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Cyclopentanoid Allylsilanes in Synthesis of Di- and Triquinanes. A Stereoselective Synthesis of (±)- Hirsutene

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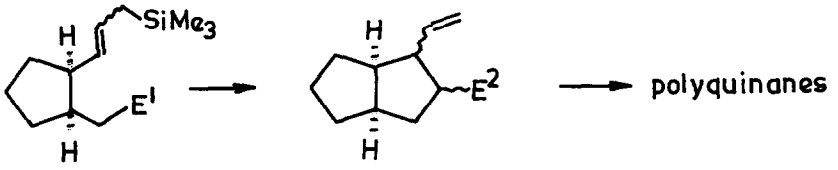
Abstract: A new general route to *cis*-1,2-disubstituted cyclopentanoid allylsilanes is described based on intramolecular ene reaction of activated 1,6-dienes featuring a homoallylsilane unit as the ene donor. In addition, application of these allylsilanes to the synthesis of some di- and triquinanes including the fungal metabolite (±)- hirsutene is presented.

As part of our research program directed toward the synthesis of polyquinane based natural products,[1] an efficient methodology for the synthesis of *cis*-1,2-disubstituted cyclopentanoid allylsilanes with a built-in electrophilic centre of the type **1** was needed (eq 1).[2,3] It appeared that such allylic silanes would allow rapid entry into functionalized diquinanes **2** which may further be elaborated into the desired polyquinanes. We report herein the details of our work that led to the development of a new approach to these species e.g., **1** based on intramolecular Alder-ene reaction of substituted 1,6-dienes featuring a homoallylsilane unit as the ene donor and application of these allylsilanes to the synthesis of some di- and triquinanes including the fungal metabolite (±)-hirsutene.[4]



(1)

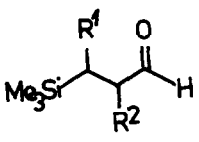
1 **2**

Our interest in this work was spurred by some special considerations : (i) in contrast to inter- and intramolecular Diels-Alder reactions which have been used by various groups[5] for the synthesis of functionalized allylsilanes, the ene reaction[6] which entails high levels of stereoselectivity has never been exploited for the synthesis of allylsilanes,[7] and (ii) although the ene reactions generally require elevated temperatures for success, these seldom exceed 500°C at which substituted allylsilanes are known to undergo scrambling by rapid 1, 3-sigmatropic shifts.[8] Thus, allylsilanes should survive the ene reaction conditons.

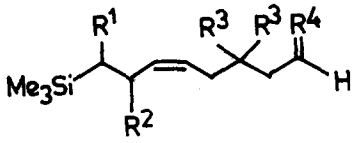
RESULTS AND DISCUSSION

The preparation of activated 1,6-dienes **15-18** used in this study is described below. Schlosser-Wittig olefination[9] of β-silyl aldehydes **3**,[10] **4**,[10] and **5**[11] with ylide **19**[9] gave carbinols **6**, **8** and **10** in 58-61% yields. Generation of the ylide **19** from **20** needs some comments. Schlosser originally reported[9] generation of **19** simply by rapid stirring of a mixture of **20** and sodium amide (2 equivalents) in tetrahydrofuran at room temperature. After a few unsuccessful runs, it was found out that *sonication*[12] *of a mixture of* **20** *and sodium amide in tetrahydrofuran at room temperature rapidly generates* **19** *as a brick-red solution.* For the preparation of carbinol

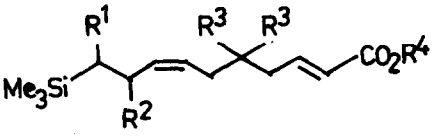
13 a somewhat different protocol was followed. Monoprotection[13] of 3,3-dimethyl-1,5-pentanediol (**21**) gave **22** (45%) after chromatographic separation from **23** (20%). **23** could be deprotected under acidic conditions to give the starting diol **21** (89%) which was recycled to improve the overall yield of **22**. Swern oxidation[14] of **22** furnished **24** (80%) which was subjected to Bestmann-Wittig olefination[15] with the ylide **25** prepared from **26**[16] with $NaN(SiMe_3)_2$ to give **12** in 61% yield. Deprotection of **12** gave **13** in almost quantitative yield. The configuration of the ene unit in **6**, **8**, **10** and **13** was tentatively assigned as *Z* since Schlosser-Wittig[9] and Bestmann-Wittig[15] condensations are well known for their high *Z*-selectivity (≥ 98%). Incidentally, in the case of **14**, double irradiation experiments confirmed the presence of the *Z* ene unit (vide experimental). Oxidation of **6**, **8**, **10** and **13** gave **7**, **9**, **11** and **14** which were transformed via Horner-Wardsworth- Emmons[17] reaction to the desired 1,6-dienes **15-18** in good overall yields. The purity of these compounds was ascertained from GC and high-field ^{1}H- and ^{13}C-NMR studies. The *Z* geometry of the ene units in these compounds was specifically chosen in view of the literature precedent[18] of enhanced *cis*-selectivity for the formation of cyclopentane ring systems.



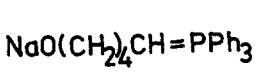
3, $R^1 = R^2 = H$
4, R^1=Me; R^2=H
5, R^1=H; R^2=Me



6, R^1=R^2=R^3=H; R^4= H,OH
7, R^1=R^2=R^3=H; R^4=O
8, R^1=Me; R^2=R^3=H; R^4= H,OH
9, R^1=Me; R^2=R^3=H; R^4=O
10, R^2=Me; R^1=R^3=H; R^4= H,OH
11, R^2=Me; R^1=R^3=H; R^4=O
12, R^1=R^2=H; R^3=Me; R^4= H,OTHP
13, R^1=R^2=H; R^3=Me; R^4= H,OH
14, R^1=R^2=H; R^3=Me; R^4=O



15, R^1=R^2=R^3=H; R^4=Et
16, R^1=R^4=Me; R^2=R^3=H
17, R^1=R^3=H; R^2=R^4=Me
18, R^1=R^2=H; R^3=Me; R^4=Et



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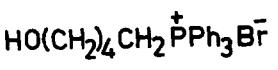
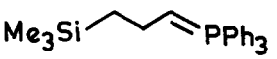


20

21, R^1=H; R^2= H,OH
22, R^1=THP; R^2=H,OH
23, R^1=THP; R^2=H,OTHP
24, R^1=THP; R^2=O



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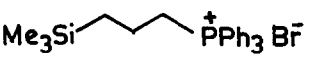


26

The thermolytic ene cyclizations were carried out in sealed pyrex tubes in an atmosphere of argon using a 5% solution of **15-18** in toluene (Table 1). As shown in the table the expected ene reactions occurred smoothly

leading to the allylsilanes **27**, **28** and **30** in near quantitative yields. It may be mentioned here that yields in these reactions suffer if air is not purged out properly with argon so as to ensure a strict inert atmosphere. Incidentally, **17** remained unchanged under these conditions and thwarted all attempts at its cyclization even at elevated temperatures for longer reaction periods.

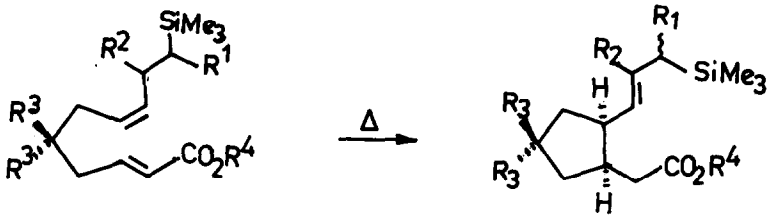


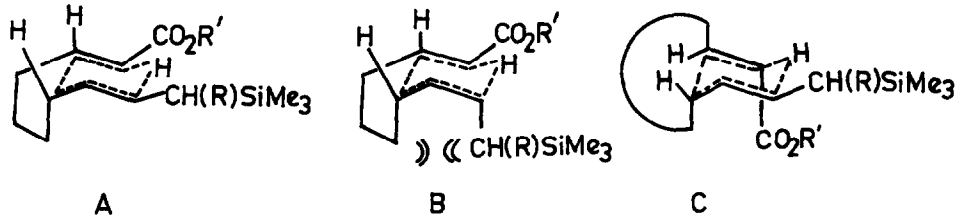
Table 1. Synthesis of Cyclopentanoid Allylsilanes.

