FUSED FURAN CONSTRUCTION *VIA* AN INTRAMOLECULAR [3+2] CYCLOADDITION REACTION: SYNTHESES OF 4*H*-CYCLOHEPTA- AND 4*H*-CYCLOPENTA[*b*]FURANS

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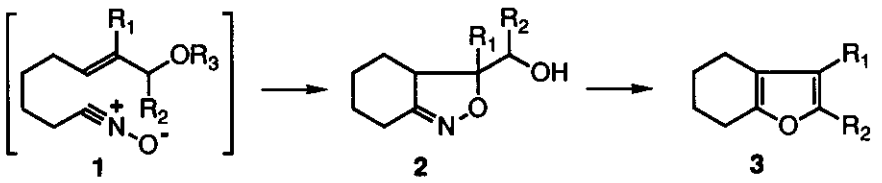
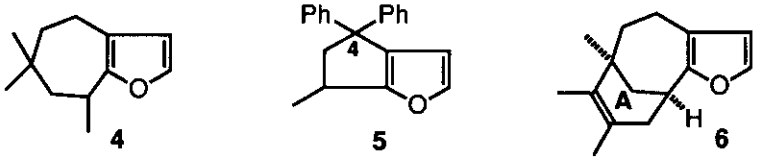
Abstract - General and efficient syntheses of 4*H*-cyclohepta- and 4*H*-cyclopenta[*b*]furans (**4** and **5**) have been accomplished employing the intramolecular [3+2] dipolar cycloaddition based fused furan construction strategy. Treatment of the oximes (**20** and **29**), readily prepared from the carboxylic acid (**7** and **23**) *via* a conventional sequence of reactions, with aqueous sodium hypochlorite produced excellent yields of the isoxazolines (**21** and **30**), which, after alkaline hydrolysis or desilylation, were exposed to the conditions of reductive hydrolysis followed by acid-catalyzed cyclization to give the corresponding fused furans (**4** and **5**) in good overall yields.

We recently reported a novel and efficient construction of the 4*H*-cyclohexa[*b*]furans (**3**)[1] from the isoxazoline alcohol (**2**), obtained *via* an intramolecular [3+2] dipolar cycloaddition reaction of the nitrile oxide (**1**), and exhibited the synthetic utility of the methodology by applying it to the syntheses of some furanoterpenes, e.g. pallescensin A,[1a] menthofuran,[1b] and the tricyclic core of tanshinones.[1c] (Scheme 1)



Scheme 1

In connection with our current synthetic studies directed toward the biologically active naturally occurring furanoterpenes having 4*H*-cyclohepta[*b*]furan framework, e.g. nakafuran-9 (**6**),[2] pallescensin E-G,[3] and gnididione,[4] and the pharmacologically promising prostacyclin analogues[5] with 4*H*-cyclopenta[*b*]furan skeleton, we planned to synthesize the two model compounds (**4** and **5**) employing our fused furan assembling strategy. The target compound (**4**) has the suitably positioned methyl groups as a model for des-A-ring nakafuran-9, and the other target (**5**) was designed to have a quaternary carbon at the C-4 position not only for pursuing the feasibility of the methodology but also for preventing the low-volatility of product. In this paper we describe experimental details of the successful syntheses of these fused furans (**4** and **5**). (Figure)

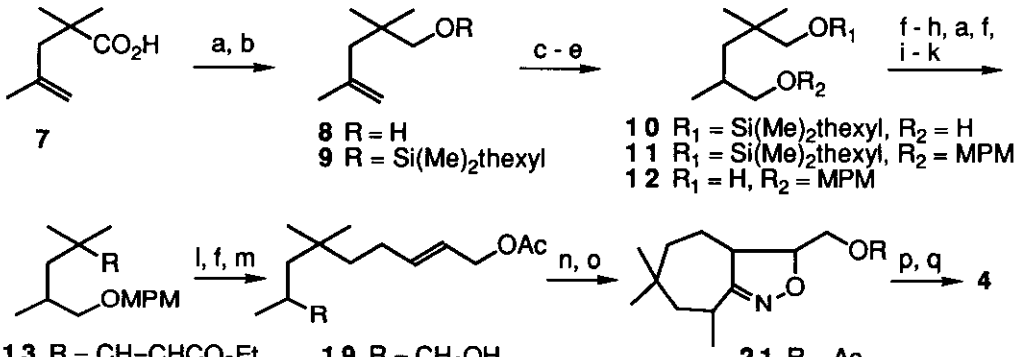


Figure

Synthesis of 5,6,7,8-tetrahydro-6,6,8-trimethyl-4*H*-cyclohepta[*b*]furan (4).

Sequential reduction of the carboxylic acid (**7**),[6] prepared from isobutyric acid dianion and methallyl chloride, with lithium aluminium hydride ($LiAlH_4$) and protection of the resulting alcohol (**8**) provided the silyl ether (**9**), which was submitted to the hydroboration-oxidation sequence to afford the primary alcohol (**10**). After protection as *p*-methoxybenzyl (MPM) ether, (**11**) was treated with tetra-*n*-butylammonium fluoride (TBAF) followed by Swern oxidation and Horner-Emmons olefination of the resultant alcohol (**12**) to provide the unsaturated ester (**13**). Chain elongation of **13** was performed by standard manipulations to give the allyl acetate (**18**) with E-configuration as shown in Scheme 2. Deprotection of MPM ether in **18** with 2,3-dichloro-5,6-dicyano-1,4-benzo-

quinone (DDQ) followed by Swern oxidation and oxime formation yielded the oxime acetate (**20**), a nitrile oxide precursor. On exposure of **20** to 7% aqueous sodium hypochlorite[7] in methylene chloride at room temperature, the expected intramolecular [3+2] dipolar cycloaddition reaction[8] smoothly occurred to provide the isoxazoline (**21**), an inseparable mixture of diastereoisomers,[9] in 98 % isolated yield. We are now able to examine the feasibility of the key transformations into the target molecule (**4**). Thus, reductive hydrolysis[10] of **22**, prepared by alkaline hydrolysis of the acetate (**21**), with a catalytic amount of Raney nickel (W-2) and methyl borate in aqueous methanol under a hydrogen pressure of 2.0 kg/cm^2 at room temperature resulted in the corresponding β,γ-dihydroxy ketone, which was immediately treated with a catalytic *p*-toluenesulfonic acid in methylene chloride at room temperature for 5 min in a one-pot operation to afford the desired furan (**4**) in 63 % overall yield from **21**. The structure of **4** was firmly established on the basis of the ^{1}H and ^{13}C nmr and the mass spectra. (Scheme 2)



