave **9**(3.5g, 86.8%). IR(neat) ν_{max}: 3445, 1726 cm^{-1}. UV λ_{max}(MeOH): 305 nm. ^1H NMR(300 MHz, $CDCl_3$): δ 6.42(dd, J_1=8.4Hz, J_2=6.6Hz, 1H, γ-H of β,γ-enone), 6.14(d, J=8.4Hz, 1H, β-H of β,γ-enone), 5.74(m, 1H, olefinic H), 5.60(m, 1H, olefinic H), 3.91(m, 1H), 3.70(complex m, 1H), 3.54(s, 3H, OCH_3), 3.15(m of d, J=8.3Hz, 1H, methine H), 3.03(m, 1H, methine H), 2.92-2.78(complex m, 2H, methylene H), 2.58(m of d, J=18Hz, 1H, methylene H), 2.33(m of d, J=18Hz, 1H, methylene H), 2.01(m, 1H). ^{13}C NMR(75 MHz, $CDCl_3$) 213.28(CO), 134.18, 133.65, 129.41, 128.26(olefinic carbons), 87.76, 64.22, 62.07, 53.95, 50.28, 39.43, 39.06, 36.33. Mass (m/z): 220(M^+), 192(M^+-18)

1-Methoxytricyclo[5.2.2.$0^{2,6}$]undeca-3,10-dien-9-one (14):

The keto alcohol **9**(2.0g, 9.2mmol) was dissolved in acetone(20ml) and treated with Jones' reagent at 0°C, till the starting material disappeared(TLC). Acetone was removed under reduced pressure, water (20ml) was added to the residue and extracted with ethyl acetate (4x20ml). The organic layer was concentrated and then treated with saturated solution of $NaHCO_3$. The aqueous layer was neutralized with Conc. HCl and extracted again with ethyl acetate. The organic extract was washed with brine and dried. Removal of solvent gave the crude acid [IR (neat)ν_{max}: 3400 cm^{-1}] which was decarboxylated by refluxing in THF-H_2O(1:4) mixture for 4h. Ethyl acetate was added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with ethyl acetate(3x20ml) and the combined organic extract was washed with brine and dried. The solvent was removed in vacuo and the residue was chromatographed on silica gel. Elution with EtOAc-light petroleum(bp 60-80°C)(2:98) gave **14**(0.63g, overall yield 34%). IR(neat) ν_{max}: 1720 cm^{-1}. ^1H NMR(300 MHz, $CDCl_3$): δ 6.33(dd, J_1=8.7Hz, J_2=6.4Hz, 1H, γ-H of β,γ-enone), 6.10(d, J=8.7Hz, 1H, β-H of β,γ-enone), 5.74(m of d, J=7.8Hz, 1H, olefinic H), 5.60(d with structure, J=7.9Hz, 1H, olefinic H), 3.57(s, 3H, OCH_3), 3.26(m of d,

J=9Hz, 1H, methine H), 2.96(m, 1H, methine H), 2.77(m of d, J=9Hz, 1H, methine H), 2.60(m of d, J=18Hz, 1H, methylene H), 2.15(d, J=2.7Hz, 2H, $COCH_2$), 2.00(m of d, J=18Hz, 1H, methylene H). ^{13}C NMR(75 MHz, $CDCl_3$): δ 210.62(CO), 133.83, 132.82, 129.58, 128.45(olefinic carbons), 87.52, 53.70, 52.48, 41.21, 40.22, 39.58, 36.70. Mass(m/z): 190(M^+)

1-Hydroxy-11-methyltricyclo[5.3.1.$0^{2,6}$]undeca-3,8-dien-10-one (15):