Educt	R^1	R^2	R^3	R^4	Reaction Conditions[a]	Product	Yield[b] [%]
15	H	H	H	Et	252°/45h	**27**	98
16	Me	H	H	Me	243°/16h	**28**	93
17	H	Me	H	Me	243°/16h	**29**	0
18	H	H	Me	Et	245°/30h	**30**	97

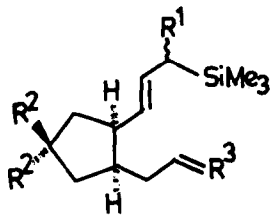
[a] Reactions were not monitored except in the case **16** → **28**.
[b] Isolated yield after distillation of crude product.

The stereochemistry of **27**, **28** and **30** rests on high-field ^{1}H- and ^{13}C-NMR as well as some chemical transformations (vide infra). **27** and **30** are essentially free from any of their stereoisomers (^{1}H- and ^{13}C-NMR, GC-MS), whereas **28** is a mixture (~1 : 1 from ^{13}C-NMR) of diastereomers. The geometry of the allylsilane unit in all these compounds (**27**, **28** and **30**) is exclusively *E* (^{1}H-NMR). This is noteworthy since literature information indicating preference for the formation of *E*- olefins in intramolecular ene reactions is sparse.[19]

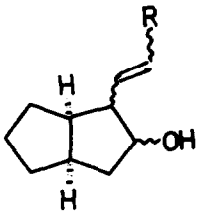
The exclusive formation of *E*-allylsilanes **27**, **28** and **30** is accountable in terms of the relevant transition states[20] namely, **A** which is favoured over **B** due to 1,3-diaxial interactions. The other transition state e.g., **C** leading to the 1,2-*trans*- disubstituted product is discarded due to obvious angle strain reasons. The recalcitrance of **17** towards cyclization is presumably due to unavoidable 1,3-diaxial interactions which result by introduction of a methyl group β to the TMS group in **A**.



The *cis*-1,2-disubstituted cyclopentanoid allylsilanes e.g., **27**, **28**, **30** and derivatives thereof should be valuable intermediates for the synthesis of various di- and triquinanes. The utility of **27** and **28** for some functionalized diquinane synthesis is shown below.



31, $R^1=R^2=H$; $R^3=H,OH$
32, $R^1=Me$; $R^2=H$; $R^3=H,OH$
33, $R^1=R^2=H$; $R^3=O$
34, $R^1=Me$; $R^2=H$; $R^3=O$
35, $R^1=H$; $R^2=Me$; $R^3=H,OH$
36, $R^1=H$; $R^2=Me$; $R^3=O$



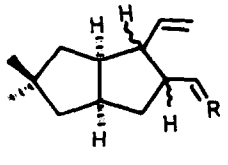
37, R = H
38, R=Me

Reduction of **27** and **28** with $LiAlH_4$ gave **31** and **32** which on subsequent oxidation furnished **33** and **34** in good overall yields. $TiCl_4$-induced ring closure[21] of **33** and **34** smoothly gave the carbinols **37** and **38**. Incidentally, this ring closure also established the *cis*-stereochemistry of the side chains in the original allylsilanes **27** and **28**. It should be pointed out that the allylsilane mediated ring closure processes (**33** → **37** and **34** → **38**) are remarkably stereoselective. GC-MS of **37** shows one major (~ 90%) isomer with two minor isomeric components. GC-MS of **38** also reveals the presence of one major (~90%) isomer with another isomeric component. However, the complete stereochemical identification of **37** and **38** was not done.

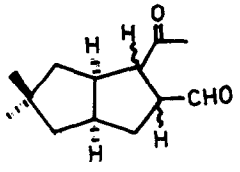
Having thus established the utility of cyclopentanoid allylsilanes for the synthesis of functionalized diquinanes, we felt well-suited to tackle a natural product total synthesis; (±)-hirsutene (**39**)[22] was selected as the initial target molecule. Incidentally, hirsutene (**39**) has served as a prototype for the synthesis of linear polyquinanes and has frequently been used to illustrate newer methods for construction of condensed cyclopentane rings.

To this end, **30** was reduced with $LiAlH_4$ to give **35** which on oxidation[23] (PDC/AcOH/4A Mol. Sieve) afforded the aldehyde **36** in good overall yield (72%). **36** was next converted[24] (Me_3SI/NaH/DMSO) to **40** (60%) which underwent a facile Lewis acid ($TiCl_4/CH_2Cl_2$/- 80°C) induced ring closure[25] to give the carbinol **41** (72%) as a mixture (vide experimental) of stereoisomers. Oxidation (PCC) of **41** furnished **42** (73%) which on further oxidation[26] ($PdCl_2/CuCl/O_2$/DMF-H_2O/55°) gave **43** (76%). Base-catalysed intramolecular aldolization[27] served to channel the stereoisomeric mixture **43** into the pure *cis, anti, cis*- triquinane **44** (mp. 63°C). Finally, catalytic hydrogenation of **44** over Pt-C yielded **45** (90%), the spectral data (IR, ^{1}H- & ^{13}C-NMR) of which were found to be identical to those for the same ketone described by Little and Muller[22j]. Since **45** has previously been converted[22j] to (±) -hirsutene (**39**), the present synthesis was complete.

40



41, R=H, OH
42, R=O



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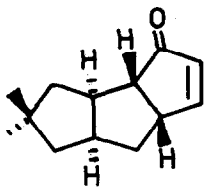

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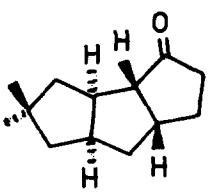

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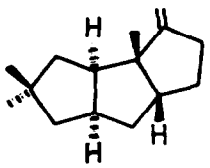

39 (hirsutene)

In conclusion, a new route to the structurally intriguing and biologically significant tricycloundecane ring system and to hirsutene itself is described which takes advantage of two rapidly growing areas of endeavour namely, intramolecular Alder ene reactions and allylsilane mediated ring closure reactions and which is potentially applicable to other members of this group of natural products.

Acknowledgement. The support of DST(SERC), New Delhi [23 (3p-17)/83/STP-II] is gratefuly acknowledged. We are also indebted to Dr. C. Fehr (Firmenich, Geneva) for high-field ^{1}H- & ^{13}C-NMR, GC-MS and capillary GC work. The CSIR, New Delhi is thanked for the award of a Senior Research Fellowship (to Satapathi). Prof. R.D. Little is thanked for providing comparison spectra (^{1}H- &^{13}C- NMR) for authentic **45**.

EXPERIMENTAL SECTION[28]

Preparation of 3, 4, 5

The β-silyl aldehydes **3** and **4** were prepared by published procedure.[10] **5**[11] was prepared from the corresponding methyl ester[29] by reduction with LAH followed by Swern oxidation of the latter.

