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Synthesis and π-Facially Selective Cycloadditions of Pinofurans

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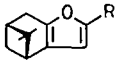
Abstract - The synthesis of the strained pinofuran (**1**) and methylpinofuran (**2**) was investigated by a number of approaches. The preferred route to **1** was via the monoprotected (*Z*)-enediol **8**, which was obtained by *Z*-selective $LiNEt_2$-induced opening of the epoxide derived from protected homoallylic alcohol **3** (nopol). Methylpinofuran (**2**) was prepared from 1,4-diketone **14**, which was obtained by a vinyl-Grignard 1,4-addition to pinocarvone (**12**) followed by ozonolysis. Pinofurans **1** and **2** entered into Diels-Alder additions with dimethyl acetylenedicarboxylate, giving **15** and **16**, respectively. Pinofuran (**1**) also reacted with allyl cations, giving [4+3] cycloadducts **19** and **20**. All cycloadditions were π-facially selective, attack occurring exclusively from the face anti to the gem-dimethyl grouping. Further, in the case of cycloadduct **19**, extended attack was slightly preferred over compact attack ($19_{\beta\beta}$: $19_{\alpha\alpha}$ = 3:2) (α, β refer to the tetrahydropyranone moiety).

Facial selectivity of attack of π-systems and its theoretical explanation have been of considerable interest recently.[1] Many of the π-systems studied have been bicyclic and polycyclic in order to maximize stereochemical preferences during attack. We here describe the synthesis of the two chiral fused furans **1** and **2**[2] from pinene, i.e. from the chiral pool. As a class of com-

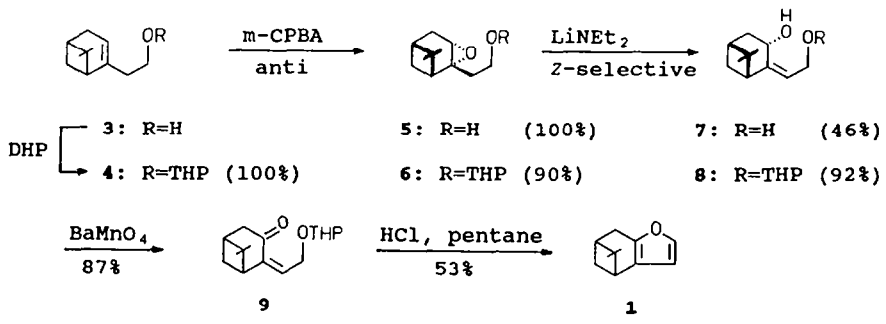


1: R=H
2: R=CH_3

pounds, furans are also of intrinsic interest, and they are ubiquitous in nature. Recently, the synthesis of a pinene-fused cyclopentadiene and fulvene, and some of their π-facially selective reactions have also been reported.[3]

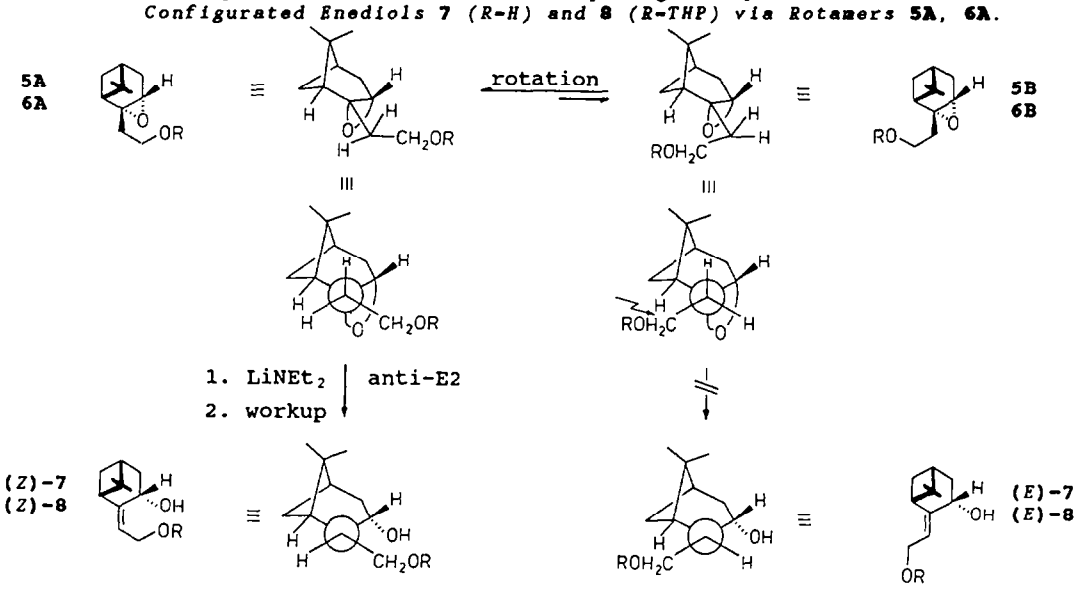
Results. Synthesis of Pinofuran (**1**) and Methylpinofuran (**2**). Starting from commercially available nopol (**3**) we prepared *Z*-enediol **7** via epoxyalcohol **5**. Attempts to convert **7** into **1** with pyridinium chlorochromate (PCC), as had been described for other sytems by K. Itoh and his co-workers,[4] were not successful, because pinofuran (**1**) proved to be too sensitive to oxidation. For this reason we decided to carry out the ring-closure to the furan under nonoxidative conditions (**9** → **1**) (Scheme 1). Accordingly, **3** was converted into THP-ether **4** and, analogously to **5**, it was transformed into anti epoxide **6**. A priori, an anti-periplanar E2 reaction of epoxide **5** and **6** can give an (*E*)- and/or a (*Z*)-configurated double bond: On treatment with $LiNEt_2$, epoxide **5** produced (*Z*)-enediol **7** only and epoxide **6** produced monoprotected (*Z*)-enediol **8**. A rationale is as follows (Scheme 2). Rotamers **5B** and **6B** should yield (*E*)-**7** and (*E*)-**8**, respectively, whereas rotamers **5A** and **6A** should afford the observed Z-configurated isomers (*Z*)-**7** and (*Z*)-**8**. Models suggest that for the B-rotamers there is an unfavorable gauche interaction between the CH_2OR group