To a solution of the methoxy ketone **10**(1.05g, 5.14mmol) in tetrahydrofuran(15ml) was added $HClO_4$(70%, 5ml) and stirred at room temperature(~30°C) for 15 minutes. Tetrahydrofuran was removed under reduced pressure and the residue neutralised with a saturated solution of $NaHCO_3$. The aqueous layer was extracted with ether(3x20ml). The combined organic extract was washed with brine and dried. Removal of the solvent and chromatography furnished **15** as a white crystalline solid(0.874 g, 89.45%) which was recrystallized from EtOAc-light petroleum(bp 60-80°C) (1:9). mp 106°C. IR(KBr) ν_{max}: 3348, 1683 cm^{-1}. UV λ_{max}(MeOH): 277.8 nm. ^1H NMR(270 MHz, $CDCl_3$): δ 7.3(m, 1H, β-H of α,β-enone), 5.98(d, J=5.3Hz, 1H, α-H of α,β-enone), 5.6(merged m, 1H, olefinic H), 5.4(merged m, 1H, olefinic H), 4.05(s, 1H, OH), 3.5 and 3.3(m, 2H, methine H), 2.85(m, 1H), 2.45(m, 1H), 2.0(m, 1H), 1.1(d, 3H, CH_3). Mass(m/z): 190(M^+), 124(M^+-C_5H_6). Analysis: Found C, 75.71; H, 7.67% Calcd. for $C_{11}H_{16}O_2$ C, 75.78; H, 7.36%.

1-Hydroxy-11,11-dimethyltricyclo[5.3.1.$0^{2,6}$]undeca-3,8-dien-10-one (16):

A solution of **11**(0.2g, 0.98mmol) in tetrahydrofuran(5ml) was treated with $HClO_4$(70%, 1.5ml) and stirred at room temperature(~30°C) for 12h. Usual workup as described above, followed by chromatography on silica gel gave the rearranged product **16**(0.15g, 86.20%). IR(neat) ν_{max}: 3355, 1676 cm^{-1}. UV λ_{max}(MeOH): 278 nm. ^1H NMR(300 MHz, $CDCl_3$): δ 7.10(dd, J_1=9Hz, J_2=7Hz, 1H, β-H of α,β-enone), 6.10(d, J=9Hz, 1H, α-H of α,β-enone), 5.60(m, 1H, olefinic H), 5.53(m, 1H, olefinic H), 4.05(br s, 1H, OH), 3.52(br m of d, J=7Hz, 1H, methine H), 3.34(complex m, 1H, methine H), 2.72(dd, J_1=J_2=7Hz, 1H, methine H), 2.44(m of dd, J_1=18Hz, J_2=10Hz, 1H, methylene H), 2.20(m of d, J=18Hz, 1H, methylene H), 1.2(s, 3H, CH_3), 0.84(s, 3H, CH_3). ^{13}C NMR(75 MHz, $CDCl_3$): δ 202.9(CO), 153.3(β-carbon of α,β-enone), 132.3, 130.2, 128.1(other olefinic carbons), 90.4, 59.0, 53.8, 50.9, 40.1, 34.3, 22.1, 19.3. Mass(m/z): 204(M^+)

1-Hydroxy-8,11,11-trimethyltricyclo[5.2.1.$0^{2,6}$]undeca-3,8-dien-10-one (17):

To a solution of **13**(0.2g, 0.91mmol) in tetrahydrofuran(5ml) was added $HClO_4$(70%, 1.5ml) and stirred at room temperature(~30°C) for 12h. Usual workup as described above, followed by chromatography on silica gel gave **17**(0.16g, 84.82%). IR(neat) ν_{max}: 3445, 1677 cm^{-1}. UV λ_{max}(MeOH): 277 nm. ^1H NMR(300 MHz, $CDCl_3$): δ 5.91(m, 1H, α-H of α,β-enone), 5.53(superimposed m, 2H, olefinic H), 4.0(s, 1H, OH), 3.52(m of d, J=9Hz, 1H, methine H), 3.33(complex m, 1H, methine H),

2.50(d, J=6.7Hz, 1H, methine H), 2.40(m of d, J_1=18Hz, J_2=9Hz, 1H, methylene H), 2.04(d, J=2Hz, 3H, CH_3), 1.95(s, 3H, CH_3), 1.93(m of d, J=18Hz, 1H, methylene H), 0.99(s, 3H, CH_3). ^{13}C NMR(75 MHz, $CDCl_3$): δ 202.2(CO), 166.7(β-carbon of α,β-enone), 132.8, 129.4, 124.4(other olefinic carbons), 89.4, 58.6, 56.9, 53.8, 39.2, 33.8, 26.73, 22.1, 19.0. Mass(m/z): 218(M^+)