(Z)-8-(Trimethylsilyl)-5-octenol (6)

A suspension of 5-hydroxypentyltriphenylphosphonium bromide **(20)**[9] (7.7 g, 17.9 mmol) and freshly prepared sodium amide [prepared from sodium metal (0.89 g, 34.8 mg atom) and dry ammonia (150 mL) following standard procedure and evaporation of ammonia followed by exhaustive pumping] in tetrahydrofuran (50 mL) was sonicated (Bransonic 221, 48 KHz) at room temperature for 30 min under argon. During this period the reaction mixture developed a brick- red colour. This was cooled to -78° C and a solution of 3- (trimethylsilyl)-propanal **(3)**[10] (2.2 g, 17.2 mmol) in dry tetrahydrofuran (10 mL) was added to it with stirring over a period of 20 min. During the addition slow disappearance of the red colour was noticed. Stirring was continued for 30 min at the same temperature and the reaction mixture brought to room temperature. This was diluted with ice-cold water (120 mL) and extracted with ether. The combined ethereal extract was washed with brine and dried ($MgSO_4$). Removal of solvent yielded a gummy residue which was dissolved in petroleum ether (60-80°C)-ethyl acetate (88:12) and filtered through a bed of silica gel (20g) to remove the major amount of triphenylphosphine oxide. Evaporation of the solvent gave a pale yellow oil which on chromatography over silica gel using ethyl acetate-petroleum ether (60-80° C) (5:95) as eluent afforded **6** as a colourless oil (2.05g, 60%) : b.p. 109-110°C/0.1 torr (bath); IR (film) 3340 (b), 3000, 2950,1260(s), 870, 840 Cm^{-1}; ^{1}H-NMR (90 MHz, $CDCl_3$) δ0.00 (s,9H), 0.40-0.75 (m,2H), 1.30-1.70 (m,4H), 1.85-2.30 (m,4H), 3.12 (bs, 1H), 3.50 (t,2H, J = 6 Hz), 5.10-5.50 (m,2H); Anal. Calcd. for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07; Found C, 65.92; H, 12.07.

(Z)-8-(Trimethylsilyl)-5-nonenol (8)

The experimental procedure for the preparation of **8** was same as that described for **6**. From 3-(trimethylsilyl)-butanal **(4)**[10] (1.56 g) was obtained **8** (1.35 g, 58.4%) as a colourless oil : b.p. 85-87°C, 0.04 torr (bath), IR (film) 3350, 3000 , 2950, 2850, 1450, 1400, 1250, 1065, 860, 840 Cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.00 (s,9H), 0.6-0.8 (m,1H), 0.95 (d,3H, J = 7.5 Hz), 1.40-1.80 (m,5H), 1.90-2.02 (m,1H), 2.04-2.30 (m,3H), 3.72 (t,2H, J = 6.5 Hz), 5.47 (m,2H); Anal. Calcd. for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22; Found C, 67.12; H, 12.20.

(Z)-7-(Trimethylsilylmethyl)-5-octenol (10)

The experimental procedure for the preparation of **10** was same as that described for **6**. From 2- (trimethylsilylmethyl)propanal **(5)**[11] (1.3 g) was obtained **10** (1.19 g, 61.26%) as a colourless oil :b.p. 88-89° C/0.04 torr; IR (film) 3350,

3000, 2950, 2860, 1450, 1410, 1250, 1210, 860, 840 Cm^{-1} ; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H), 0.54 (d,2H, J = 6.5 Hz), 0.94 (d,3H, J = 6.5 Hz), 1.50 (m,4H), 1.99 (m,2H), 2.48 (bs,1H), 2.50 (m,1H), 3.50 (t,2H, J = 6.5 Hz), 5.00- 5.35 (m,2H); Anal. Calcd. for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22; Found C, 67.21; H, 12.20.

(Z)-8-(Trimethylsilyl)-5-octenal (7)

To a stirred suspension of pyridinium chlorochromate (1.8 g, 7.8 mmol) and sodium acetate (640 mg, 7.8 mmol) in dry dichloromethane (7 mL) was added a solution of **6** (1 g, 5 mmol) in dry dichloromethane (2 mL) in one portion. The reaction mixture was stirred at room temperature for 2 h and then diluted with dry ether (25 mL). The supernant liquid was filtered through a bed of silica gel and the filtrate concentrated in vacuo to give **7** as a pale yellow oil (820 mg, 82%). The product was homogeneous on TLC (silica gel) and sufficiently pure for next step : IR (film) 3000, 2960(s), 2720, 1730(s), 1260(s), 870 an d 840 Cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s,9H), 0.38-0.66 (m,2H), 1.30-1.79 (m,2H), 1.88-2.24 (m,4H), 2.37 (t,2H, J = 7 Hz), 5.06- 5.60 (m,2H), 9.86 (unresolved triplet, 1H).

(Z)-8-(Trimethylsilyl)-5-nonenal (9)

The experimental procedure for the preparation of **9** was same as that described for **7**. From **8** (650 mg) was obtained **9** (620 mg, 95%) as a pale yellow oil which was homogeneous on TLC (silica gel) and sufficiently pure for next step :IR (film) 3004, 2954, 2869, 1720, 1454, 1421, 1249, 1055, 982, 855 and 834 Cm^{-1} ; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s,9H), 0.60-0.80 (m,1H), 0.95 (d,3H, J = 7.5 Hz), 1.50-1.83 (m,2H), 1.84-2.22 (m,4H), 2.36 (t,2H, J = 6.5 Hz), 5.2-5.6 (m,2H), 9.72 (unresolved triplet, 1H).

(Z)-7-(Trimethylsilylmethyl)-5-octenal (11)

The experimental procedure for the preparation of **11** was same as that described for **7**. From **10** (550 mg) was obtained **11** (520 mg, 95%) as a pale yellow oil which was homogeneous on TLC (silica gel) and sufficiently pure for next step : IR (film) 3004, 2954, 2869, 1720, 1454, 1421, 1249, 1055, 982, 855, 834 Cm^{-1} ; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s,9H), 0.54 (d,2H, J = 6.5 Hz), 0.94 (d,3H, J = 6.5 Hz), 1.50- 1.80 (m,2H), 1.9-2.2 (m,2H), 2.21-2.80 (m,3H), 5.0-5.4 (m,2H), 9.75 (unresolved triplet, 1H).

5-(Tetrahydropyranyloxy)-3,3-dimethylpentanol (22)

To a refluxing solution of 3,3-dimethyl-1,5-pentanediol (**21**) (10 g, 75.7 mmol) in dry ether (100 mL) containing p-toluenesulfonic acid (0.54 g) was added dropwise a solution of 3,4-dihydro-2H-pyran (6.35g, 75.5 mmol) in dry ether (20 mL). The reaction mixture was heated under reflux for 5 h. The ethereal solution was washed with 10% aqueous sodium bicarbonate, brine, dried ($MgSO_4$) and concentrated to give a mixture of products (16 g), which was chromatographed over silica gel. Elution with petroleum ether (60-80° C)-ethyl acetate (9:1) gave 1,5-ditetrahydro- pyranyloxy-3,3-dimethylpentane (**23**) (4.6 g, 20%); ^{1}H-NMR (90 MHz, CCl_4) δ 0.98 (s,6H), 1.31-1.90 (m,16H), 3.15-3.53 (m,4H), 3.60-3.86 (m,4H), 4.50 (bs, 2H). Further elution with petroleum ether (60-80°C)-ethyl acetate (9:1) gave **22** (7.3 g, 45%) : IR (film) 3400(b), 2950, 1475, 1460, 1440, 1390, 1370, 1360, 1200, 1125, 1040(s), 910(s), 815 Cm^{-1} ; ^{1}H-NMR (90 MHz, CCl_4) δ1.00 (s,6H), 1.40-1.80 (m,1OH), 2.82 ((s,1H), 3.20-3.95 (m,6H), 4.51 (bs, 1H). Anal. Calcd. for $C_{12}H_{24}O_3$: C, 66.63; H, 11.18; Found C, 66.51; H, 11.16. Final elution with chloroform gave unconverted diol **21** (1.5 g, 15%). Compound **23** (4.6 g) obtained above was hydrolysed by refluxing in methanol (120 mL) containing catalytic amount of p-toluenesulfonic acid (340 mg) for 5 h to give the diol **21** (1.89 g, 89%) after usual work-up.