Scheme 1. Five-Step Synthesis of Pinofuran (1) from Nopol (3).



and the neighboring bridgehead hydrogen. In fact, the C-CH_2OR σ bond and the bridgehead C-H σ bond are approximately parallel (Newman projections, Scheme 2). In contrast, for the A-rotamer, the gauche interaction between CH_2OR group and the C(3) carbon of the pinane skeleton is less severe, and elimination from this rotamer is preferred.

Scheme 2. $LiNEt_2$-Induced Stereoselective Opening of Epoxides 5 and 6 to Z-Configurated Enediols 7 (R=H) and 8 (R=THP) via Rotamers 5A, 6A.

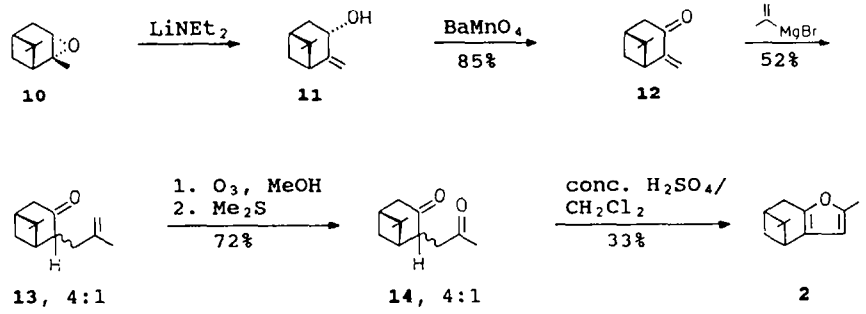


A further important step was the oxidation of 8 to 9, and anhydrous $BaMnO_4$ (cf. also below) was the agent of choice for oxidizing this allylic alcohol. Thus, functionalized enone 9 was obtained in 87% yield. The acid-catalyzed two-phase cyclization of 9 at room temperature proved to be sufficiently mild for the isolation of pinofuran (1) in 53% yield. Pinofuran (1) was optically active and its structure was proved spectroscopically (^1H NMR, ^{13}C NMR) and chemically as a 4π component in cycloadditions.

The 1,4-diketone route (Scheme 3) was successful for preparing methylpinofuran (2). α-Pinene oxide (10) was opened to allylic alcohol 11.[5] Previously, the oxidation of 11 with activated MnO_2 had been reported to give enone 12 in 83% yield.[6] In our hands, the yields of 12 fluctuated between 30 and 70%. Again, oxidation with $BaMnO_4$ was more efficient. Under these conditions, shorter reaction times and only 5 equiv. of anhydrous $BaMnO_4$ (instead of 15 equiv. MnO_2) sufficed to produce 12 in 85% yield.

More than 40 years ago Treibs reported the conjugate addition of RMgX to enone 12 and suggested that in the major of two isomeric products the group R was syn to the gem-dimethyl group.[7] Reaction of 12 with isopropylmagnesium

Scheme 3. *Five-Step Route to Methylpinofuran (2) via 1,4-Diketone 14*.

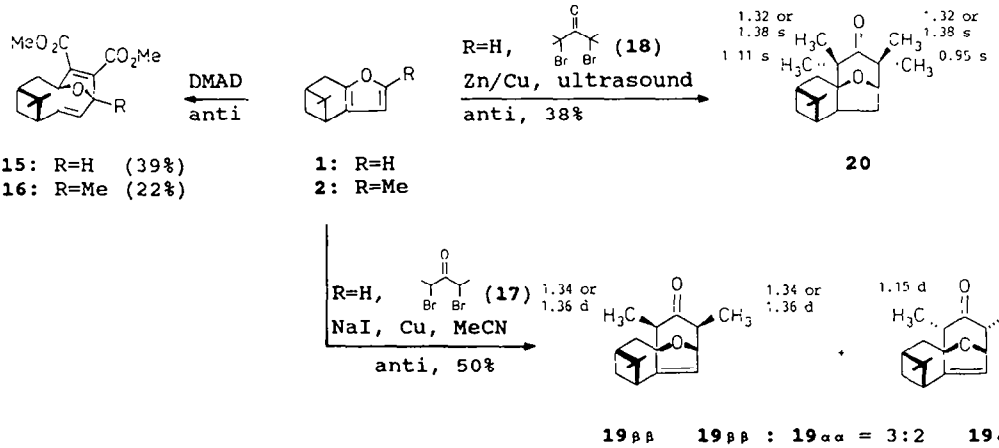


bromide gave **13** (4:1 isomeric mixture) *without* addition of Cu(I) salts. Again, the major isomer is assumed to have the side chain syn to the gem-dimethyl group.[8-10]

Ozonolysis of **13** in methanol produced 1,4-diketone **14** (4:1 stereochemistry retained), the cyclization of which required *concentrated sulfuric acid/dichloromethane* between 0°C and room temperature.[11] Both pinofurans **1** and **2** are strained and sensitive to oxygen and were obtained optically active. Their ^{1}H and ^{13}C NMR spectra are similar.