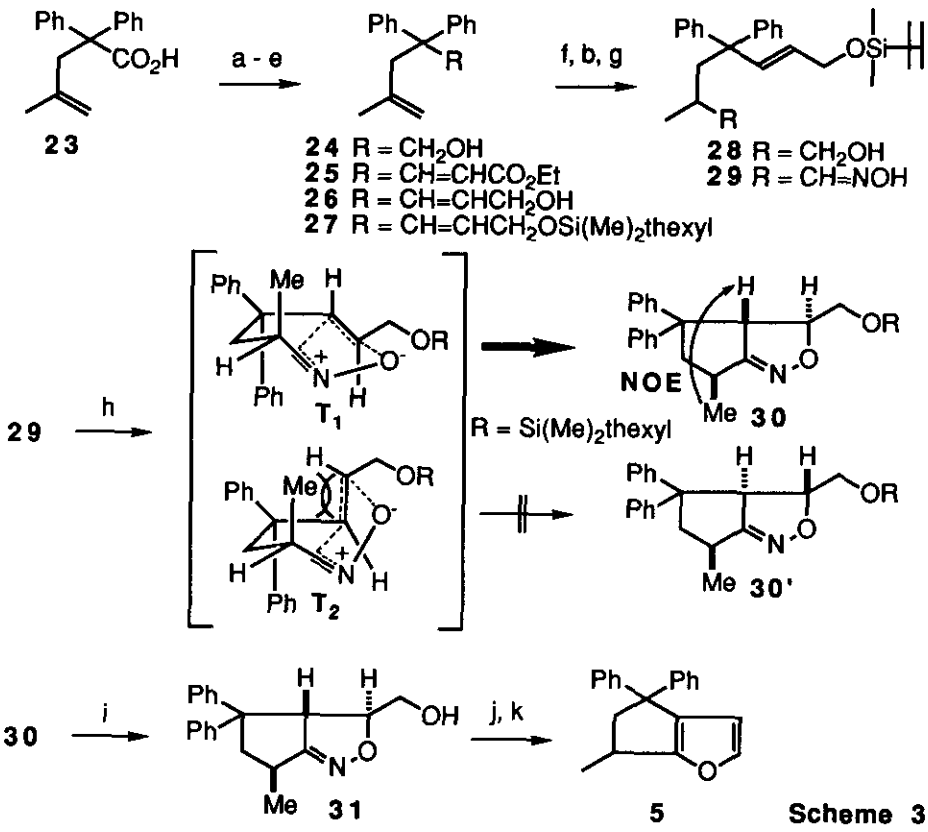
Scheme 2

Reagents: a, $LiAlH_4$, 86 %; b, $ClSi(Me)_2$thexyl, imidazole, 98 %; c, BH_3•THF then NaOH, H_2O_2, 95 %; d, NaH, *p*-$MeOC_6H_4CH_2Cl$, 86 %; e, $^nBu_4NF$, 92 %; f, Swern ox.; g, NaH, $(EtO)_2P(O)CH_2CO_2Et$, 89 % for the 2 steps; h, H_2, 10% Pd-C, 98 %; i, $Ph_3P{=}CHCO_2Me$; j, $^iBu_2AlH$, 98 %; k, Ac_2O, pyridine, 100 %; l, DDQ, 92 %; m, NH_2OH•HCl, AcONa, 78 % for the 2 steps; n, 7% aq. NaOCl, CH_2Cl_2, 98 %; o, LiOH•H_2O, aq.THF, 88 %; p, H_2, Raney Ni, $(MeO)_3B$, aq. MeOH; q, *p*-TsOH, CH_2Cl_2, 71 % for the 2 steps.

Synthesis of 5,6-dihydro-6-methyl-4,4-diphenyl-4*H*-cyclopenta[*b*]furan (5).

With the successful route to the 4*H*-cyclohepta[*b*]furan in hand, we next turned our attention to evaluate if the methodology would also be applicable to the construction of the lower homologue, i.e. 4*H*-cyclopenta[*b*]furan (**5**). As a starting material, we chose the carboxylic acid (**23**), similarly prepared from diphenylacetic acid dianion and methallyl chloride. Sequential $LiAlH_4$ reduction, Swern oxidation, Horner-Emmons reaction, and reduction with diisobutylaluminium hydride produced the allyl alcohol (**26**). At this point, we decided to use the dimethylthexylsilyl ether as the protective group of allylic alcohol in **26**, since the acetate used for the protection in **17** seemed to be difficult to survive in the next hydroboration. Thus, **26** was treated with dimethylthexylsilyl chloride and imidazole in methylene chloride to give the silyl ether (**27**) in 69 % overall yield from **23**. Chemoselective hydroboration using 9-borabicyclo[3.3.1]nonane (9-BBN) cleanly provided the primary alcohol (**28**), which was then transformed to the oxime (**29**). The oxime silyl ether (**28**) thus obtained was exposed to the same conditions as used for **20** to produce the isoxazoline (**30**) as a single product in 98 % yield. The exact configuration of the newly formed stereogenic centers in **30** could be determined by the observation of distinct NOE between C-6 methyl protons and C-3a methine proton as shown in Scheme 3. The remarkable diastereoselectivity in the cycloaddition reaction may be rationalized by considering the transition state.[11] That is to say, the transition state T_1, leading to **30**, would be more sterically favored than the other one, T_2, that provides the diastereoisomer (**30'**). Finally, the isoxazoline alcohol (**31**), derived from **30** by treatment with TBAF, was converted uneventfully to the desired fused furan (**5**), whose spectral data supported the structure. (Scheme 3)

In summary, we have demonstrated the efficient synthetic routes to 4*H*-cyclohepta- and 4*H*-cyclopenta[*b*]furans, which are important bicyclic ring systems present in the biologically active compounds, as an extension of our fused furan construction methodology. The syntheses described here are quite flexible because the introduction of a variety of functionalities to the requisite positions of the product would be easy, so that the application to the synthesis of natural furanoids such as nakafuran-9 are under way in our laboratories.



Scheme 3

Reagents: a, $LiAlH_4$, 80 %; b, Swern ox.; c, NaH, $(EtO)_2P(O)CH_2CO_2Et$, 93 % for the 2 steps; d, $^iBu_2AlH$, 96 %; e, $ClSi(Me)_2$thexyl, imidazole, 96 %; f, 9-BBN then NaOH, H_2O_2, 88 %; g, NH_2OH•HCl, AcONa, 82 % for the 2 steps; h, 7% aq. NaOCl, CH_2Cl_2, 98 %; i, $^nBu_4NF$, 97 %; j, H_2, Raney Ni, $(MeO)_3B$, aq. MeOH; k, *p*-TsOH, 61 % for the 2 steps.

EXPERIMENTAL SECTION

Melting points were determined by a Yanagimoto MP-S2 apparatus and are uncorrected. Ir spectra were recorded on a Parkin Elmer 1720FT-IR spectrophotometers. ^{1}H-Nmr spectra were recorded at 200 MHz on a JEOL JNM-FX200 spectrometer in deuteriochloroform solutions with tetramethylsilane (TMS) as an internal standard. ^{13}C-Nmr spectra were recorded at 100 MHz on a JEOL GSX400 spectrometer in deuteriochloroform solutions with TMS as an internal standard. Chemical shifts are reported in ppm (from TMS). When peak multiplicities are reported, the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br,

broadened. Ordinary mass spectra and high resolution mass spectra were measured with a JEOL JMS-D300 mass spectrometer. Tlc was carried out with E. Merck Silica gel GOF-254 (0. 25 mm thickness) precoated tlc plates. Columun chromatography was carried out with silica gel (Kieselgel 60, 70-230 mesh, E. Merck). All reactions were run under an atmosphere of nitrogen. Solvents were freshly distilled prior to use: tetrahydrofuran (THF), toluene, benzene, ether (Et_2O) and 1,2-dimethoxyethane (DME) were distilled from sodium and benzophenone: methylene chloride (CH_2Cl_2) was distilled from phosphorus pentoxide. Unless otherwise noted, all reaction mixture were dried, after workup, over anhydrous magnesium sulfate.

2,2,4-Trimethyl-4-penten-1-ol (8). A solution of the carboxylic acid (**7**)[6] (23. 30 g, 0. 16 mol) in dry THF (100 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (6. 22 g, 0. 16 mol) in dry THF (160 ml) at 0 °C. After being stirred at room temperature for 3 h, the mixture was quenched by addition of aq. Et_2O. After filtration through a pad of Celite, the filtrate was dried. Evaporation of the solvent followed by distillation (bp_{15} 74 - 75 °C) gave the alcohol (**8**) (18. 05 g, 86 %) as a colorless oil: Ir (neat) 3436 cm^{-1} (OH); ^{1}H-nmr (200 MHz) δ 0. 92 (6H, s, Me×2), 1. 80 (3H, br s, Me), 2. 02 (2H, br s, CH_2), 3. 36 (2H, s, $C\underline{H_2}OH$), 4. 70 (1H, m, olefinic H), 4. 87 (1H, m, olefinic H); ms m/z 111 (M^+- OH); HRms Calcd for C_8H_{15}: 111. 1174. Found: 111. 1179.