5-(Tetrahydropyranyloxy) - 3,3-dimethylpentanal (24)

To a solution of oxalyl chloride (2.32 mL, 26.5 mmol) in dry dichloremethane (55 mL) at -60°C was added dropwise with stirring a solution of DMSO (3.5 mL) in dichloromethane (4 mL) under an atmosphere of nitrogen over a period of 20 min. To this after stirring for 5 min was added **22** (5 g, 23.1 mmol) in dichloromethane (5 mL) over a period of 10 min. Stirring was continued for an additional 15 min and triethylamine (15 mL) was added at that temperature. After 10 min the reaction mixture was allowed to attain room temperature, diluted with water (125 mL) and aqueous phase was extracted with dichloromethane. The organic extract was washed with 5% aqueous hydrochloric acid, saturated aqueous sodium bicarbonate, brine and dried ($MgSO_4$). Removal of solvent gave a pale yellow oil **24** (3.95 g, 80%) which was sufficiently pure for next step : IR (film) 2940, 2860, 2725, 1720(s), 1470, 1450, 1440, 1390, 1365, 1350, 1140, 1120, 1035 Cm^{-1}; ^{1}H-NMR (60 MHz, CCl_4) δ 1.10 (s,6H), 1.20-1.85 (m,8H), 2.30 (d,2H, J = 3 Hz), 3.15-4.15 (m,4H), 4.51 (bs, 1H), 9.86 (t,1H, J = 3 Hz).

(Z)-8-(Trimethylsilyl)-3,3-dimethyl-1-(tetrahydropyranyloxy)-5-octene (12)

A mixture of 3-bromopropyltrimethylsilane (9.3 g, 47.6 mmol) and triphenylphosphine (11.9 g, 45.3 mmol) in dry xylene (65 mL) was heated under reflux with stirring for 14 h. After cooling to room temperature, part of the xylene was removed in vacuo and the precipitated salt separated by filtration. The salt was thoroughly washed with xylene and dried under vacuo to give 3-(trimethylsilyl)-propyltriphenylphosphonium bromide (**26**)[16] as a white crystalline solid (14 g, 67.6%), m.p. 239-240°C. To a mixture of the phosphonium salt **26** (7.29 g, 15.9 mmol) and sodium hexamethyl disilazide (2.92 g, 15.9 mmol) was added dry tetrahydrofuran (35 mL) under an atmosphere of argon. The reaction mixture was stirred for 1 h; during this period the mixture developed a bright orange colour indicating the formation of the ylide **25**. This was cooled to -78°C and the aldehyde **24** (3.4 g, 15.8 mmol) in tetrahydrofuran (10 mL) was added over a period of 15 min. The reaction mixture was slowly brought to room temperature and stirring continued overnight whereby the orange colour disappeared and a whitish suspension formed. This was diluted with petroleum ether (60-80°C) and the precipitated triphenylphosphine oxide separated by filtration. The filtrate was concentrated and the residue passed through a bed of silica gel. The crude oil thereby obtained was chromatographed over silica gel and eluted with ethyl acetate- petroleum ether (60-80°C) (5:95) to give **12** as an oil (2.98 g, 61%) : IR (film) 2940, 1385, 1365, 1350, 1250, 1200, 1140, 1120, 1035(s), 865, 840 Cm^{-1} ; ^{1}H-NMR (60 MHz, $CDCl_3$) δ 0.00 (s,9H), 0.30-0.65 (m,2H), 1.20-1.70 (m,8H), 1.71-2.25 (m,4H), 3.15-4.10 (m,4H), 4.42-4.75 (m,1H), 5.15-5.60 (m,2H); MS, m/z 313(M+1), 312(M^+), 294, 277, 136(2.5), 103(9.8), 86(22.5), 85(100), 73(99.8),69(30.5), 67 (25.2), 57(21.4), 55(20). Anal. Calcd. for $C_{18}H_{36}O_2Si$: C, 69.17; H, 11.61; Found C, 69.11; H, 11.60.

(Z)-8-(Trimethylsilyl)-3,3-dimethyl-5-octenol (13)

A solution of **12** (2.1 g, 6.73 mmol) in methanol (75 mL) containing p-toluenesulfonic acid (200 mg) was heated to reflux for 1.5 h. Methanol was removed in vacuo and the residue taken up in ether. The ethereal layer was washed with dilute aqueous sodium bicarbonate, brine, dried ($MgSO_4$) and concentrated to give **13** as an oil (1.5 g, 97%) : b.p. 85-90°C/0.01 torr (bath); IR (film) 3335, 2960, 1650(w), 1250(s), 1030,840 Cm^{-1} ; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.00 (s,9H), 0.552 (t,2H), 0.900 (s,6H), 1.476 (t,2H), 1.909 (d,2H, J = 7.1 Hz), 1.963-2.103 (m,2H), 3.577 (t,2H, J = 7 Hz), 3.672 (bs, 1H), 5.252-5.370 (m,1H), 5.382-5.503 (m,1H); MS, m/z 228(M^+), 213(M-15), 195, 169, 157, 123(6.4), 109(11.5), 73(97.3), 69(100). Anal. Calcd. for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35; Found C, 68.21; H, 12.39.

(Z)-8-(Trimethylsilyl)-3,3-dimethyl-5-octenal (14)

The experimental procedure for the preparation of **14** from **13** was same as that described for the preparation of **7**. From **13** (1.45 g) was obtained **14** (1.25 g, 87%) as an oil which was sufficiently pure for the next step : IR (film) 3020, 2970, 2720, 1725(s), 1250(s), 830 Cm^{-1} ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.00 (s,9H), 0.40-0.66 (m,2H), 1.03 (s,6H), 1.80-2.12 (m,4H), 2.25 (d,2H), 5.31-5.37 (m,1H), 5.38-5.58 (m,1H), 9.85 (t,1H). Irradiation at δ 2.05 : the multiplet at δ 5.31-5.37 collapses into a broad doublet at δ 5.34 (J = 11 Hz), the multiplet at δ 5.38-5.58 collapses into a doublet at δ 5.55 (J = 11 Hz) and the multiplet at δ 0.40-0.66 collapses into a singlet at δ 0.55.

Ethyl (2E,7Z)-10-(trimethylsilyl)-2,7-decadienoate (15)

To a stirred suspension of sodium hydride (230 mg, 3.83 mmol, 40% in oil, washed with 5 mL of dry benzene) in dry DME (10 mL), under argon at room temperature was added a solution of triethyl phosphonoacetate (960 mg, 4 mmol) in DME (3 mL) and the mixture stirred for an additional hour. To the resulting white semisolid mass was added a solution of **7** (700 mg, 4 mmol) in DME (3 mL) over a period of 15 min and stirring continued for 1.5 h at the same temperature. The reaction mixture was quenched with cold water and extracted with ether. The combined ether extracts were washed with brine, dried ($MgSO_4$) and concentrated to afford a pale yellow oil. This was chromatographed over silica gel and eluted with ethyl acetate - petroleum ether (60- 80°C) (5:95) to give **15** (815 mg, 87%) containing 3% of the *Z*-isomer (GLC). Pure *(E)*-**15** (722 mg, 77%) was isolated by preparative layer chromatography over silica gel [ethyl acetate-petroleum ether (40-60°C) (5:95) as developing solvent] : b.p. 140-145° C/0.05 torr (bath); IR (film) 1730(s), 1655(s), 1370, 1260, 1250(s), 1050, 980(s), 865, 840 Cm^{-1} ; ^{1}H- NMR (500 MHz, $CDCl_3$) δ 0.00 (s,9H), 0.54-0.59 (m,2H), 1.28 (t,3H, J = 7 Hz), 1.53 (m,2H), 1.99-2.11 (m,4H), 2.21-2.24 (m,2H), 4.19 (q,2H, J = 7 Hz), 5.22-5.28 (m,1H), 5.40-5.44 (m,1H), 5.83 (d,1H, J = 16 Hz), 6.96 (dt, 1H, J = 16 & 7 Hz); MS, m/z No(M^+), 263(M-15), 253, 121, 73, 68; Anal. Calcd. for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.51; Found C, 67.21; H, 10.56.