Cycloadditions. Pinofuran (**1**) and methylpinofuran (**2**) entered into Diels-Alder additions with dimethyl acetylenedicarboxylate, giving **15** and **16**, respectively. Oxyallyl cation cycloadditions to pinofuran (**1**) were also examined (Scheme 4). Thus, treatment of dibromo ketone **17** with NaI/Cu in the presence of **1** afforded two stereoisomeric cycloadducts **19**. A priori, 8 diastereomers of **19** are possible. As shown below, the cycloaddition is *anti*-selective with respect to the *gem*-dimethyl bridge and *cis*-selective with respect to the two methyl groups, which are introduced via the oxyallyl moiety. Cycloadducts $\mathbf{19}_{\alpha\alpha}$ and $\mathbf{19}_{\beta\beta}$ (2:3) are the two diastereomers formed.

Scheme 4. *Stereoselective Cycloadditions of Pinofuran (1)*.

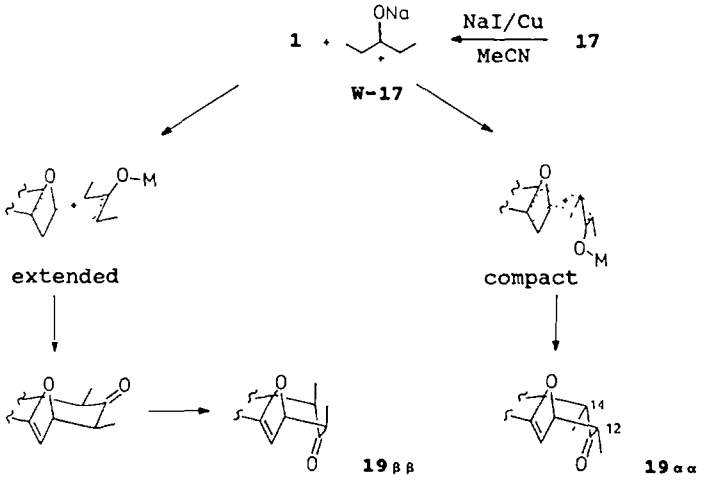


Spectroscopic Identification of the Cycloadducts. In the Diels-Alder additions producing **15** and **16**, we found one isomer each, using ^{13}C NMR and also ^{1}H NMR spectroscopy. Since *anti*-attack is general for bicyclic [3.1.1] pinene types (see also epoxides **5** and **10**), we assume that the fused pinene systems **1** and **2** behave similarly, giving anti-configurated cycloadducts only.[12] For the same reason, *anti*-selectivity is presupposed for the oxyallyl cation cycloadditions. Given *anti*-addition, the two methyl groups at C-12 and C-14 could

be oriented αα, αβ, βα, and ββ with respect to the bridged 7-membered ring. In the 200 MHz ^{1}H NMR spectrum, the methyl protons of the two isomers appear at δ 0.97, 1.15, 1.34, and 1.36 ppm. Integration shows that the signals at 0.97 and 1.15 ppm belong to one diastereomer, and the signals at 1.34 and 1.36 ppm to another (ratio 2:3). In 8-oxabicyclo[3.2.1]oct-6-en-3-ones the axial methyl protons resonate downfield from the signals of the equatorial methyl protons.[13] Thus, the assignment of the major **19ββ** isomer is secure, and is confirmed by further spectroscopic criteria listed below. The second, minor diastereomer could have been **19αα**, **19αβ** and **19βα**. Isomer **19βα** (methyl group β at C-12) could be ruled out, because of the pattern of the furan bridgehead proton (dd, ^3J = 5 Hz, ^3J = 2 Hz), which demands an α-configurated methyl group at C-12. In **19ββ**, the corresponding proton appeared as a simple doublet, ^3J = 2 Hz (coupling with the neighboring olefinic proton, whereas ^3J coupling with the C(12)-H proton is approximately zero) (cf. model compounds[13]). Is the signal of the methyl group at C-14 in the minor diastereomer due to an α- or β-configuration? In the tetracyclic *model* compound **20**, the signal of the α-configurated methyl group at C-14 appears at 1.11 ppm, compared to 1.15 ppm in the minor diastereomer, which must be **19αα**. Confirmatory evidence comes from the ^{13}C signals of the quasi-equatorial methyl carbons in **19αα** (10.35, 12.48 ppm), which are upfield[14,15] from the signals of the quasi-axial methyl carbons in **19ββ** (14.55, 17.96 ppm). The carbonyl carbon in **19αα** is also upfield (209.3 ppm) from the corresponding signal in **19ββ** (215.1 ppm).[14]

Discussion. All cycloadducts (**15**, **16**, **19αα**, **19ββ**, **20**) are formed π-face selectively. In addition, in **19αα** and **19ββ** the newly introduced methyl groups are *cis* to one another. The stereochemistry of the isomer formation can be explained *via* the compact and extended transition states and the W-configurated allyl cation intermediate **W-17** (Scheme 5). However, in contrast to cycloadditions involving simple furans,[13] cycloaddition to pinofuran **1** occurs via the extended transition state preferentially (extended : compact = 3:2). We suggest that in the compact transition state leading to **19αα**, the methyl group destined to be at C-14 suffers steric repulsion due to the presence of

Scheme 5. The Compact and Extended Model of Allyl Cation Cycloaddition.



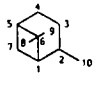
the pinene skeleton. Note also that the proton signals of the equatorial methyl groups at C-14 in **19**αα and also in the model tetracycle **20** are *downfield* by 0.18 and 0.16 ppm, respectively from the signals of the equatorial methyl protons at C-12. The downfield shift is accounted for by van der Waals repulsion, which we also postulate for the transition state leading to **19**αα.