1-Hydroxytricyclo[5.2.1.$0^{2,6}$]undeca-3,8-dien-10-one (18):

The ketone **14**(0.5g, 2.6mmol) was rearranged as described for **15** to give the hydroxy enone **18** as a white solid(0.362g, 78.3%) which was recrystallized with EtOAc-light petroleum(bp 60-80°C)(1.5:8.5). mp 126-128°C. IR(KBr) ν_{max}: 3453, 1683 cm^{-1}. UV λ_{max}(MeOH): 274.4 nm. ^{1}H NMR(500 MHz, $CDCl_3$): δ 7.25(m of d, J=6Hz, 1H, β-H of α,β-enone), 6.15(d, J=6Hz, 1H, α-H of α,β-enone), 5.6(m, 1H, olefinic H), 5.55(m, 1H, olefinic H), 4.14(s, 1H, OH), 3.43(m of d, J=9Hz, 1H, methine H), 3.3(m, 1H), 3.1(m, 1H), 2.43(d of ddd, J_1=18Hz, J_2=9Hz, J_3=6Hz, 1H, methylene H), 2.16(m, 1H), 2.05(cluster of m, 2H). ^{13}C NMR(125 MHz, $CDCl_3$): δ 203.4(CO), 156.9, 133.0, 131.0, 128.7(olefinic carbons), 87.7, 60.74, 47.8, 43.5, 41.2, 35.4. Mass(m/z): 176(M^+)

1-Hydroxypentacyclo[5.3.1.0.^{2,6}0.^{3,9}0^{4,8}]undeca-10-one (20):

A solution of **16**(0.2 g, 0.98 mmol) in acetone(200ml) was irradiated with a mercury vapour lamp(200 W, medium pressure) in a pyrex vessel for 2h. Removal of the solvent and chromatography on silica gel gave **20**(0.13 g, 65%). mp 80°C. IR ν_{max}(KBr): 3460, 1749 cm^{-1}. UV λ_{max}(MeOH): 293.8 nm. ^{1}H NMR(60 MHz, $CDCl_3$): δ 3.2-2.6(m, 6H), 2.35(m, 1H), 1.7(m, 2H), 1.05(s, 3H, CH_3), 0.95(s, 3H, CH_3). Mass(m/z): 204(M^+)

1,10-Dihydroxy-11-methyltricyclo[5.3.1.$0^{2,6}$]undeca-3-ene (21):

To a solution of the enone **15**(0.18g, 0.94mmol) in dry methanol(10ml) at -10°C was added $NaBH_4$(0.53g, 1.41mmol) and stirred for 0.5h. Methanol was removed under reduced presure, water(5ml) was added to the residue and extracted with $CHCl_3$(4x10 ml). The organic extract was washed with brine and dried. Removal of the solvent followed by chromatography gave **21** as a white solid(0.158g, 86.5%), which was recrystallized from EtOAc-light petroleum(bp 60-80°C)(2:8). mp 97-98°C. IR(KBr) ν_{max}: 3369 cm^{-1}. ^{1}H NMR(270 MHz, $CDCl_3$): δ 5.8(merged m, 2H, olefinic H), 3.6 and 3.3(m, 1H, H-COH), 3.1(m, 1H, methine H), 2.8-2.0(cluster of m, 4H), 1.9-1.2(cluster of m, 6H), 1.0(d, J=7Hz, 3H, CH_3). Mass(m/z): 194(M^+). Analysis: Found C, 74.5; H, 9.4%; $C_{12}H_{18}O_2$ requires C, 74.2; H, 9.2%.

1,10-Dihydroxytricyclo[5.3.1.$0^{2,6}$]undeca-3-ene (22):

To a solution of the rearranged enone **18**(0.23g, 1.3mmol) in dry methanol at -10°C was added $NaBH_4$(0.74g, 1.95mmol) and stirred for 0.5h. Usual workup as described for **21**, followed by

chromatography gave **22**(0.166g, 70.2%) as a white solid which was recrystallized from EtOAc-light petroleum(bp 60-80°C)(2:8). mp 183-185°C. IR(KBr)ν_{max}: 3401 cm^{-1}. ^1H NMR(60 MHz, $CDCl_3$): δ 5.8(m, 2H, olefinic H), 3.7(m, 1H), 3.15(m, 2H), 2.75(m, 1H), 2.4-1.4(cluster of m, 8H). Mass(m/z): 180(M^+), 162(M^+-18)