Methyl (2*E*,7*Z*)-10-(trimethylsilyl)-2,7- undecadienoate (16)

The experimental procedure for the preparation of **16** was same as that described for **15**. From **9** (765 mg) and trimethyl phosphonoacetate (800 mg) was obtained **16** (810 mg, 81.6%) as a colourless oil : b.p. 130-132°C/0.3 torr (bath); IR (film)

2955, 1730, 1650, 1450, 1390, 1250, 1060, 980, 860, 840 Cm^{-1} ; ^{1}H-NMR (200 MHz, $CDCl_3$) 0.00 (s,9H), 0.65 (m,1H), 0.88 (d,3H, J = 7.5 Hz), 1.4-1.6 (m,2H), 1.75-1.94 (m,1H), 2.03-2.25 (m,5H), 3.71 (s,3H), 5.37 (m,2H), 5.81 (d,1H, J =16.5 Hz), 6.98 (dt,1H, J = 16.5 & 8.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ167.105(s), 149.447(d), 131.150(d), 128.839(d), 121.000(d), 51.382(q), 31.717(t), 29.340(t), 28.012(t), 26.608 (t), 20.438(d), 14.003(q); MS, m/z No(M^+), 253 (M-Me,3.6), 200(2.2), 186(2.0), 185(4.1), 172(2.1), 164(1.8), 159(1.6), 147(2.2), 146(2.8), 136(2.1), 135(7.5), 121(8.3), 120(2.9), 119(2.2), 108(5.5), 107(6.9), 96(10.5), 95(7.3), 89(22.8), 82(16.3), 81(57.8), 79(12.4), 75(7.2), 74(11.0), 73(100), 68(37.2), 67(10.8), 59(20.5), 55(14.5), 45(24.7). Anal. Calcd. for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.51; Found C, 67.18; H, 10.53.

Methyl (2*E*,7*Z*)-9(trimethylsilylmethyl)-2,7- decadienoate (17)

The experimental procedure for the preparation of **17** was same as that described for **16.** From **11** (450 mg) was obtained **17** (460 mg, 80.9%) as a colourless oil : b.p. 130-132° C/0.3 torr (bath); IR (film) 2960, 1730, 1650, 1445, 1395, 1250, 1060, 985, 860, 842 Cm^{-1} ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ -0.02 (s,9H), 0.57 (d,2H, J = 6.5 Hz), 0.95 (d,3H, J = 6.5 Hz), 1.51 (m,2H), 2.00-2.26 (m,4H), 2.55 (m, 1H), 3.71 (s,3H), 5.18 (m,2H), 5.81 (d,1H, J = 16.5 Hz), 6.96 (dt, 1H, J = 16.5 & 8.2 Hz), ^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.092(s), 149.379(d), 139.565(d), 125.173(d), 120.991(d), 51.373(q), 31.804(t), 28.156(t), 28.116(d), 26.785(t), 25.966(t), 25.037(q), -0.702(3q); MS, m/z No(M^+), 253 (M-Me), 185(1.8), 159(1.5), 149(1.6), 135(1.9), 122(1.9), 121(6.3), 109(2.7), 108(4.8), 107(4.2), 95(4.7), 93(7.6), 89(18.8), 81(28.5), 79(9.5), 75(6.6), 74(8.2), 73(100), 68(12.7), 55(13.8), 45(18.0).

Ethyl (2*E*,7*Z*)-10-(trimethylsilyl)-5,5-dimethyl-2,7- decadienoate (18)

The experimental procedure for the preparation of **18** was same as that described for **15.** From **14** (1.3 g) was obtained **18** (1.3 g, 76%) as an oil : b.p. 120-125°C/0.01 torr (bath); IR (film) 2960(s), 1729(s), 1650(s), 1385, 1365, 1260(s), 1050, 980(s), 830, 755 Cm^{-1} ; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.00 (s,9H), 0.547 (t,2H, J = 8.2 Hz), 0.940 (s,6H), 1.279 (t,3H), 1.95 (d,2H), 1.969-2.041 (m,2H), 2.081 (d,2H, J = 7.7 Hz), 4.13 (q,2H, J = 7 Hz), 5.24-5.359 (m,1H), 5.399-5.521 (m,1H), 5.72 (d,1H, J = 15.2 Hz), 6.88 (dt, 1H, J = 15.2 & 7.7 Hz); MS, m/z 297(M+1), 296(M^+), 281(M-15, 5.6), 268, 251, 149(10.6), 109(31.5), 73(100), 69(18.1); Anal. Calcd. for $C_{17}H_{32}O_2Si$: C, 68.91; H, 10.80; Found C, 68.95; H, 10.82.

General procedure for thermolytic ene cyclization

A 5% solution of the diene e.g., **15-18** in dry toluene was taken in a pyrex tube, purged with argon and sealed. The tube was heated in a constant temperature tubular furnace at a temperature/time as given in Table 1. After cooling to room temperature, the solvent was removed in vacuo and the residue distilled to give the product **27-30.**

Cis-Ethyl 2-[2-[(*E*)-3-(trimethylsilyl-1- propenyl]cyclopentyl]acetate (27)

b.p. 115-120°C/0.01 torr (bath); IR (film) 2970, 1740(s), 1655(w), 1250(s), 980(s), 800 and 770 Cm^{-1} ; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.00 (s,9H), 1.26 (t,3H, J = 7 Hz), 1.28- 1.40 (m,1H), 1.42 (d,2H, J = 8 Hz), 1.44-1.83 (m,5H), 2.11- 2.16 (m,1H), 2.28-2.37 (m ,2H), 2.58-2.62 (m,1H), 4.12 (q,2H, J = 7 Hz), 5.15 (dd,1H, J = 16 & 8.5 Hz), 5.37 (dt, 1H, J = 16 & 8 Hz); ^{13}C-NMR (90.5 MHz, $CDCl_3$) δ 129.179(d), 126.882(d), 60.043(t), 45.918(d), 40.356(d), 36.395(t), 31.662(t), 30.543(t), 22.923(2t), 14.293(q), -1.914(3q); MS, m/z 268(M\+), 253(M-15), 240, 223, 200(3.3), 173, 150, 135(2.4), 117(11.0), 107(12.2), 93(7), 82(26.8), 73(100), 67(7.3), 55(6), 45(10.3); Anal. Calcd. for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.52; Found C, 67.15; H, 10.46.