The cycloaddition of the tetramethyloxyallyl cation derived from dibromo ketone **18** presented a challenge from the steric point of view and also, because the more electrophilic zinc-oxyallyl cation[13] generated from **18** and zinc-copper under sonication[16] could have entered into undesirable side reactions with the strained pinofuran (**1**). In fact, the sterically demanding cycloadduct **20** was obtained in 38% unoptimized yield.

Conclusions. The synthesis of pinofuran (**1**) via monoprotected enediol **8** is an efficient process. Starting from nopol, an inexpensive homoallylic alcohol, **1** is obtained in 5 simple stages in 38% overall yield. Key steps are the *Z*-selective epoxide opening to **8** and the mild oxidation of the resulting allylic alcohol with $BaMnO_4$. The routes to **1** and **2** should be useful models for the construction of other strained and sensitive furans, which are to be grafted upon pre-existing cyclic olefin frameworks. Cycloadditions occurred with oxyallyl cations using the mild NaI/Cu and the more electrophilic Zn/Cu procedure. All cycloadditions were π-facially selective from the face *anti* to the *gem*-dimethyl group. The *anti-cis*-extended mode of attack was slightly preferred over the *anti-cis*-compact alternative, due to steric repulsion of the methyl group at C-14.

Experimental Section

Numbering of the pinane carbon skeleton:[19]



In the tricyclic and tetracyclic derivatives, this numbering is retained, in contrast to the systematic name, because the spectral data can be compared more easily. Nopol (**3**) (Janssen, 98%, $[\alpha]_D^{20}$ -37°, neat) and α-pinene oxide (**10**) (Janssen, 95%, $[\alpha]_D^{20}$ -64°, neat) were used without further purification; r.t. (room temperature).

2,3-Epoxy-2-(2-hydroxyethyl)-6,6-dimethylbicyclo[3.1.1]heptane (Nopol-2,3-oxide) (**5**). A solution of $NaHCO_3$ (15.2 g, 181 mmol) in water (80 mL) was added to nopol (**3**) (15 g, 90.4 mmol) in CH_2Cl_2 (60 mL). Into the resulting two-phase system, a solution of m-chloroperbenzoic acid (18.7 g, 108.5 mmol) in CH_2Cl_2 (100 mL) was dropped in. After being stirred for 18 h at r.t. the reaction mixture was partitioned between pentane (150 mL) and water (100 mL). The aqueous phase was washed with pentane (3 x 80 mL) and the combined organic phase was washed with 10% aqueous NaOH (4 x 100 mL), aqueous saturated NaCl solution (2 x and dried ($MgSO_4$). After removal of the solvent the residue was distilled under reduced pressure (100°C, oil pump) to give **5** (16.4 g, quantitative). IR (CCl_4, cm^{-1}) 3620 (w), 3500 (bm), 2970 (s), 2910 (vs), 2860 (m), 1460 (m), 1420 (m), 1380 (m), 1360 (m), 1090 (m), 1060 (s), 1035 (s), 850 (m); 200 MHz ^1H NMR ($CDCl_3$) δ 0.95 (s, 3H-9), 1.32 (s, 3H-8), 1.61 (d, J = 8.4 Hz, *endo* H-7), 1.7 - 2.2 (m, H-1, 2H-4, H-5, *exo* H-7, 2H-10), 2.7 (bs, OH), 3.34 (d, J = 4 Hz, H-3), 3.7 (t, J = 6 Hz, 2H-11); 50 MHz ^{13}C NMR ($CDCl_3$) δ 20.19 (q, C-9), 25.63 (t, C-7), 26.73 (q, C-8), 27.54 (t, C-4), 36.58 (t, C-10), 40.08 (d, C-5), 40.67 (s, C-6), 44.49 (d, C-1), 54.95 (d, C-3), 58.67 (t, C-11), 63.12 (s, C-2); mass spectrum (70 eV, r.t.), *m/z* (relative intensity) 182 (2, M^+), 167 (12), 149 (10), 105 (29), 91 (70), 79 (93), 77 (87), 67 (100), 65(66), 56 (81), 43 (94). Exact mass calcd. for $C_{11}H_{18}O_2$, 182.1305. Found 182.1306.

2-(2-Hydroxyethylidene)-6,6-dimethylbicyclo[3.1.1]heptan-3-ol (**7**). A 500 mL three-necked flask equipped with reflux condenser and gas inlet, pressure equalizing dropping funnel and septum was charged with diethylamine (3.9 g, 55 mmol) in abs. ether (150 mL) at 0°C under N_2. A 1.5 M solution of n-BuLi (40 mL, 60 mmol) was carefully introduced by syringe. The mixture was stirred for 30 min at 0°C, the ice bath was removed and nopol-2,3-oxide (**5**) (5 g, 27.5 mmol) in abs. ether (55 mL) was stirred dropwise into the solution. The solution was heated at 50°C for 3.5 h, cooled to 0°C and carefully treated with water (25 mL). The organic phase was separated and washed with 1 N HCl (4 x 150 mL), water (2 x 150 mL), saturated $NaHCO_3$ (2 x 150 mL) and water (2 x 100 mL). The aqueous phases were each washed with ether (50 mL). The united