2,4,4-Trimethyl-5-dimethylthexylsilyloxy-1-pentene (9). Imidazole (8. 17 g, 0. 12 mol) and dimethylthexylsilyl chloride (19. 73 g, 0. 11 mol) were added to a stirred solution of **8** (12. 81 g, 0. 10 mol) in dry CH_2Cl_2 (130 ml) at 0 °C. After being stirred at room temperature for 4 h, the mixture was extracted with CH_2Cl_2 after addition of water. The extracts were washed with brine and dried. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 19 : 1, v/v) gave the silyl ether (**9**) (26. 53 g, 98 %) as a colorless oil: ^{1}H-Nmr (200 MHz) δ 0. 06 (6H, s, $SiMe_2$), 0. 85 (12H, s, $SiCMe_2$ and Me×2), 0. 90 (6H, d, J=6. 8 Hz, $C\underline{H_3}CHC\underline{H_3}$), 1. 61 (1H, q, J=6. 8 Hz, $CH_3C\underline{H}CH_3$), 1. 77 (3H, s, Me), 1. 98 (2H, s, CH_2), 3. 22 (2H, s, $C\underline{H_2}OSi$), 4. 65 (1H, br s, olefinic H), 4. 83 (1H, br s, olefinic H); ms m/z 255 (M^+- Me); HRms Calcd for $C_{15}H_{31}OSi$: 255. 2144. Found: 255. 2173.

2,4,4-Trimethyl-5-dimethylthexylsilyloxy-1-pentanol (10). Boran-THF complex (1. 0 M in THF, 19. 6 ml, 19. 6 mmol) was added dropwise to a stirred solution of **9** (16. 0 g, 59. 1 mmol) in dry THF (400 ml) at 0 °C. After being stirred at the same temperature for 20 min and at room temperature for 1 h, 1 N NaOH (19. 6 ml, 19. 6 mmol) and 30 % H_2O_2 (7. 38 ml, 65. 1 mmol) were added dropwise and the mixture was stirred at the same temperature for 1 h. The reaction mixture was poured into water and extracted with Et_2O. The extracts were washed with brine and dried. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 9 : 1, v/v) gave the alcohol (**10**) (16. 3 g, 95 %) as a colorless oil: Ir (neat) 3338 cm^{-1} (OH); ^{1}H-nmr (200 MHz) δ 0. 08 (6H, s, $SiMe_2$), 0. 84 (3H, s, Me), 0. 85 (6H, s, $SiCMe_2$), 0. 87 (3H, s, Me), 0. 89 (6H, d, J=6. 8 Hz, $C\underline{H}_3CHC\underline{H}_3$), 0. 95 (3H, d, J=6. 6 Hz, $C\underline{H}_3CH$), 1. 39 (1H, m, C<u>H</u>H), 1. 62 (2H, m, CH<u>H</u> and $CH_3C\underline{H}CH_3$), 1. 81 (2H, m, $CH_3C\underline{H}$ and OH, D_2O exchangeable), 3. 23 (1H, d, J=19. 8 Hz, C<u>H</u>HOSi), 3. 28 (1H, d, J=19. 8 Hz, CH<u>H</u>OSi), 3. 38 (2H, m, $C\underline{H}_2OH$); ms m/z 203 (M^+- thexyl). Anal. Calcd for $C_{16}H_{36}O_2Si$: C, 66. 60; H, 12. 58. Found: C, 66. 12; H, 12. 97.

5-(4-Methoxybenzyloxy)-2,2,4-trimethyl-1-dimethylthexylsilyloxypentane (11). A solution of **10** (14. 8 g, 51. 3 mmol) in dry DME (120 ml) was added dropwise to a stirred suspension of 60 % sodium hydride (1. 48 g, 61. 7 mmol) in dry DME (40 ml) at 0 °C. After being stirred at 70 °C for 2 h, 4-methoxybenzyl chloride (10. 0 g, 63. 9 mmol) was added dropwise and the mixture was stirred at the same temperature for 18 h. The mixture was extracted with Et_2O after addition of water. The extracts were washed with brine and dried. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 19 : 1, v/v) gave the MPM ether (**11**) (18. 0 g, 86 %) as a colorless oil: ^{1}H-Nmr (200 MHz) δ 0. 04 (6H, s, $SiMe_2$), 0. 83 (12H, s, $SiCMe_2$ and Me×2), 0. 88 (6H, d, J=6. 8 Hz, $C\underline{H}_3CHC\underline{H}_3$), 0. 97 (3H, d, J=6. 6 Hz, $C\underline{H}_3CH$), 1. 26 (1H, m, C<u>H</u>H), 1. 59 (2H, m, CH<u>H</u> and $CH_3C\underline{H}CH_3$), 1. 79 (1H, m, $CH_3C\underline{H}$), 3.10 (1H, m, C<u>H</u>HOMPM), 3. 20 (2H, s, $C\underline{H}_2OSi$), 3. 30 (1H, m, CH<u>H</u>OMPM), 3. 80 (3H, s, OMe), 4. 42 (2H, s, benzylic H), 6. 87 (2H, d, J=8. 6 Hz, PhH), 7. 26 (2H, d, J=8. 6 Hz, PhH); ms m/z 408 (M^+). Anal. Calcd for $C_{24}H_{44}O_3Si$: C, 70. 53; H, 10. 85. Found: C, 70. 12; H, 11. 11.

5-(4-Methoxybenzyloxy)-2,2,4-trimethyl-1-pentanol (12). TBAF (1. 0 M in THF, 2. 50 ml, 2. 50 mmol) was added dropwise to a stirred solution of **11** (850 mg, 2. 08 mmol) in dry THF (12 ml) at 0 °C. After being stirred at room temperature for 3 h, the mixture was extracted with ethyl acetate after addition of water. The extracts were washed with brine and dried. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 4 : 1, v/v) gave the alcohol (**12**) (510 mg, 92 %) as a colorless oil: Ir (neat) 3419 cm^{-1} (OH); ^{1}H-nmr (200MHz) δ 0. 81 (3H, s, Me), 0. 90 (3H, d, J=6. 8Hz, C$\underline{H_3}$CH), 0. 91 (3H, s, Me), 1. 25 (1H, m, C$\underline{H}$H), 1. 63 (1H, m, CH$\underline{H}$), 1. 77 (1H, m, $CH_3C\underline{H}$), 2. 86 (1H, dd, J=9. 0 and 4. 9 Hz, OH, D_2O exchangeable), 3. 08 (1H, dd, J=11. 2 and 9. 0 Hz, C$\underline{H}$HOH), 3. 12 (1H, dd, J=8. 8 and 8. 8 Hz, C$\underline{H}$HOMOM), 3. 29 (1H, dd, J=8. 8 and 4. 9 Hz, CH$\underline{H}$OMOM), 3. 42 (1H, dd, J=11. 2 and 4. 9 Hz, CH$\underline{H}$OH), 3. 80 (3H, s, OMe), 4. 45 (2H, s, benzylic H), 6. 88 (2H, d, J=8. 9 Hz, PhH), 7. 25 (2H, d, J=8. 9 Hz, PhH); ms m/z 266 (M^+). Anal. Calcd for $C_{16}H_{26}O_3$: C, 72. 14; H, 9. 84. Found: C, 72. 14; H, 10. 01.