Cis-Methyl 2-[2-[(*E*)-3-(trimethylsilyl)-1-butenyl]- cyclopentyl]acetate (28)

b.p. 130-131°C/0.3 torr (bath); IR (film) 2960, 1740, 1655, 1250, 980. 840, 770 Cm^{-1} ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ -0.05 (s,9H), 1.01 (d,3H, J = 7.3 Hz), 1.28-1.79 (m,6H), 2.10-2.40 (m,4H), 2.60 (m,1H), 3.64 (s,3H), 5.06 (dd,1H, J = 14.86 & 8.60 Hz), 5.42 (m,1H); ^{13}C-NMR (90 MHz, $CDCl_3$) δ 174.214(s), 133.600(d), 126.389(d), 51.235(q), 45.970(d), 40.237(d), 36.053(t), 31.658(t), 30.567(t), 26.120(d), 22.662(t), 13.756(q), -3.498(3q); ^{13}C-NMR for other diastereomer (partial) : δ 45.875(d), 26.249(d); MS, m/z No(M^+), 253(M-Me, 2.3), 239(3.0), 200(3.9), 185(4.4), 164(2.5), 149(5.0), 146(4.4), 135(8.4), 131(3.3), 122(3.4), 121(13.5), 120(5.2), 119(3.3), 109(5.6), 108(5.4), 107(7.6), 105(8.6), 96 (16.0), 89(10.6), 83(10.6), 82(13.1), 81(29.0), 75(9.5), 74(10.2), 73(100), 57(22.9), 55(24.3), 45(20.2). Anal. Calcd. for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.51; Found C, 67.14; H, 10.55.

Cis-Ethyl 2-[2-[(E)-3-(trimethylsilyl)-1-propenyl]-4,4- dimethylcyclopentyl]acetate (30)

b.p. 125-130°C/0.01 torr (bath); IR (film) 2965, 1740(s), 1655(w), 1250(s), 975, 830, 770 Cm^{-1} :^{1}H-NMR (500 MHz, $CDCl_3$) : δ 0.00 (s,9H), 1.019 (s,3H), 1.097 (s,3H), 1.234 (t,3H, J = 7 Hz), 1.274-1.356 (m,2H), 1.394 (d,2H, J= 7.6 Hz), 1.535-1.718 (m,2H), 2.142 (dd,1H, J= 15.5 & 8.4 Hz), 2.36 (dd, 1H, J = 15.5 & 6.8 Hz), 2.5-2. 63 (m,1H), 2.73-2.84 (m,1H),

4.1 (q,2H, J = 7 Hz), 5.17 (dd, 1H, J = 15.5 & 8.5 Hz), 5.33 (dt, 1H, J = 15.5 & 8.5 Hz); ^{13}C-NMR (90.5 MHz, $CDCl_3$) : δ 173.8(s), 130.007(d), 126.729(d), 60.001(t), 47.733(t), 46.956(t), 45.423(d), 39.167(d), 37.616(s), 36.999(t), 31.075(q), 30.101(q), 22.811(t), 14.278(q), - 1.922(3q); MS, m/z 296(M^+), 281(M-15), 268, 251, 227, 200(3.04), 163(2.4), 135(4.56), 117(8.5), 109(18.3), 95(11.5), 82(16.1), 73(100), 55(6). Anal. Calcd. for $C_{17}H_{32}O_2Si$: C, 68.91; H, 10.80; Found C, 68.90; H, 10.84.

Cis-2-[2-[(*E*)-3-(trimethylsilyl)-1-propenyl]cyclopentyl]ethanol (31)

To a suspension of lithium aluminum hydride (100 mg, 2.63 mmol) in dry ether (12 mL) at room temperature was added dropwise with stirring a solution of **27** (700 mg, 2.61 mmol) in ether (2 mL). The reaction mixture was stirred for 3 h and heated under reflux for 2 h. This was decomposed with saturated aqueous sodium sulfate solution and the product worked-up in ether to give **31** as a colourless oil (550 mg, 93%) : b.p. 92°C/0.01 torr (bath); IR (film) 3330, 2950, 1650(w), 1250(s), 1155, 870 Cm^{-1} ; ^{1}H-NMR (500 MHz, $CDCl_3$) : δ 0.00 (s,9H), 1.247-1.455 (m,3H), 1.405 (d,2H, J ~ 7.8 Hz), 1.462-1.504 (m,1H), 1.507-1.657 (m,2H), 1.664-1.837 (m,3H), 1.853-1.957 (m,1H), 2.503 (m,1H), 3.51 (t,2H), 5.153 (dd,1H, J = 15.8 & 9.1 Hz), 5.333 (dt, 1H, J = 15.8 & 7.5 Hz); MS, m/z 227(M+1), 211(M-15), 208(M-18), 195, 184, 179, 167, 151(15.9), 125(26.3), 111(64.9), 107(20.8), 95(44), 81(33), 73(100), 67(49.7), 55(67.9), 41(47.1). Anal. Calcd. for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57; Found C, 68.92; H, 11.59.

Cis-2-[2-[(E)-3-(trimethylsilyl)-1-butenyl]cyclopentyl]ethanol (32)

The experimental procedure for the preparation of **32** from **28** was same as that described for **31**. From **28** (200 mg) was obtained **32** (diastereomeric mixture) (190 mg, 94%) as a colourless thick oil; IR (film) 3350, 2955, 2870, 1655, 1450, 1250, 840 Cm^{-1} ; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s,9H), 1.02 (d, 3H, J = 7.3 Hz), 1.18-2.08 (m,9H), 2.12-2.66 (m,3H), 3.58 (t,2H, J = 7.5 Hz), 4.90-5.50 (m,2H); ^{13}C- NMR (100 MHz, $CDCl_3$) δ 132.938(d), 127.001(d), 62.475(t), 46.156(d), 40.383(d), 34.518(t), 32.288(t), 30.508(t), 26.042(d), 22.884(t), 13.874(q); ^{13}C-NMR for other diastereomer (partial) δ 132.915(d), 46.074(d), 32.262(t), 30.452(t), 22.814(t), 13.781(q); MS, m/z 239(M-1, 6), 213(7), 149(34), 121(32), 111(37), 97(38), 95(47), 83(40), 81(50), 73(100), 71(54), 57(93), 55(77).

Cis-2-[2-[(*E*)-3-(trimethylsilyl)-1-propenyl]cyclopentyl]ethanal (33)

To a well-stirred suspension of pyridinium dichromate (0.832 g, 2.21 mmol) in dry dichloromethane (6 mL) was added **31** (0.25 g, 1.1 mmol) in dichloromethane (2.5 mL). The reaction mixture was stirred for 10 h at room temperature and then diluted with dry ether (15 mL). The organic layer was separated and filtered through a bed of silica gel and the filtrate concentrated to give a pale yellow oil **33** (0.185 g, 75%) which was sufficiently pure for the next step : IR (film) 2980, 2890, 1720, 1420, 1255, 845 cm^{-1} ; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s,9H), 1.04-2.00 (m,6H), 1.35 (d,2H, J = 7.8 Hz), 2.02-2.74 (m,4H), 4.90-5.55 (m, 2H), 9.78 (unresolved triplet, 1H).

Cis-2-[2-[(*E*)-3-(trimethylsilyl)-1-butenyl]cyclopentyl]ethanal (34)

To a vigorously stirred suspension of chromium trioxide (1 g, 10 mmol) in dichloromethane (8 mL) under argon, pyridine (1.2 mL) was added and the mixture stirred at room temperature for 1.5 h. The resulting red solution was transferred to another reaction flask via hypodermic syringe and to this was added **32** (155 mg, 0.64 mmol) in dichloromethane (1 mL) and the mixture stirred for 2.5 h. This was diluted with dry ether (30 mL) and the organic layer passed through a bed of silica gel and the filtrate concentrated. Preparative layer chromatography [silica gel, 5% ethyl acetate-petroleum ether (60-80°C) as developing solvent] of the residue gave **34** (95 mg, 60%) as a colourless oil : IR (film) 2955, 2870, 2710, 1730, 1650, 1450, 1250, 840 Cm^{-1} ; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s,9H), 1.02 (d,3H, J = 7.3 Hz), 1.12-2.00 (m,7H), 2.00-2.70 (m,4H), 4.86-5.53 (m,2H), 9.66 (unresolved triplet, 1H).