organic phase was dried ($MgSO_4$) and the solvent was removed to leave the crude product which was distilled (Kugelrohr, 130°C, oil pump), giving **7** (2.3 g, 46%) as a viscous oil. IR (CCl_4, cm^{-1}) 3600 (w), 3350 (bm), 2930 (vs), 1390 (m), 1370 (m), 1010 (m); 200 MHz ^1H NMR ($CDCl_3$) δ 0.62 (s, 3H-9), 1.25 (s, 3H-8), 1.70 (d, J = 10 Hz, *endo* H-7), 1.85 (dd, J = 19 Hz, J = 4 Hz, H-4t), 2.0 (m, H-5), 2.18 - 2.48 (m, H-4c, *exo* H-7, H-1), 4.02 (dd, J = 12 Hz, J = 7 Hz, H-11), 4.3 (dd and bs, J = 12 Hz, J = 8 Hz, H-11 and 2 OH), 4.7 (d, J = 8 Hz, H-3), 5.45 (dd, J = 8 Hz, J = 7 Hz, H-10); 50 MHz ^{13}C NMR ($CDCl_3$) δ 22.07 (q, C-9), 25.88 (q, C-8), 27.69 (t, C-7), 35.06 (t, C-4), 40.21 (s and d, C-6 and C-5), 51.66 (d, C-1), 57.62 (t, C-11), 62.27 (d, C-3), 125.3 (d, C-10), 150.4 (s, C-2); mass spectrum (70 eV, r.t.), *m/z* (relative intensity) 182 (2, M^+), 164 (14), 146 (31), 131 (33), 121 (98), 95 (100), 67 (97), 41 (78).

2-[2-(Tetrahydropyran-2-yloxy)ethyl]-6,6-dimethylbicyclo[3.1.1]hept-2-ene (4). Dihydropyran (1.43 g, 12 mmol) and nopol (2 g, 12 mmol) were mixed and treated with 2-3 drops of conc. HCl. The reaction started immediately with self-heating; the temperature was maintained at 30°C with an ice bath. After 3 h at r.t., K_2CO_3 (20 mg) was added and the product was isolated by distillation (Kugelrohr, 100°C, oil pump) (lit.[17] 160-167°C/14 Torr), giving **4** as a diastereomeric mixture (3.0 g, quantitative). For spectroscopic data see ref. 17.

2,3-Epoxy-2-[2-(tetrahydropyran-2-yloxy)ethyl]-6,6-dimethylbicyclo[3.1.1]heptane (6). A solution of $NaHCO_3$ (4.7 g, 56 mmol) in water (31 mL) was added to **4** (7 g, 28 mmol) in CH_2Cl_2 (20 mL). Into the resulting two-phase system a solution of m-chloroperbenzoic acid (5.8 g, 33.6 mmol) in CH_2Cl_2 (60 ml) was dropped in. After being stirred for 18 h at r.t. the mixture was partitioned between light petroleum (50 mL) and water (15 mL). The aqueous phase was washed with light petroleum (3 x 20 mL). The united organic phase was washed with 10% aqueous NaOH (4 x 40 mL), saturated NaCl (2 x 30 mL) and dried ($MgSO_4$). The solvent was removed and the residue was distilled (Kugelrohr, 120°C, oil pump) to give **6** as a diastereomeric mixture, 6.7 g (90%). IR (CCl_4, cm^{-1}) 2980 (s), 2950 (s), 2920 (s), 2880 (m), 1200 (m), 1140 (s), 1130 (s), 1080 (m), 1040 (vs), 870 (m); 200 MHz ^1H NMR ($CDCl_3$) δ 0.96 (s, 3H-9), 1.29 (s, 3H-8), 1.45 - 2.15 (m, 14 H), 3.18 (dd, J = 8 Hz, J = 4 Hz, H-3), 3.35 - 3.90 (2m, 2H-11, 2H-16), 4.56 (m, H-12); 50 MHz ^{13}C NMR ($CDCl_3$) δ 19.62/19.67 (t, C-pyran), 20.12 (q, C-9), 25.56 (t, C-7), 25.73 (t, C-pyran), 26.86 (q, C-8), 27.77 (t, C-4), 30.81 (t, C-pyran), 35.06/35.11 (t, C-10), 40.11 (d, C-5), 40.69 (s, C-6), 44.12 (d, C-1), 55.67/55.83 (d, C-3), 61.29 (s, C-2), 62.23/62.33 (t, C-11), 62.77/63.08 (t, C-16), 94.58/98.84 (d, C-12); mass spectrum (70 eV, r.t.), *m/z* (relative intensity) 266 (0.07 after enhancement, M^+), 223 (1.4), 197 (19), 181 (6), 165 (3), 121 (8), 105 (12), 85 (100), 67 (38), 42 (38).

2-[2-(Tetrahydropyran-2-yloxy)ethylidene]-6,6-dimethylbicyclo[3.1.1]heptan-3-ol (8). A 150 mL three-necked flask equipped with reflux condenser and gas inlet, pressure-equalizing dropping funnel and septum was charged with diethylamine (0.76 g, 10.4 mmol) in abs. ether (70 mL) under N_2 at 0°C. A 1.4 M solution of n-BuLi (7.64 mL, 10.7 mmol) was carefully introduced by syringe. The mixture was stirred for 40 min at 0°C and the ice bath was removed while epoxide **6** (2.7 g, 10.1 mmol) in abs. ether (20 mL) was stirred in dropwise. The mixture was heated at 55°C for 3.5 h, cooled to 0°C and treated carefully with water (15 mL). The organic phase was separated and washed with 1 N HCl (4 x 30 mL), water (2 x 30 mL), saturated aqueous $NaHCO_3$ solution (2 x 30 mL) and water (2 x 20 mL). The aqueous layers were extracted with each 10 mL of ether, and the united organic phase was dried ($MgSO_4$). After removal of the solvent, Kugelrohr distillation (130°C, oil pump) gave **8** as a diastereomeric mixture (ca. 1:1), 2.47 g (92%). IR (CCl_4, cm^{-1}) 3460 (bm), 2950 (s), 2880 (m), 1660 (w), 1390 (m), 1370 (m), 1205 (m), 1120 (m), 1015 (vs), 970 (m); 200 MHz ^1H NMR ($CDCl_3$) δ 0.62/0.63 (s, 3H-9), 1.27 (s, 3H-8), 1.5 - 2.4 (series of m, 11 H), 2.45 (dd, 2xJ = 5 Hz, H-1), 3.39/3.68 (bs, OH), 3.44 - 4.84 (series of m, H-3, 2H-11, H-12, 2H-16), 5.32/5.47 (td, J_t = 7 Hz, J_d = 1 Hz, H-10); 50 MHz ^{13}C NMR ($CDCl_3$) δ 18.91/19.32 (t, C-pyran), 21.98/22.06 (q, C-9), 25.34 (t, C-7), 25.94 (q, C-8), 27.26/27.42 (t, C-pyran), 30.2730.52 (t, C-pyran), 34.24/34.40 (t, C-4), 40.13/40.17 (d, C-5), 40.33/40.51 (s, C-6), 51.66/51.72 (d, C-1), 61.62/61.87/61.96/62.05/62.10/62.93 (2xt and d, C-11, C-16, C-3), 95.58/98.43 (d, C-12), 121.1/121.8 (d, C-10), 152.5/153.0 (s, C-2); mass spectrum (70 eV, r.t.), *m/z* (relative intensity) 266 (0, M^+), 250 (1), 180 (3), 169 (6), 146 (5), 131 (5), 121 (9), 105 (20), 91 (14), 85 (100), 67 (23), 55 (18), 41 (21).