Ethyl (*E*)-7-(4-methoxybenzyloxy)-4,4,6-trimethyl-2-heptenoate (13). Dimethyl sulfoxide (4. 08 g, 52. 2 mmol) was added to a stirred solution of oxalyl chloride (3. 32 g, 26. 2 mmol) in dry CH_2Cl_2 (30 ml) at -78 °C, and a solution of **12** (5. 36 g, 20. 1 mmol) in dry CH_2Cl_2 (70 ml) was then added dropwise to the chilled solution. After the solution had been stirred at the same temperature for 30 min, triethylamine (10. 16 g, 0. 10 mol) was added dropwise and the resulting mixture was warmed to room temperature for 40 min. The mixture was extracted with CH_2Cl_2 after addition of water and the extracts were washed with brine and dried. Evaporation of the solvent gave the crude aldehyde (5. 38 g, 100 %), an yellow oil, which was used to next reaction without further purification: Ir (neat) 1726 cm^{-1} (C=O); ^{1}H-nmr (200 MHz) δ 0. 88 (3H, d, J=6. 7Hz, C$\underline{H_3}$CH), 1. 05 (3H, s, Me), 1. 06 (3H, s, Me), 1. 71 (3H, m, CH_2 and $CH_3C\underline{H}$), 3. 18 (2H, d, J=5. 9 Hz, C$\underline{H_2}$OMPM), 3. 81 (3H, s, OMe), 4. 38 (2H, s, benzylic H), 6. 86 (2H, d, J=8. 5 Hz, PhH), 7. 24 (2H, d, J=8. 5 Hz, PhH), 9. 44 (1H, s, CHO).

Triethyl phosphonoacetate (5. 41 g, 24. 1 mmol) was added dropwise to a stirred suspension of 60 % sodium hydride (580 mg, 24. 2 mmol) in dry DME (50 ml) at room temperature. After being stirred at the same temperature for 1 h, the crude aldehyde in dry DME (80 ml) was added dropwise and the mixture was stirred at the same temperature for 12 h. The mixture was extracted with Et_2O after

addition of water. The extracts were washed with brine and dried. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 9 : 1, v/v) gave the unsaturated ester (**13**) (5. 98 g, 89 %) as a colorless oil: Ir (neat) 1718 cm^{-1} (C=O); ^{1}H-nmr (200 MHz) δ 0. 92 (3H, d, J=6. 8 Hz, C$\underline{H_3}$CH), 1. 06 (6H, s, Me×2), 1. 28 (3H, t, J=7. 1 Hz, $CO_2CH_2C\underline{H_3}$), 1. 58 (2H, m, CH_2), 1. 72 (1H, m, $CH_3C\underline{H}$), 3. 18 (2H, m, C$\underline{H_2}$OMPM), 3. 80 (3H, s, OMe), 4. 18 (2H, q, J=7. 1 Hz, $CO_2C\underline{H_2}CH_3$), 4. 40 (2H, s, benzylic H), 5. 72 (1H, d, J=16. 1 Hz, CH=C$\underline{H}CO_2$Et), 6. 87 (2H, d, J=8. 8 Hz, PhH), 6.95 (1H, d, J=16. 1 Hz, C$\underline{H}$=CHCO$_2$Et), 7. 25 (2H, d, J=8. 8 Hz, PhH); ms m/z 334 (M^+). Anal. Calcd for $C_{20}H_{30}O_4$: C, 71. 82; H, 9. 04. Found: C, 71. 45; H, 9. 17.

Ethyl 7-(4-methoxybenzyloxy)-4,4,6-trimethylheptanoate (14). A mixture of **13** (5. 00 g, 14. 9 mmol) and 10 % palladium on carbon (500 mg) in EtOH (150 ml) was stirred at room temperature for 12 h under an atmosphere of hydrogen. The reaction mixture was filtrated and the filtrate was evaporated. A residue was chromatographed on silica gel (hexane - ethyl acetate, 4 : 1, v/v) to afford the ester (**14**) (4. 91 g, 98 %) as a colorless oil: Ir (neat) 1735 cm^{-1} (C=O); ^{1}H-nmr (200 MHz) δ 0. 87 (6H, s, Me×2), 0. 97 (3H, d, J=6. 6 Hz, C$\underline{H_3}$CH), 1. 25 (3H, t, J=7. 1 Hz, $CO_2CH_2C\underline{H_3}$), 1. 56 (4H, m, CH_2×2), 1. 80 (1H, m, $CH_3C\underline{H}$), 2.25 (2H, m, C$\underline{H_2}CO_2$Et), 3. 14 (1H, dd, J=9. 0 and 7. 1 Hz, C$\underline{H}$HOMPM), 3. 26 (1H, dd, J=9. 0 and 5. 9 Hz, CH$\underline{H}$OMPM), 3. 80 (3H, s, OMe), 4. 11 (2H, q, J=7. 1 Hz, $CO_2C\underline{H_2}CH_3$), 4. 42 (2H, s, benzylic H), 6. 87 (2H, d, J=8. 5 Hz, PhH), 7. 25 (2H, d, J=8. 5 Hz, PhH); ms m/z 336 (M^+). Anal. Calcd for $C_{20}H_{32}O_4$: C, 71. 39; H, 9. 59. Found: C, 70. 92; H, 9. 92.

7-(4-Methoxybenzyloxy)-4,4,6-trimethyl-1-heptanol (15). A solution of **14** (4. 80 g, 14. 3 mmol) in dry THF (40 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (540 mg, 14. 2 mol) in dry THF (20 ml) at 0 °C. After being stirred at room temperature for 1 h, the mixture was quenched by addition of aq. Et_2O. After filtration through a pad of Celite, the filtrate was dried. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 2 : 1, v/v) gave the alcohol (**15**) (4. 11 g, 98 %) as a colorless oil: Ir (neat) 3392 cm^{-1} (OH); ^{1}H-nmr (200 MHz) δ 0. 88 (6H, s, Me×2), 0. 97 (3H, d, J=6. 6 Hz, C$\underline{H_3}$CH), 1. 27 (4H, m, CH_2×2), 1. 51 (2H, m, CH_2), 1. 80 (1H, m, $CH_3C\underline{H}$), 3. 13 (1H, dd, J=9. 0 and 7. 3 Hz, C$\underline{H}$HOMPM), 3. 26 (1H, dd, J=9. 0 and 5. 9 Hz, CH$\underline{H}$OMPM), 3. 80 (3H, s, OMe), 4. 43 (2H, s, benzylic H), 6. 88 (2H, d, J=8. 6 Hz, PhH),

7. 26 (2H, d, J=8. 6 Hz, PhH); ms m/z 294 (M^+). Anal. Calcd for $C_{18}H_{30}O_3$: C, 73. 43; H, 10. 27. Found: C, 73. 45; H, 10. 63.

Methyl (*E*)-9-(4-methoxybenzyloxy)-6,6,8-trimethyl-2-nonenoate (16). According to the procedure described for oxidation of **12**, the alcohol (**15**) (4. 00 g, 13. 6 mmol) was converted to the corresponding aldehyde (4. 06 g, 100 %), which was used for the next reaction without further purification: Ir (neat) 1724 cm^{-1} (C=O).

A mixture of the crude aldehyde and methyl triphenylphosphoranylideneacetate (5. 45 g, 16. 30 mmol) in dry benzene (80 ml) was stirred under reflux for 3 h. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 4 : 1, v/v) gave the unsaturated ester (**16**) (4. 49 g, 95 %) as a colorless oil: Ir (neat) 1725 cm^{-1} (C=O); ^{1}H-nmr (200 MHz) δ 0. 88 (6H, s, Me×2), 0. 97 (3H, d, J=6. 6 Hz, $C\underline{H}_3CH$), 1. 33 (4H, m, $CH_2\times2$), 1. 77 (1H, m, $CH_3C\underline{H}$), 2. 14 (2H, m, CH_2C=C), 3. 13 (1H, dd, J=9. 0 and 7. 1 Hz, C$\underline{H}$HOMPM), 3. 25 (1H, dd, J=9. 0 and 5. 9 Hz, CH$\underline{H}$OMPM), 3. 72 (3H, s, CO_2Me), 3. 80 (3H, s, OMe), 4. 42 (2H, s, benzylic H), 5. 79 (1H, dt, J=15. 6 and 1. 3 Hz, CH=C$\underline{H}CO_2Me$), 6. 87 (2H, d, J=8. 5 Hz, PhH), 6. 96 (1H, dt, J=15. 6 and 6. 8 Hz, C$\underline{H}$=CHCO_2Me), 7. 25 (2H, d, J=8. 5 Hz, PhH); ms m/z 348. Anal. Calcd for $C_{21}H_{32}O_4$: C, 72. 38; H, 9. 26. Found: C, 72. 84; H, 9. 47.