2-Vinyl-cis-bicyclo[3.3.0]octan-3-ol (37)

To a solution of **33** (135 mg, 0.60 mmol) in dry dichloromethane (10 mL) was added with stirring at -78° C under argon $TiCl_4$ (1.9 mL of a 0.315M solution in dichloromethane). After 45 min at - 78°C the reaction mixture was quenched with saturated aqueous ammonium chloride and extracted with dichloromethane. The combined organic phase was washed with brine, dried ($MgSO_4$) and concentrated in vacuo. Preparative layer chromatography [silica gel, 7% ethyl acetate- petroleum ether (60-80°C) as developing solvent] of the residue afforded **37** (65 mg, 70%) as a colourless oil : IR ($CHCl_3$) 3600(w), 3420(b), 2950, 1650(w), 1225, 925 Cm^{-1} ; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.332-1.483 (m,3H), 1.499- 1.616(m,4H), 1.699 (q,1H), 2.016-2.183 (m,2H), 2.201- 2.332(m,1H), 2.816 (bs), 3.491-3.624 (m,1H), 4.946 (d,1H, J = 10 Hz), 5.00 (d,1H, J = 17.1 Hz), 5.643 (ddd, 1H, J = 17.3, 9.6 & 7.9 Hz); MS, m/z 152(M^+), 134, 124, 119, 108, 105, 93, 79, 70, 67(100), 55,

41. MS of two other minor isomers : m/z 152(M^+), 134, 123, 119, 108, 93, 79, 70, 67(100), 55, 41; m/z 152(M^+), 134, 124, 119, 108, 93, 79, 70, 67(100), 55, 41.

2-(1-propenyl)-cis-bicyclo[3.3.0]octan-3-ol (38)

The experimental procedure for the preparation of **38** from **34** was same as that described for **37**. From **34** (85 mg) was obtained **38** (45 mg, 80%) as a colourless oil : IR (film) 3430, 2950, 1650, 1220, 1020, 925 Cm^{-1} ; ^{1}H-NMR (300 MHz, $CDCl_3$) δ1.05- 1.78 (m,11H), 1.87-2.80 (m,4H), 3.64 (m,1H, from major isomer), 3.83 (m,1H, from minor isomer), 5.24-5.70 (m,2H); MS, m/z 166 (M, 3.7), 151(M-Me, 1.8), 149(3.9), 148(15.6), 137(18.9), 124 (23.3), 122(13.7), 119(13.2), 108(13.0), 107(12.6), 96(12.1), 95 (48.0), 93(42.8), 91(23.5), 84(34.4), 83(28.8), 82(20.2), 81(49.0), 79(57.2), 67 (100), 55(59.5), 43(30.3), 41(84.4). MS for minor isomer : m/z 166 (M^+, 2.5), 151(M-Me, 1.7), 149 (1.8), 148(11.2), 137(17.5), 124(20.0), 122(9.4), 119(10.6), 108 (10.0), 107(10.4), 96(10.3), 95(45.6), 93(38.0), 91(23.7), 84(34.0), 83(29.8), 82(19.5), 81(44.6), 79(56.1), 67(100), 55(67.8), 43(37.9), 41(99.1).

Cis-2-[2-[(*E*)-3-(trimethylsilyl)-1-propenyl]-4,4- dimethylcyclopentyl]ethanol (35)

The experimental procedure for the preparation of **35** from **30** was same as that described for **31**. From **30** (300 mg) was obtained **35** (230 mg, 90%) as an oil : b.p. 100- 105°C/0.01 torr (bath); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.00 (s,9H), 1.01 (s,3H), 1.10 (s,3H), 1.18- 1.38 (m,2H), 1.43 (d,2H, J ~ 8 Hz), 1.52-1.74 (m,4H), 2.08-2.22 (m,1H), 2.62-2.74 (m,1H), 3.63 (t,2H), 5.2-5.4 (m,2H). Anal. Calcd. for $C_{15}H_{30}OSi$: C, 70.80; H, 11.88; Found C, 70.83; H, 11.86.

Cis-2-[2-[(*E*)-3-(trimethylsilyl)-1-propenyl]-4,4-dimethyl- cyclopentyl]ethanal (36)

To a stirred mixture of pyridinium dichromate (4.45 g, 11.8 mmol) and freshly activated molecular sieve (4A°) powder (6 g) in dry dichloromethane (40 mL) at 0-5°C was added a solution of **35** (2.0 g, 7.87 mmol) and acetic acid (0.8 mL) in dichloromethane (10 mL) over a period of 10 min. After the addition was over, the reaction mixture was stirred at the same temperature for 15 min., at room temperature for 25 min and then diluted with dry ether. The supernant liquid was decanted and passed through bed of florisil (25 g). Removal of solvent afforded **36** (1.62 g, 82%) as a colourless oil which was sufficiently pure for next step : IR (film) 2960, 2940, 2870, 2710, 1730, 1650, 1460,1400, 1380, 1360, 1250, 1155, 970, 860 Cm^{-1} ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.00 (s,9H), 1.02 (s,3H), 1.09 (s,3H), 1.15-1.36 (m,2H), 1.42 (d,2H, J ~ 8 Hz), 1.50-1.80 (m,3H), 2.00-2.95 (m, 3H), 5.15 (dd,1H, J ~ 16 & 7 Hz), 5.31 (dt, 1H, J ~ 16 & 8 Hz), 9.74 (bs, 1H); MS, m/z 252 (M^+ ,1.2), 238(1.7), 237(M-15, 8.5), 95 (13.8), 93(10.2), 79(10.1), 75(27.6), 73(100), 59(10.9), 55(13.6), 45(27.3), 43(16.8).

Cis-1-(2,3-epoxypropyl)-2-[(*E*)-3-(trimethylsilyl)-1- propenyl]-4,4- dimethylcyclopentane (40)

A mixture of sodium hydride (125 mg, 2.6 mmol, 50% in oil, washed free of mineral oil with petroleum ether) and DMSO (3 mL) was heated with stirring at 55-60°C for 1 h. To this pale green solution at room temperature was added THF (2 mL) followed by a solution of Me_3SI (640 mg, 3.12 mmol) in DMSO (2 mL) at 0°C over 3 min. The mixture was stirred at 0°C for 15 min and then a solution of **36** (460 mg, 1.8 mmol) in THF (2 mL) was added in one portion. Stirring was continued for 15 min at 0°C and then at room temperature for 30 min. The reaction mixture was diluted with cold water and extracted with hexane. Removal of solvent in vacuo followed by chromatography (Gr.II alumina, neutral) of the residue and eluting with 1% hexane-ethyl acetate gave **40** (192 mg,61%) : IR (film) 2950, 2930, 2860, 1650, 1460, 1385, 1370, 1250, 1160, 970, 860 Cm^{-1} ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.00 (s,9H), 0.99 (s,3H), 1.07 (s,3H), 1.15-1.37 (m,3H), 1.39 (d,2H, J ~ 7 Hz), 1.52-1.73 (m,3H), 1.97-2.39 (m ,1H), 2.40-2.46 (m,1H), 2.60-2.77 (m,2H), 2.80-2.95 (m,1H), 5.06- 5.40 (m,2H); MS, m/z 266(M° ,2.1), 251(M-15,1.7), 129(10.7), 75(35.3), 73(100), 67(20.2), 59(16.8), 55(20.7), 45(38.8), 43(24.5).