8-Methyl-9-hydroxytricyclo[6.3.0.$0^{2,6}$]undeca-4-en-7-one (23):

To a solution of the diol **21**(0.40g, 2.08mmol) in 1:1 THF-H_2O(20ml), $NaIO_4$(0.629g, 3.09mmol) was added and stirred at 10°C for 0.5h. The reaction mixture was filtered and the filtrate saturated with NaCl. The organic layer was separated and the aqueous layer extracted with ether(3x20ml). The combined organic extract was washed with brine and dried. Removal of the solvent gave a keto aldehyde [IR(neat) ν_{max}: 1730 cm^{-1}. ^1H NMR(60 MHz, $CDCl_3$): δ 9.8(1H, CHO)] which was used for the next step without further purification as follows. The aldehyde thus obtained was dissolved in acetone(50ml), HCl(3N, 3ml) was added and stirred under nitrogen atmosphere at room temperature(~30°C) for 12h. $NaHCO_3$(5g) was added and stirring was further continued for 15 min. The reaction mixture was filtered and the solvent was removed under reduced pressure. Water(10ml) was added to the residue and extracted with CH_2Cl_2(3x10ml). The organic extract was washed with brine and dried. Removal of the solvent gave a 1:1 stereoisomeric mixture of aldol products(0.32g, 80%) which were seperated on silica gel. Elution with EtOAc-light petroleum(bp 60-80°C) (0.5:9.5) gave the keto alcohol **23**(fast moving isomer). IR(neat) ν_{max}: 3500, 1720 cm^{-1}. UV λ_{max}(MeOH): 290 nm. ^1H NMR(300 MHz, $CDCl_3$): δ 5.80(m, 1H, olefinic H), 5.68(m, 1H, olefinic H), 3.83(dd, $J_1=J_2=6Hz$, 1H, H-COH), 3.56(m of d, J=9Hz, 1H, methine H), 3.48(br s, 1H, OH), 3.06(d of ddd, $J_1=18Hz$, $J_2=\sim7.5Hz$, $J_3=\sim2Hz$, 1H, methylene H), 2.56(m of d, J=9Hz, 1H, methine H), 2.46-2.28(cluster of m, 2H), 1.84(m, 1H), 1.70-1.28 (complex m, 3H), 1.24(s, 3H, CH_3). Mass(m/z): 192(M^+). Further elution with EtOAc-light petroleum(bp 60-80°C)(1:9) gave the other stereoisomer of **23**. IR(neat) ν_{max}: 3440, 1720 cm^{-1}. UV λ_{max}(MeOH): 294.8 nm. ^1H NMR(300 MHz, $CDCl_3$): δ 5.76 (m, 1H, olefinic H), 5.70(m, 1H, olefinic H), 4.21(dd, $J_1=J_2=6Hz$, 1H, H-COH), 3.57(m of d, J=9Hz, 1H, methine H), 3.1(d of ddd, $J_1=18Hz$, $J_2=\sim7.5Hz$, $J_3=\sim2Hz$, 1H, methylene H), 2.64-2.40(cluster of m, 3H), 1.8(m, 3H), 1.7(br s, 1H, OH), 1.52(m, 1H), 1.24(m, 1H), 1.17(s, 3H, CH_3). Mass(m/z): 192(M^+)

9-Hydroxytricyclo[6.3.0.$0^{2,6}$]undeca-4-en-7-one (24):

To a solution of the diol **22**(0.5g, 2.8mmol) in 1:1 THF-H_2O(20ml), $NaIO_4$ (1.40g, 6.5mmol) was added and stirred at room temperature(~30°C) for 0.5h. The reaction mixture was filtered and the filtrate saturated with NaCl. The organic layer was separated and the aqueous layer extracted with ether(3x20ml). The combined organic extract was washed with brine and dried. Removal of the solvent gave a keto aldehyde [IR(neat) ν_{max}: 1700 cm^{-1}. ^1H NMR(60 MHz, $CDCl_3$): 9.8(1H, CHO)]. Without further purification the keto aldehyde was dissolved in THF(50ml) and HCl(3N, 3ml) was added. The