(*E*)-9-(4-Methoxybenzyloxy)-6,6,8-trimethyl-2-nonen-1-ol (17). Diisobutylaluminium hydride (1. 0 M in toluene, 2. 15 ml, 2. 15 mmol) was added dropwise to a stirred solution of **16** (326 mg, 0. 94 mmol) in dry toluene (8 ml) at -78 °C. After being stirred at the same temperature for 30 min, the mixture was treated with water (2. 15 ml) at room temperature for 1 h, then filtered through a pad of Celite. The filtrate was dried and concentrated to give a residue which was chromatographed on silica gel (hexane - ethyl acetate, 4 : 1, v/v) gave the allyl alcohol (**17**) (293 mg, 98 %) as a colorless oil: Ir (neat) 3401 cm^{-1} (OH); ^{1}H-nmr (200 MHz) δ 0. 86 (6H, s, Me×2), 0. 97 (3H, d, J=6. 6 Hz, $C\underline{H}_3CH$), 1. 28 (4H, m, $CH_2\times2$), 1. 56 (1H, br, OH, D_2O exchangeable), 1. 79 (1H, m, $CH_3C\underline{H}$), 1. 99 (2H, m, CH_2C=C), 3. 12 (1H, dd, J=9. 0 and 7. 6 Hz, C$\underline{H}$HOMPM), 3. 27 (1H, dd, J=9. 0 and 5. 9 Hz, CH$\underline{H}$OMPM), 3. 80 (3H, s, OMe), 4. 43 (2H, s, benzylic H), 5. 63 (2H, m, olefinic H), 6. 87 (2H, d, J=8. 5 Hz, PhH), 7. 26 (2H, d, J=8. 5 Hz, PhH); ms m/z 320. Anal. Calcd for

$C_{20}H_{32}O_3$: C, 74. 96; H, 10. 06. Found: C, 74. 98; H, 10. 36.

(*E*)-1-Acetoxy-9-(4-methoxybenzyloxy)-6,6,8-trimethyl-2-nonene (18). Acetic anhydride (2. 16 g, 21. 2 mmol) was added to a stirred solution of **17** (285 mg, 0. 89 mmol) in pyridine (2. 0 ml, 24. 5 mmol) at 0 °C. After being stirred at room temperature for 2 h, the solvent was evaporated and the residue was extracted with CH_2Cl_2 after addition of water. The extracts were washed with brine and dried. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 4 : 1, v/v) gave the acetate (**18**) (322 mg, 100 %) as a colorless oil: Ir (neat) 1741 cm^{-1} (C=O); ^{1}H-nmr (200 MHz) δ 0. 86 (6H, s, Me×2), 0. 97 (3H, d, J=6. 6 Hz, C<u>H</u>$_3$CH), 1. 26 (4H, m, CH_2 ×2), 1. 79 (1H, m, CH_3C<u>H</u>), 2. 01 (2H, m, CH_2C=C), 2. 02 (3H, s, COMe), 3. 12 (1H, dd, J=9. 0 and 7. 6 Hz, C<u>H</u>HOMPM), 3. 26 (1H, dd, J=9. 0 and 5. 6 Hz, CH<u>H</u>OMPM), 3. 80 (3H, s, OMe), 4. 43 (2H, s, benzylic H), 4. 49 (2H, d, J=6. 1 Hz, C<u>H</u>$_2$OAc), 5. 64 (2H, m, olefinic H), 6. 87 (2H, d, J=8. 5 Hz, PhH), 7. 26 (2H, d, J=8. 5 Hz, PhH); ms m/z 362. Anal. Calcd for $C_{22}H_{34}O_4$: C, 72. 89; H, 9. 45. Found: C, 72. 45; H, 9. 73.

(*E*)-9-Acetoxy-2,4,4-trimethyl-7-nonen-1-ol (19). DDQ (2. 68 g, 11. 8 mmol) was added to a stirred solution of **18** (3. 89 g, 10. 7 mmol) in CH_2Cl_2 (72 ml) - water (4 ml) at 0 °C. After being stirred at room temperature for 1 h, the reaction mixture was filtered and the filtrate was extracted with CH_2Cl_2. The extracts were successively washed with sat. aq. $NaHCO_3$ and brine and dried. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 19 : 1, v/v) gave the alcohol (**19**) (2. 40 g, 92 %) as a colorless oil: Ir (neat) 3442 (OH) and 1742 cm^{-1} (C=O); ^{1}H-nmr (200 MHz) δ 0. 89 (6H, s, Me×2), 0. 98 (3H, d, J=6. 6 Hz, C<u>H</u>$_3$CH), 1. 31 (4H, m, CH_2 ×2), 1. 57 (1H, br, OH, D_2O exchangeable), 1. 65 (1H, m, CH_3C<u>H</u>), 2. 00 (2H, m, CH_2C=C), 2. 06 (3H, s, COMe), 3. 33 (1H, dd, J=10. 5 and 7. 3 Hz, C<u>H</u>HOH), 3. 47 (1H, dd, J=10. 5 and 5. 6 Hz, CH<u>H</u>OH), 4. 50 (2H, d, J=6. 4 Hz, C<u>H</u>$_2$OAc), 5. 67 (2H, m, olefinic H); ms m/z 242 (M^+). Anal. Calcd for $C_{14}H_{26}O_3$: C, 69. 38; H, 10. 81. Found: C, 69. 85; H, 11. 02.

(*E*)-1-Acetoxy-9-hydroxyimino-6,6,8-trimethyl-2-nonene (20). A solution of the crude aldehyde (2. 28 g, 9. 5mmol), obtained from **19** (2. 30 g, 9. 5 mmol) by the same procedure as

described for **12**, in dry benzene (40 ml) was added to a stirred solution of hydroxylamine hydrochloride (1. 32 g, 19. 0 mmol) and sodium acetate (1. 95 g, 23. 8 mmol) in dry benzene (40 ml). After being stirred at room temperature for 48 h, the solvent was evaporated and the residue was extracted with $CHCl_3$ after addition of water. The extracts were washed with brine and dried. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 9 : 1, v/v) gave the oxime (**20**) (1. 89 g, 78 %) as a colorless oil; aldehyde: Ir (neat) 1741 (C=O) and 1728 cm^{-1} (C=O); ^{1}H-nmr (200 MHz) δ 0. 87 (6H, s, Me×2), 1. 10 (3H, d, J=7. 0 Hz, $C\underline{H}_3CH$), 1. 29 (2H, m, CH_2), 1. 84 (2H, m, CH_2), 2. 02 (2H, m, CH_2C=C), 2. 06 (3H, s, COMe), 2. 41 (1H, m, $CH_3C\underline{H}$), 4. 50 (2H, d, J=6. 2 Hz, $C\underline{H}_2OAc$), 5. 66 (2H, m, olefinic H), 9. 56 (1H, d, J=2. 6 Hz, CHO); oxime: Ir (neat) 3418 (OH) and 1741 cm^{-1} (C=O); ^{1}H-nmr (200 MHz) δ 0. 88 (6H, s, Me×2), 1. 03 (3/2H, d, J=6. 8 Hz, $C\underline{H}_3CH$), 1. 08 (3/2H, d, J=6. 8 Hz, $C\underline{H}_3CH$), 1. 35 (4H, m, CH_2×2), 2. 02 (2H, m, CH_2C=C), 2. 06 (3H, s, COMe), 2. 51 (1/2H, m, $CH_3C\underline{H}$), 3. 25 (1/2H, m, $CH_3C\underline{H}$), 4. 50 (2H, d, J=6. 4 Hz, $C\underline{H}_2OAc$), 5. 67 (2H, m, olefinic H), 6. 54 (1/2H, d, J=8. 1 Hz, CH=N), 7. 14 (1/2H, br, OH, D_2O exchangeable), 7. 25 (1/2H, d, J=7. 8 Hz, CH=N), 7. 43 (1/2H, br, OH, D_2O exchangeable); ms m/z 255 (M^+). Anal. Calcd for $C_{14}H_{25}NO_3$: C, 65. 85; H, 9. 87; N, 5. 49. Found: C, 65. 38; H, 10. 02; N, 5. 10.