7,7-Dimethyl-2-vinyl-3-hydroxymethyl-cis-bicyclo[3.3.0]octane (41)

To a solution of **40** (1.14 g, 4.28 mmol) in dry dichloromethane (25 mL) at -78°C under argon was added dropwise with stirring $TiCl_4$ (2.5 mL of a 1.8M solution in dichloromethane, 4.5 mmol) (initially cooled to -40°C). The reaction mixture was stirred for 1 h and then quenched at the same temperature with saturated aqueous sodium bicarbonate (10 mL). Extraction with ether followed by removal of solvent and chromatography of the residue over silica gel eluting with 10% ethyl acetate-petroleum ether (60-80° C) gave **41** (600 mg, 72%) as a mixture (42:50:8) (from GLC) of three diastereomers : IR (film) 3350(b), 3080, 2960, 2940, 2875, 1645, 1475, 1390, 1370, 1050, 915; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.88, 0.89, 0.92 (three singlets,3H), 1.03, 1.04, 1.05 (three singlets,3H), 1.30-2.71 (m,11H), 3.52- 3.71 (m,2H), 4.94-5.11 (m,2H), 5.71-5.93 (m,1H); MS, m/z 194(M^+ ,1.1), 176 (9.3), 164(51.0), 162(24.8), 161(14.8), 136(21.9), 135(14.5), 121 (13.9), 107(28.8), 105(16.6), 95(35.4), 93(27.1), 91(26.0), 81(26.1), 79(33.8), 77(20.9), 69(25.1), 67(34.3), 53(20.3), 43(30.6), 41(100).

7,7-Dimethyl-2-vinyl-3-methanoyl-cis-bicyclo[3.3.0]octane (42)

A mixture of **41** (195 mg, 1 mmol), PCC (325 mg, 1.5 mmol) in dichloromethane (4 ml) was stirred at room temperature for 1.5 h. This was diluted with ether (15 mL) and filtered through a bed of florisil (10 g). Removal of solvent gave **42** (140 mg, 70%) as a colourless oil which appeared from GLC to be a mixture (67:17:16) of diastereomers : IR (film) 3070, 2950, 2930, 2860, 2700, 1720, 1630, 1460, 1380, 1360, 910; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.88-0.93 (group of singlets, 3H), 1.03-1.07 (group of singlets, 3H), 1.10-3.10 (m,10H), 4.95-5.09 (m,2H), 5.67-5.80 (m,1H), 9.51 (d, J ~ 3.8 Hz, 1H, from one diastereomer), 9.55 (d, J~ 3.5 Hz, 1H, from one diastereomer), 9.72 (d, J ~ 2.4 Hz, 1H, from one diastereomer); MS, m/z 193 (M^+1,7.7), 192(M^+ ,2.1), 179(5.0), 177(5.2), 163(10.0), 122(10.1), 107(21.0), 105(10.5), 95(32.7), 93(21.2), 91(21.7), 81(19.3), 77(21.6), 69(17.9), 67(26.0), 55(37.5), 53(21.7), 43(49.5), 41(100), 39(53.4), 29(63.0), 28(24.5).

7,7-Dimethyl-2-ethanoyl-3-methanoyl-cis-bicyclo[3.3.0]octane (43)

A mixture of $PdCl_2$ (70 mg, 0.38 mmol), $CuCl_2$ (126 mg, 1.25 mmol) in DMF-water (5.0:0.6, 1.2 mL) was stirred under oxygen for 3.5 h at room temperature. The mixture was warmed to 55-57°C and to this was added a solution of **42** (200 mg, 1.04 mmol) in DMF-water (5.0:0.6, 3 mL) over a period of 5 min. This was stirred under the same condition for 1 h, cooled to room temperature and diluted with ice-cold water. Extraction with ether followed by removal of solvent gave **43** (165 mg, 77%) as a mixture of diastereomers which was sufficiently pure for next step : IR (film) 2960, 2940, 2880, 2720, 1725, 1460, 1390, 1370 Cm^{-1}; ^{1}H- NMR (300 MHz, $CDCl_3$) δ 0.91 & 0.92 (two singlets,3H), 1.02, 1.06, 1.07 (three singlets, 3H), 1.09-1.22 (m ,1H), 1.34- 2.0(m,4H), 2.17, 2.19, 2.2 (three singlets, 3H), 2.22-2.32 (m,1H), 2.58-2.80 (m,2H), 2.90-3.00 (m,1H), 3.16-3.36 (m,1H), 9.71 (d, J~1.1 Hz, 1H, from one diastereomer), 9.77 (d, J~ 1.5 Hz, 1H, from one diastereomer), 9.81 (d, J ~ 0.7 Hz, 1H, from one diastereomer).

Cis-anti-cis-10,10-dimethyltricyclo[6.3.0.$0^{2,6}$]undec-4-en-3-one (44)

A mixture of **43** (70 mg, 0.33 mmol) and 5% KOH solution (H_2O : EtOH, 1:1, 1 mL, initially purged with argon for 0.5 h at 0°C) under argon was stirred at 50-55°C for 1.5 h. This was cooled to room temperature, ethanol removed under vacuo and the residue acidified with dil. aqueous hydrochloric acid. The product was worked up in ether in the usual way and purified by preparative layer chromatography using 8% ethyl acetate-petroleum ether (60- 80°C) as developing solvent to give **44** (26 mg, 40%) : m.p. 63.5°C; IR ($CHCl_3$) 2950, 2930, 2850, 1700, 1580, 1460, 1380, 1360 Cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.94 (s, 3H), 1.09 (s, 3H), 1.27-1.41 (m,2H), 1.58-1.89 (m,4H), 2.25- 2.37 (m,1H), 2.57-2.65 (m,2H), 3.44-3.51 (m,1H), 6.08 (dd,1H, J~5.5 & 1.83 Hz), 7.51 (dd,1H, J~5.5 & 2.56 Hz); MS, m/z 191(M+1, 7.8), 190(M^+, 44.7), 176(6.3), 175(44.8), 149(12.4), 148(12.4), 135(16.9), 134(20.9), 133(39.3),79(45.7), 78(22.7), 77(50.5), 67(25.1), 66(28.6), 56(89.8), 54(41.9), 53(29.8), 45(27.9), 43(100), 41(91.2); Anal. Calcd. for $C_{13}H_{18}O$: C, 82.05; H, 9.53; Found C, 81.97; H, 9.61.

Cis-anti-cis-10,10-dimethyltricyclo[6.3.0.$0^{2,6}$]undecan-3-one (45)

A mixture of **44** (25 mg, 0.13 mmol), 10% Pt-C (5 mg) in ethyl acetate (2 mL) was stirred under hydrogen at room temperature and atmospheric pressure for 1 h. Filtration of the catalyst through a bed of celite followed by removal of solvent gave **45** as an oil (25 mg, 98%) : IR (film) 2950, 2865, 1735, 1460, 1380, 1365 Cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.89 (s,3H), 1.02 (s,3H), 1.03- 1.12 (m,1H), 1.31-1.42 (m,1H), 1.54-1.66 (m,3H), 1.72-1.85 (m,2H), 1.98-2.12 (m,1H), 2.19-2.31 (m,3H), 2.60-2.70 (m,1H), 2.78-2.96 (m,2H); ^{13}C-NMR (50.26 MHz, $CDCl_3$) 23.85, 26.64, 28.87, 35.86, 37.03, 40.62, 41.48, 43.96, 45.92, 48.04, 49.12, 61.30, 222.58; MS, m/z 193(M+1,6.3), 192(M^+,39.2), 178(12.2), 163(22.1), 150(12.3), 149 (14.6), 136(18.0), 133(14.4), 121(10.5), 110(22.2), 109(26.4), 108(12.9), 107(22.9), 69(21.3), 67(41.9), 66(20.5), 57(53.8), 55(58.2), 53(23.2), 44(27.5), 43(64.8), 41(100); Anal. Calcd. for $C_{13}H_{20}O$: C, 81.19; H, 10.48; Found C, 81.02; H, 10.52.

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