reaction mixture was stirred at room temperature(~30°C) under inert atmosphere for two days after which $NaHCO_3$(5g) was added and stirring continued for 15 minutes. The reaction mixture was filtered and the solvent removed under reduced pressure. Water(10ml) was added to the residue and extracted with CH_2Cl_2(3x10ml). Removal of the solvent gave a 1:1 mixture of stereoisomeric aldol products **24**(0.22g, 44%) which was separated on silica gel. Elution with EtOAc-light petroleum(bp 60-80°C)(0.7:9.3) gave the fast moving isomer of **24**. IR(neat) ν_{max}: 3450, 1733 cm^{-1}. UV λ_{max}(MeOH): 277.2 nm. ^1H NMR(300 MHz, $CDCl_3$): δ 5.82(m, 1H, olefinic H), 5.69(m, 1H, olefinic H), 4.38(br s, 1H, OH), 3.51(m, 1H), 3.22(m, 1H, H-COH), 3.1(m of d, J=18Hz, 1H, methylene H), 2.86(m, 2H), 2.6-2.44(cluster of m, 2H), 1.76-1.58(complex m, 4H). Mass(m/z): 178(M^+), 160(M^+-18). Further elution with EtOAc:light petroleum(bp 60-80°C)(1:9) gave another isomer of **24**. IR(neat) ν_{max}: 3430, 1733 cm^{-1}. ^1H NMR(60 MHz, $CDCl_3$): δ 5.85(m, 2H, olefinic H), 4.4(m, 1H), 3.5(m, 1H), 3.2-2.4(cluster of m, 5H), 2.2-1.3(cluster of m, 5H). Mass(m/z): 178(M^+)

8-Methyltricyclo[6.3.0.$0^{2,6}$]undeca-4-en-7,9-dione (25):

To a solution of **23**(0.4g, 2.08mmol) in acetone(15ml), Jones' reagent was added at 0°C while stirring. Acetone was removed under reduced pressure. Water(10ml) was added and extracted with ether(3x10ml). The ether extract was washed with brine and dried. The solvent was removed and the residue chromatographed on silica gel to furnish the tricyclic dione **25** as a white crystalline solid(0.37g, 89%). mp 86°C. IR(KBr) ν_{max}: 1758 and 1710 cm^{-1}. UV λ_{max}(MeOH): 310.6 nm. ^1H NMR(300 MHz, $CDCl_3$): δ 3.6(d of ddd, J_1=18Hz, J_2=~7.5Hz, J_3=~2Hz, 1H, methylene H), 2.74(m, 1H), 2.64(m of d, J=9Hz, 1H, methine H), 2.52(m of d, J=18Hz, 1H, methylene H), 2.36-2.01 (cluster of m, 3H), 1.58(m of d, J=18Hz, 1H, methylene H), 1.24(s, 3H, CH_3). ^{13}C NMR(75 MHz, $CDCl_3$): δ 212.8 and 212.09(CO), 133.63, 128.52(olefinic carbons), 66.72, 59.05, 49.08, 37.23, 36.24, 34.60, 21.28, 18.58. Mass (m/z): 190(M^+)

Tricyclo[6.3.0.$0^{2,6}$]undeca-4-en-7,9-dione (26):

To a solution of **24**(0.11g, 0.61mmol) in acetone(10ml) at 0°C was added Jones' reagent while stirring. Acetone was removed under reduced pressure, water(10ml) was added and extracted with ether(3x10ml). The ether extract was washed with brine and dried. Removal of the solvent followed by chromatography on silica gel gave the dione **26**(0.08g, 74%). IR(neat) ν_{max}: 1760 and 1716 cm^{-1}. UV λ_{max}(MeOH): 303.8 nm. ^1H NMR(300 MHz, $CDCl_3$): δ 5.84(m, 1H, olefinic H), 5.78(m, 1H, olefinic H), 3.6(m, 1H, methine H), 3.31-3.18(merged m, 3H), 2.62(m, 1H), 2.52(m of d, J=18Hz, 1H, methylene H), 2.34-2.12(complex m, 3H), 1.64(m, 1H). Mass(m/z): 176(M^+)

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