2-[2-(Tetrahydropyran-2-yloxy)ethylidene]-6,6-dimethylbicyclo[3.1.1]heptan-3-one (9). Anhydrous $BaMnO_4$[18] (2.4 g, 9.4 mmol) was suspended in CH_2Cl_2 (50 mL) and allyl alcohol **8** (0.5 g, 1.9 mmol) was added. The mixture was stirred for 21 h at r.t. with exclusion of moisture and suction-filtered through a glass filter covered with coarse silica gel. After removal of the solvent the crude product was distilled (Kugelrohr, 150°C, oil pump) giving a diastereomeric (1:1) mixture of **9**, 0.43 g (87%). IR ($CHCl_3$, cm^{-1}) 3020 (m), 2950 (s), 2880 (m), 1700 (s), 1630 (m), 1370 (m), 1360 (m), 1120 (s), 1080 (s), 1055 (m), 1030 (vs); 200 MHz ^1H NMR ($CDCl_3$) δ 0.81 (s, 3H-9), 1.28 (d, J = 10 Hz, *endo* H-7), 1.35 (s, 3H-8), 1.45 - 1.9 (m, 6 pyran-H), 2.17 (ddt, $J_{5/1}$ = 6 Hz,

$J_{5/exo-7}$ = 6 Hz, $J_{5/4}$ = 3 Hz, H-5), 2.47 (dd, J = 19 Hz, J = 3 Hz, H-4t), 2.55 - 2.75 (m, H-1, H-4c, *exo* H-7), 3.52 (m, H-16), 3.87 (m, H-16), 4.55 - 4.9 (series of m, 2H-11, H-12), 5.81 (t, J = 5 Hz, H-10); 50 MHz ^{13}C NMR ($CDCl_3$) δ 19.65/19.75 (t, C-pyran), 21.55 (q, C-9), 25.48 (t, C-pyran), 26.0 (q, C-8), 30.77/30.97 (t, C-pyran), 32.38/32.48 (t, C-7), 38.39 (d, C-5), 40.81 (s, C-6), 43.06/43.10 (t, C-4), 49.51 (d, C-1), 62.28/62.42 (t) and 66.44/66.50 (t) (C-11 and C-16), 98.64/98.83 (d, C-12), 138.6 (d, C-10), 139.6/139.7 (s, C-2), 200.8 (s, C-3); mass spectrum (70 eV, r.t.), *m/z* (relative intensity) 264 (0, M^+), 180 (16), 162 (16), 146 (18), 119 (25), 91 (36), 85 (100), 67 (26), 55 (33), 40 (53). Exact mass calcd. for M^+-84, 180.1149. Found 180.1150.

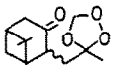
9,9-Dimethyl-5-oxatricyclo[6.1.1.$0^{2,6}$]deca-2(6),3-diene (1) (Pinofuran). In a 100 mL round-bottomed flask the THP-ether protected enone **9** (1.5 g, 5.68 mmol) was dissolved in pentane (15 mL) and treated with 3 N HCl (35 mL). The mixture was stirred for 4 h (TLC) at r.t. and after complete reaction the aqueous phase was separated and extracted with pentane (3 x 20 mL). The united organic phase was washed with water (2 x 10 mL), saturated aqueous $NaHCO_3$ solution (3 x 10 mL), saturated aqueous NaCl solution (10 mL) and dried ($CaCl_2$). The solvent was carefully evaporated at 50°C and the residue was distilled (Kugelrohr, r.t., oil pump) to give pinofuran (**1**) as a colorless liquid, 0.49 g (52.8%), $[\alpha]_D^{24}$-41.99° in CH_2Cl_2, c = 0.905. IR (CCl_4, cm^{-1}) 2940 (vs), 1615 (w), 1490 (m), 1470 (m), 1370 (m), 1230 (m), 1130 (m), 1035 (m), 900 (m), 720 (s); 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.64 (s, 3H-9), 1.35 (d, obscured, *endo* H-7), 1.37 (s, 3H-8), 2.31 (m, H-5), 2.58 (dd, $J_{1/5}$ = $J_{1/exo-7}$ = 6 Hz, H-1), 2.65 (m, *exo* H-7), 2.72 (dd, obscured, $J_{4/5}$ = 3 Hz, H-4), 2.86 (dd, J_{gem} = 16 Hz, $J_{4/5}$ = 3 Hz, H-4), 6.21 (d, J = 2 Hz, H-10), 7.21 (d, J = 2 Hz, H-11); 50 MHz ^{13}C NMR ($CDCl_3$) δ 20.91 (q, C-9), 26.68 (q, C-8), 28.45 (t) and 34.40 (t) (C-4 and C-7), 39.76 (d) and 41.59 (d) (C-1 and C-5), 42.15 (s, C-6), 109.6 (d, C-10), 127.4 (s, C-2), 140.1 (d, C-11), 149.2 (s, C-3); mass spectrum (70 eV, r.t.), *m/z* (relative intensity) 163 (7, M^++1), 162 (62, M^+), 147 (66), 133 (15), 119 (100), 118 (26), 105 (22), 94 (35), 91 (90), 77 (21), 65 (16), 55 (19), 42 (19).