3-Acetoxymethyl-3,3a,5,6,7,8-hexahydro-6,6,8-trimethyl-4*H*-cyclohepta[*c*]isoxazole (21). 7% Aq. sodium hypochlorite (0. 88 ml, 0. 83 mmol) was added slowly to a stirred solution of **20** (140 mg, 0. 55 mmol) in CH_2Cl_2 (10 ml) at room temperature. After being stirred at the same temperature for 16 h, the mixture was extracted with CH_2Cl_2, and the extracts were washed with brine and dried. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 9 : 1, v/v) gave the isoxazoline acetate (**21**) (136 mg, 98 %) as a colorless oil: Ir (neat) 1746 cm^{-1} (C=O); ^{1}H-nmr (200 MHz) δ 0. 89 (3H, s, Me), 0. 95 (3H, s, Me), 1. 16 (3H, d, J=6. 8 Hz, $C\underline{H}_3CH$), 1. 42 (4H, m, CH_2×2), 1. 69 (1H, m, $C\underline{H}H$), 2. 06 (1H, m, $CH\underline{H}$), 2. 08 (3H, s, $COCH_3$), 2. 89 (2H, m, $CH_3C\underline{H}$ and CHC=N), 4. 05 (2H, m, $C\underline{H}_2OAc$), 4. 31 (1H, m, CHON); ms m/z 253 (M^+); HRms Calcd for $C_{14}H_{23}NO_3$: 253. 1678. Found: 253. 1681.

3,3a,5,6,7,8-Hexahydro-3-hydroxymethyl-6,6,8-trimethyl-4*H*-cyclohepta[*c*]isoxazole (22). Lithium hydroxide monohydrate (65 mg, 1. 55 mmol) was added to a stirred solution of **21**

(130 mg, 0. 51 mmol) in THF (2. 7 ml) - water (0. 9 ml) at room temperature. After being stirred at the same temperature for 2 h, the solvent was evaporated to leave a residue which was extracted with $CHCl_3$, and the extracts were washed with brine and dried. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 2 : 1, v/v) gave the alcohol (**22**) (95 mg, 88 %) as a colorless oil: Ir (neat) 3392 cm^{-1} (OH); ^{1}H-nmr (200 MHz) δ 0. 90 (3H, s, Me), 0. 95 (3H, s, Me), 1. 18 (3H, d, J=7. 1 Hz, $C\underline{H}_3CH$), 1. 42 (4H, m, $CH_2\times2$), 1. 68 (2H, m, CH_2), 1. 89 (1H, m, OH, D_2O exchangeable), 2. 91 (2H, m, $CH_3C\underline{H}$ and CHC=N), 3. 52 (1H, dd, J=12. 0 and 5. 4 Hz, $C\underline{H}HOH$), 3. 65 (1H, dd, J=12. 0 and 5. 1 Hz, $CH\underline{H}OH$), 4. 20 (1H, m, CHON); ms m/z 211 (M^+); HRms Calcd for $C_{12}H_{21}NO_2$: 211. 1572. Found: 211. 1571.

5,6,7,8-Tetrahydro-6,6,8-trimethyl-4*H*-cyclohepta[*b*]furan (4). Trimethyl borate (247 mg, 2. 38 mmol) was added to a suspension of **22** (50 mg, 0. 24 mmol) and a catalytic amount of Raney nickel (W-2) in MeOH (4 ml) - water (0. 3 ml). The resulting mixture was stirred under a hydrogen pressure (2. 0 kg/cm^2) at room temperature for 13 h. After filtration through a pad of Celite, the filtrate was concentrated to give a residue which was extracted with $CHCl_3$. The extracts were washed with brine, dried, and evaporated to leave a residue which was taken up into dry CH_2Cl_2 (3 ml). A catalytic amount of p-toluenesulfonic acid was added to the solution and the mixture was stirred at room temperature for 5 min. After addition of water, the mixture was extracted with CH_2Cl_2. The extracts were washed with brine and dried. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 19 : 1, v/v) gave the furan (**4**) (30 mg, 71 %) as a colorless oil: ^{1}H-Nmr (200 MHz) δ 0. 98 (6H, s, Me×2), 1. 28 (3H, d, J=6. 8 Hz, $C\underline{H}_3CH$), 1. 49 (4H, m, $CH_2\times2$), 2. 92 (1H, m, $CH_3C\underline{H}$), 6. 12 (1H, d, J=1. 7 Hz, $C\underline{H}$=CHO), 7. 16 (1H, d, J=1. 7 Hz, CH=C$\underline{H}$O); ^{13}C-nmr (100 MHz) δ 19. 29, 21. 39, 25. 38, 29. 28, 33. 18, 33. 49, 40. 74, 49. 06, 112. 87, 119. 43, 138. 51, 155. 13; ms m/z 178 (M^+); HRms Calcd for $C_{12}H_{18}O$: 178. 1358. Found: 178. 1359.

4-Methyl-2,2-diphenyl-4-pentenoic acid (23). Diisopropylamine (12. 4 g, 0. 12 mol) and diphenylacetic acid (25. 0 g, 0. 12 mol) were added to a stirred suspension of 60 % sodium hydride (2. 95 g, 0. 12 mol) in dry THF (600 ml) at room temperature. After refluxing for 1 h, the mixture was stirred at room temperature for 3 h with *n*-BuLi (1. 6 M in hexane, 73. 6 ml, 0. 12 mol). The resulting

lithio compound was allowed to react with methallyl chloride (11. 5 g, 0. 13 mol) by stirring overnight at 30 °C. Water was added to the reaction mixture at 0 °C and aqueous phase was extracted with CH_2Cl_2 under acidic condition. The extracts were washed with brine and dried. Evaporation of the solvent followed by chromatography on silica gel (CH_2Cl_2 - MeOH, 30 : 1, v/v) gave the carboxylic acid (**23**) (27. 0 g, 86 %) as a white powder (mp 114 - 115 °C): Ir (KBr) 1697 cm^{-1} (C=O); ^{1}H-nmr (200 MHz) δ 1. 34 (3H, s, Me), 3. 18 (2H, s, CH_2), 4. 55 (1H, br s, olefinic H), 4. 70 (1H, br s, olefinic H), 7. 28 (10H, m, PhH); ms m/z 266 (M^+). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81. 17; H, 6. 81. Found: C, 81. 07; H, 6. 92.