6,6-Dimethyl-2-methylenebicyclo[3.1.1]heptan-3-one (12) (Pinocarvone). A round-bottomed flask was charged with anhydrous $BaMnO_4$[18] (42.15 g, 164 mmol, 5 equiv) and pinocarveol[5] (from α-pinene oxide **10**) (5 g, 32.9 mmol) in CH_2Cl_2 (150 mL). The mixture was stirred with exclusion of moisture. After 19 h at r.t. the alcohol had disappeared completely (TLC) and the solid was suction-filtered through a glass filter covered with coarse silica. The filtrate was concentrated and distilled (Kugelrohr, bp 70°C/1 Torr) to give **12**[19] (4.2 g, 85%). IR (CCl_4, cm^{-1}) 2930 (s), 1710 (vs), 1630 (m), 940 (m); 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.81 (s, 3H-9), 1.29 (d, J = 10 Hz, *endo* H-7), 1.38 (s, 3H-8), 2.21 (ddt, $J_{5/1}$ = $J_{5/exo-7}$ = 6 Hz, J_t = 3 Hz, H-5), 2.5 (dd, J = 19 Hz, J = 3 Hz, H-4t), 2.6 - 2.83 (m, H-1, H-4c, *exo* H-7),5.0 (d, J = 2 Hz, H-10); ^{13}C NMR (cf. ref. 19); mass spectrum (70 eV, r.t.), *m/z* (relative intensity) 150 (14, M^+), 135 (19), 122 (11), 108 (51), 81 (61), 53 (100).

6,6-Dimethyl-2-(2-methylprop-2-enyl)bicyclo[3.1.1]heptan-3-one (13). A 25 mL two-necked flask equipped with septum and reflux condenser with $CaCl_2$ tube was charged with Mg turnings (0.73 g, 30 mmol), catalytic I_2 and abs. tetrahydrofuran (7 mL). Neat 2-bromo-2-propene was syringed in carefully. After the reaction had started the remaining 2-bromo-2-propene (altogether 4.54 g, 37.5 mmol) was diluted with abs. THF (2.8 mL) and dropped in so as to maintain boiling of the reaction mixture. Formation of the Grignard compound was completed by heating at 50°C, and the mixture was cooled to r.t.. Pinocarvone **12** (3.75 g, 25 mmol) in abs. THF (4 mL) was syringed in, the reaction mixture was heated to 50°C for 1 h, allowed to reach r.t. overnight, cooled to 0°C and treated with ice-cold aqueous NH_4Cl. The organic phase was washed with saturated aqueous NH_4Cl (2x) and the aqueous layers were rewashed with ether. The combined organic phase was shaken with saturated NaCl (2x) and dried ($MgSO_4$). After removal of the solvent the residue was distilled (Kugelrohr, 85°C, oil pump vacuum) to give **13** (2.5 g, 52%) as an epimeric mixture (4:1). IR (CCl_4, cm^{-1}) 3070 (w), 2930 (s), 1715 (vs), 1645 (w), 990 (m); 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.87/0.88 (s, 3H-9), 1.18/1.20 (d, J = 10 Hz, *endo* H-7), 1.31/-1.33 (s, 3H-8), 1.68 (bs, 3H-13), 1.95 - 2.24 (m, 3H), 2.40 - 2.93 (series of m, 5H), 4.64 (m, H-12), 4.77 (m, H-12); a distinction of *trans*- and *cis*-**13** was made by ^{13}C NMR following Coxon[19] who described the spectra of isopinocamphone (*cis* methyl group) and pinocamphone (*trans* methyl group). The first signals refer to the *cis* compound. 50 MHz ^{13}C NMR ($CDCl_3$) δ 21.93/19.85 (q) and 22.13/21.80 (q) (C-9 and C-13), 27.04/26.49 (q, C-8), 34.08/28.89 (t, C-7), 38.87/38.14 (d, C-5), 39.13/39.02 (s, C-6), 39.24/37.50 (t, C-10), 41.13/40.71 (d, C-1), 44.77/44.53 (t, C-4), 54.57/49.70 (d, C-2), 112.1/112.3 (t, C-12), 143.6/142.9 (s, C-11), 213.2/213.8 (s, C-3); mass spectrum (70 eV, r.t.), *m/z* (relative intensity) 192 (7, M^+), 177 (8), 149 (10), 122 (41), 95 (89), 81 (82), 69 (87), 67 (62), 55 (60), 42 (200). Exact mass calcd. for $C_{13}H_{20}O$, 192.1513. Found 192.1513.