4-Methyl-2,2-diphenyl-4-penten-1-ol (24). A solution of **23** (10. 00 g, 37. 6 mmol) in dry THF (50 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (2. 85 g, 75. 1 mmol) in dry THF (250 ml) at 0 °C. After refluxing for 12 h, the mixture was quenched by addition of aq. Et_2O at 0 °C. After filtration through a pad of Celite, the filtrate was dried. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 9 : 1, v/v) gave the alcohol (**24**) (7. 59 g, 80 %) as a colorless oil: Ir (neat) 3436 cm^{-1} (OH); ^{1}H-nmr (200 MHz) δ 1. 11 (3H, s, Me), 1. 11 (IH, m, OH, D_2O exchangeable), 2. 96 (2H, s, CH_2), 4. 25 (2H, d, J=6. 8 Hz, C$\underline{H_2}$OH), 4. 67 (1H, br s, olefinic H), 4. 85 (1H, br s, olefinic H), 7. 21 (10H, m, PhH); ms m/z 252 (M^+). Anal. Calcd for $C_{18}H_{20}O$: C, 85. 67; H, 7. 99. Found: C, 85. 41; H, 8. 19.

Ethyl (*E*)-6-methyl-4,4-diphenyl-2,6-heptadienoate (25). The unsaturated ester (**25**) (6. 23 g, 93 %) was obtained as a colorless oil *via* the aldehyde from **24** (5. 29 g, 21. 0 mmol) according to the procedure used for **13**; aldehyde: Ir (neat) 1724 cm^{-1} (C=O); ^{1}H-nmr (200 MHz) δ 1. 32 (3H, s, Me), 3. 14 (2H, s, CH_2), 4. 53 (1H, br s, olefinic H), 4. 70 (1H, br s, olefinic H), 7. 24 (10H, m, PhH), 9. 86 (1H, s, CHO); unsaturated ester (**25**): Ir (neat) 1719 cm^{-1} (C=O); ^{1}H-nmr (200 MHz) δ 1. 27 (3H, t, J=7. 1 Hz, $CO_2CH_2C\underline{H_3}$), 1. 35 (3H, s, Me), 3. 08 (2H, s, CH_2), 4. 18 (2H, q, J=7. 1 Hz, $CO_2C\underline{H_2}CH_3$), 4. 54 (1H, br s, olefinic H), 4. 82 (1H, br s, olefinic H), 5. 39 (1H, d, J=15. 9 Hz, CH=C$\underline{H}$$CO_2$Et), 7. 25 (10H, m, PhH), 7. 79 (1H, d, J=15. 9 Hz, C_H=CHCO_2Et); ms m/z 320 (M^+). Anal. Calcd for $C_{22}H_{24}O_2$: C, 82. 46; H, 7. 55. Found: C, 82. 00; H, 7. 76.

(*E*)-6-Methyl-4,4-diphenyl-2,6-heptadien-1-ol (26). The allyl alcohol (**26**) (5. 01 g, 96 %) was obtained as a colorless oil from **25** (6. 00 g, 43. 1 mmol) according to the experimental conditions used for **17**: Ir (neat) 3327 cm^{-1} (OH); ^{1}H-nmr (200 MHz) δ 1. 26 (1H, m, OH, D_2O exchangeable), 1. 32 (3H, s, Me), 3. 05 (2H, s, CH_2), 4. 17 (2H, m, $C\underline{H}_2OH$), 4. 53 (1H, br s, olefinic H), 4. 78 (1H, br s, olefinic H), 5. 17 (1H, dt, J=15. 6 and 5. 6 Hz, CH=C$\underline{H}$CH_2OH), 6. 52 (1H, d, J=15. 6 Hz, C$\underline{H}$=CHCH_2OH), 7. 21 (10H, m, PhH); ms m/z 278 (M^+). Anal. Calcd for $C_{20}H_{22}O$: C, 86. 29; H, 7. 97. Found: C, 85. 90; H, 8. 16.

(*E*)-2-Methyl-7-dimethylthexylsilyloxy-4,4-diphenyl-1,5-heptadiene (27). The silyl ether (**27**) (7. 05 g, 96 %) was obtained as a colorless oil from **26** (4. 90 g, 17. 6 mmol) according to the procedure used for **9**: ^{1}H-Nmr (200 MHz) δ 0. 08 (6H, s, $SiMe_2$), 0. 84 (6H, s, $SiCMe_2$), 0. 88 (6H, d, J=7. 1 Hz, C$\underline{H}_3$CH$\underline{C}$H$_3$), 1. 32 (3H, s, Me), 1. 61 (1H, q, J=7. 1 Hz, $CH_3C\underline{H}CH_3$), 3. 03 (2H, s, CH_2), 4. 16 (2H, dd, J=4. 8 and 1. 6 Hz, C$\underline{H}_2$OSi), 4. 52 (1H, br s, olefinic H), 4. 76 (1H, br s, olefinic H), 5. 03 (1H, dt, J=15. 6 and 4. 6 Hz, CH=C$\underline{H}$CH_2OSi), 6. 51 (1H, d, J=15. 6 Hz, C$\underline{H}$=CHCH_2OSi), 7. 21 (10H, m, PhH); ms m/z 420 (M^+). Anal. Calcd for $C_{28}H_{40}OSi$: C, 79. 94; H, 9. 58. Found: C, 79. 67; H, 9. 64.

(*E*)-2-Methyl-7-dimethylthexylsilyloxy-4,4-diphenyl-5-hepten-1-ol (28). 9-BBN (0. 5 M in hexane, 28. 8 ml, 14. 4 mmol) was added dropwise to a stirred solution of **27** (5. 76 g, 13. 7 mmol) in dry THF (130 ml) at 0 °C. After being stirred at room temperature for 3 h, 1 N NaOH (14. 4 ml, 14. 4 mmol) and 30 % aq. H_2O_2 (4. 7 ml, 41. 3 mmol) were successively added and the resulting mixture was then stirred at the same temperature for 1 h. The reaction mixture was poured into water and aqueous phase was extracted with Et_2O. The extracts were washed with brine and dried. Evaporation of the solvent followed by chromatography on silica gel (hexane - ethyl acetate, 4 : 1, v/v) gave the alcohol (**28**) (5. 28 g, 88 %) as a colorless oil: Ir (neat) 3387 cm^{-1} (OH); ^{1}H-nmr (200 MHz) δ 0. 07 (6H, s, $SiMe_2$), 0. 76 (3H, d, J=6. 8 Hz, C$\underline{H}_3$CH), 0. 85 (6H, s, $SiCMe_2$), 0. 88 (6H, d, J=6. 8 Hz, C$\underline{H}_3$CH$\underline{C}$H$_3$), 1. 10 (1H, m, OH, D_2O exchangeable), 1. 56 (1H, m, $CH_3C\underline{H}$), 1. 61 (1H, q, J=6. 8 Hz, $CH_3C\underline{H}CH_3$), 2. 07 (1H, dd, J=13. 7 and 5. 4 Hz, C$\underline{H}$H), 2. 39 (1H, dd, J=13. 7 and 4. 6 Hz, CH$\underline{H}$), 3. 23 (2H, m, C$\underline{H}_2$OH), 4. 16 (2H, dd, J=4. 6 and 1. 7 Hz, C$\underline{H}_2$OSi), 5. 20 (1H, dt, J=15. 6 and 4. 6 Hz, CH=C$\underline{H}$CH_2OSi), 6. 42 (1H, d, J=15. 6 Hz, C$\underline{H}$=CHCH_2OSi), 7. 22 (10H, m, PhH); ms m/z

438 (M^+). Anal. Calcd for $C_{28}H_{42}O_2Si$: C, 76. 66; H, 9. 65. Found: C, 76. 19; H, 9. 97.

(*E*)-7-Hydroxyimino-6-methyl-1-dimethylthexylsilyloxy-4,4-diphenyl-2-heptene (29). The oxime (**29**) (4. 26 g, 82 %) was obtained as a colorless oil *via* the corresponding aldehyde from **28** (5. 07 g, 11. 6 mmol) utilizing the same procedure as described for **20**; aldehyde: Ir (neat) 1724 cm^{-1} (C=O); ^{1}H-nmr (200 MHz) δ 0. 06 (6H, s, $SiMe_2$), 0. 84 (6H, s, $SiCMe_2$), 0. 89 (6H, d, J=7. 0 Hz, $C\underline{H}_3CH\underline{C}H_3$), 0. 95 (3H, d, J=7. 3 Hz, $C\underline{H}_3CH$), 1. 61 (1H, q, J=7. 0 Hz, $CH_3C\underline{H}CH_3$), 2. 22 (1H, dd, J=14. 1 and 3. 5 Hz, C<u>H</u>H), 2. 42 (1H, m, $CH_3C\underline{H}$), 2. 91 (1H, dd, J=14. 1 and 7. 0 Hz, CH<u>H</u>), 4. 16 (2H, dd, J=4. 7 and 1. 8 Hz, $C\underline{H}_2OSi$), 5. 27 (1H, dt, J=15. 8 and 4. 7 Hz, CH=C<u>H</u>CH_2OSi), 6. 29 (1H, d, J=15. 8 Hz, C<u>H</u>=CHCH_2OSi), 7. 21 (10H, m, PhH), 9. 08 (1H, d, J=2. 3 Hz, CHO); oxime: Ir (neat) 3317 cm^{-1} (OH); ^{1}H-nmr (200 MHz) δ 0. 06 (6H, s, $SiMe_2$), 0. 84 (6H, s, $SiCMe_2$), 0. 88 (6H, d, J=7. 1 Hz, $C\underline{H}_3CH\underline{C}H_3$), 0. 92 (3/2H, d, J=6. 6 Hz, $C\underline{H}_3CH$), 0. 99 (3/2H, d, J=6. 6 Hz, $C\underline{H}_3CH$), 1. 25 (1H, m, OH, D_2O exchangeable), 1. 63 (1H, q, J=7. 1 Hz, $CH_3C\underline{H}CH_3$), 2. 30 (1/2H, m, $CH_3C\underline{H}$), 2. 41 (1H, m, C<u>H</u>H), 2. 60 (1H, dd, J=16. 0 and 7. 8 Hz, CH<u>H</u>), 3. 20 (1/2H, m, $CH_3C\underline{H}$), 4. 17 (2H, d, J=3. 4 Hz, $C\underline{H}_2OSi$), 5. 20 (1H, dt, J=15. 4 and 4. 6 Hz, CH=C<u>H</u>CH_2OSi), 6. 13 (1/2H, d, J=8. 1 Hz, CH=N), 6. 36 (1H, d, J=15. 4 Hz, C<u>H</u>=CHCH_2OSi), 6. 95 (1/2H, d, J=6. 6 Hz, CH=N), 7. 21 (10H, m, PhH); ms m/z 451 (M^+). Anal. Calcd for $C_{28}H_{41}NO_2Si$: C, 74. 45; H, 9. 15; N, 3. 10. Found: C, 73. 97; H, 9. 33; N, 2. 74.

(3RS,3aRS,6SR)-3,3a,5,6-Tetrahydro-6-methyl-3-dimethylthexylsilyloxymethyl-4,4-diphenyl-4*H*-cyclopenta[*c*]isoxazole (30). The isoxazoline (**30**) (307 mg, 98 %) was obtained as colorless needles [mp 122 - 124 °C (from hexane - ethyl acetate)] from **29** (315 mg, 0. 70 mmol) as described for **21**: ^{1}H-Nmr (200 MHz) δ 0. 17 (3H, s, SiMe), 0. 19 (3H, s, SiMe), 0. 90 (3H, s, SiCMe), 0. 91 (3H, s, SiCMe), 0. 92 (3H, d, J=7. 1 Hz, $C\underline{H}_3CHCH_3$), 0. 93 (3H, d, J=7. 1 Hz, $CH_3CHC\underline{H}_3$), 1. 31 (3H, d, J=6. 8 Hz, $C\underline{H}_3CH$), 1. 66 (1H, q, J=7. 1 Hz, $CH_3C\underline{H}CH_3$), 2. 25 (1H, dd, J=13. 9 and 8. 3 Hz, C<u>H</u>H), 3. 18 (1H, m, $CH_3C\underline{H}$), 3. 46 (1H, dd, J=13. 9 and 8. 1 Hz, CH<u>H</u>), 3. 96 (2H, m, C<u>H</u>HOSi and CHON), 4. 02 (1H, m, CH<u>H</u>OSi), 4. 82 (1H, d, J=10. 5 Hz, CHC=N), 6. 90 (2H, m, PhH), 7. 24 (8H, m, PhH); ms m/z 364 (M^+ - thexyl). Anal. Calcd for $C_{28}H_{39}NO_2Si$: C, 74. 78; H, 8. 74; N, 3. 11. Found: C, 74. 46; H, 8. 96; N, 2. 88.

(3RS,3aRS,6SR)-3,3a,5,6-Tetrahydro-3-hydroxymethyl-6-methyl-4,4-diphenyl-4*H*-cyclopenta[*c*]isoxazole (31). The alcohol (**31**) (973 mg, 97 %) was obtained as colorless prisms [mp 149 - 150 °C (from hexane - ethyl acetate)] from **30** (1. 47 g, 3. 27 mmol) according to the conditions for **12**: Ir (KBr) 3367 cm^{-1} (OH); ^{1}H-nmr (200 MHz) δ 1. 34 (3H, d, J=6. 8 Hz, $C\underline{H}_3CH$), 2. 05 (1H, *m, OH, D_2O exchangeable*), 2. 29 (1H, dd, J=13. 9 and 8. 3 Hz, $CH\underline{H}$), 3. 20 (1H, m, $CH_3C\underline{H}$), 3. 46 (1H, dd, J=13. 9 and 8. 1 Hz, $CH\underline{H}$), 3. 90 (1H, m, $C\underline{H}HOH$), 4. 10 (2H, m, $CH\underline{H}OH$ and CHON), 4. 78 (1H, d, J=10. 5 Hz, CHC=N), 6. 91 (2H, m, PhH), 7. 22 (8H, m, PhH); ms m/z 307 (M^+). Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78. 15; H, 6. 89; N, 4. 56. Found: C, 77. 99; H, 6. 84; N, 4. 20.

5,6-Dihydro-6-methyl-4,4-diphenyl-4*H*-cyclopenta[*b*]furan (5). The furan (**5**) (100 mg, 61 %) was obtained as a white powder (mp 62. 5 - 63. 5 °C) from **31** (185 mg, 0. 60 mmol) according to the experimental procedure used for **22**: ^{1}H-Nmr (200 MHz) δ 1. 28 (3H, d, J=6. 6 Hz, $C\underline{H}_3CH$), 2. 60 (1H, dd, J=12. 5 and 6. 8 Hz, $CH\underline{H}$), 3. 25 (1H, ddq, J=7. 1, 6. 8 and 6. 6 Hz, $CH_3C\underline{H}$), 3. 40 (1H, dd, J=12. 5 and 7. 1 Hz, $CH\underline{H}$), 6. 44 (1H, d, J=2. 0 Hz, $C\underline{H}$=CHO), 7. 24 (10H, m, PhH), 7. 40 (1H, d, J=2. 0 Hz, CH=$C\underline{H}$O); ^{13}C-nmr (100 MHz) δ 18. 58, 32. 28, 54. 23, 54. 84, 108. 76, 125. 85, 125. 91, 127. 14, 127. 31, 128. 11, 128. 18, 130. 05, 146. 00, 148. 08, 149. 10, 161. 95; ms m/z 274 (M^+). Anal. Calcd for $C_{20}H_{18}O$: C, 87. 56; H, 6. 61. Found: C, 87. 36; H, 6. 68.

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