6,6-Dimethyl-2-(2-oxopropanyl)bicyclo[3.1.1]heptan-3-one (14). A 100 mL two-necked flask equipped with gas inlet, outlet and drying tube was charged with γ,δ-unsaturated ketone **13** (3.7 g, 19.3 mmol) in methanol (80 mL) at -60°C. An

ozone/oxygen mixture was passed through the stirred solution until the blue coloration persisted (30 min). The ozone was then driven off with oxygen and finally nitrogen. After addition of dimethyl sulfide (8.8 mL, 96.4 mmol) the solution was allowed to reach r.t overnight. After evaporation of the methanol the product was taken up in ether, washed with 10% $NaHSO_3$ solution, saturated $NaHCO_3$ solution, saturated NaCl solution and dried ($MgSO_4$). The solvent was evaporated and the crude product was purified by flash column chromatography (silica gel, ether/light petroleum, 1:1) to give **14** (2.7 g, 72%), epimeric mixture (*cis* : *trans* = 4:1). IR (CCl_4, cm^{-1}) 2930 (s), 1715 (vs), 1410 (m), 1360 (m), 1160 (m); 200 MHz ^1H NMR ($CDCl_3$) δ 0.85/0.97 (s, 3H-9), 1.30/1.33 (s, 3H-8), 1.34 (d, J = 9 Hz, *endo*-H-7), 2.15 (m, 1H), 2.17/2.19 (s, 3H-12), 2.30 (dd, J = 19 Hz, J = 7 Hz, 1 H), 2.49 (m, 1H), 2.55- 3.25 (series of m, 6H); 50 MHz ^{13}C NMR ($CDCl_3$) δ (the epimers were distinguished as in **13**. The more intense first signals refer to the *cis* isomer) 21.88/19.78 (q, C-9), 26.79/26.24 (q, C-8), 29.97/30.08 (q, C-12), 34.28/29.11 (t, C-7), 38.87/38.23 (d, C-5), 38.89/39.39 (s, C-6), 43.65/42.46 (d, C-1), 44.49/43.40 (t) and 45.58/44.15 (t) (C-4 and C-10), 51.48/47.85 (d, C-2), 206.2/206.2 (s, C-11), 212.9/213.1 (s, C-3); mass spectrum (70 eV, r.t.), *m/z* (relative intensity) 194 (5, M^+), 179 (3), 151 (18), 150 (11), 125 (71), 97 (25), 69 (61), 44 (100). Exact mass calcd. for $C_{12}H_{18}O_2$, 194.1306. Found 194.1307.



vi

When the ozonolysis was carried out in CH_2Cl_2 instead of MeOH, diketone **14** was isolated in 66% yield and ozonide **vi** in 16% yield after chromatography (silica gel, ether/light petroleum, 1:1). After treatment of **vi** with zinc powder in acetic acid at 50°C, diketone **14** was isolated in 88% yield.

4,9,9-Trimethyl-5-oxatricyclo[6.1.1.$0^{2,6}$]deca-2(6),3-diene (**2**) (Methylpinofuran). A 5 mL round-bottomed flask with reflux condenser was charged with diketone **14** (0.24 g, 1.23 mmol) in CH_2Cl_2 (2 mL) at 0°C. Concentrated sulfuric acid (1 mL) was carefully stirred in. The two-phase mixture was stirred for another 3.5 h, allowed to reach r.t., diluted with pentane (5 mL) and poured onto ice. The organic phase was separated, the aqueous layer neutralized with saturated $NaHCO_3$ solution and extracted with pentane (4 x 20 mL). The united organic phase was washed with NaCl solution, dried ($CaCl_2$) and the solvent was evaporated carefully at 50°C under atmospheric pressure. Distillation of the remaining yellow liquid in a Kugelrohr apparatus at r.t. and under reduced pressure gave colorless methylpinofuran (**2**), 60 mg, 33%, $[\alpha]_D^{21}$ -31.58° in CH_2Cl_2, c = 0.915. IR (CCl_4, cm^{-1}) 2960 (s), 2930 (vs), 2870 (m), 1470 (m), 1380 (m), 1365 (m), 1230 (m); 200 MHz ^1H NMR ($CDCl_3$) δ 0.67 (s, 3H-9), 1.36 (s and d, 3H-8, J = 9 Hz, *endo* H-7), 2.27 (dd, 2xJ = 1 Hz, 3H-12), 2.29 (m, H-5), 2.49 (dd, $J_{1/5} = J_{1/exo-7} = 5.5$ Hz, H-1), 2.60 (m, *exo* H-7), 2.70 (dd, obscured, J = 3 Hz, H-4), 2.84 (dd, $J_{gem} = 16$ Hz, $J_{4/5} = 3$ Hz, H-4), 5.78 (bd, J = 1 Hz, H-10); 50 MHz ^{13}C NMR ($CDCl_3$) δ 13.76 (s, C-12), 20.97 (q, C-9), 26.73 (q, C-8), 28.49 (t) and 34.45 (t) (C-4 and C-7), 39.74 (d) and 41.67 (d) (C-1 and C-5), 42.10 (s, C-6), 105.8 (d, C-10), 129.3 (s, C-2), 147.1 (s) and 149.5 (s) (C-11 and C-3); mass spectrum (70 eV, r.t.), *m/z* (relative intensity) 176 (44, M^+), 161 (60), 133 (71), 108 (63), 105 (74), 91 (48), 44 (100). Exact mass calcd. for $C_{12}H_{16}O$, 176.1200. Found 176.1201.

10,10-Dimethyl-12-oxatetracyclo[7.1.1.1.$^{4,7}0^{2,7}$]dodeca-2(3),5-diene-5,6-dicarboxylic Acid, Dimethyl Ester (**15**). Pinofuran (**1**) (0.1 g, 1.1 mmol) and dimethyl acetylenedicarboxylate (0.17 g, 1.2 mmmol) were dissolved in CH_2Cl_2 (1 mL) and heated at 60°C. After 6 h (TLC) the solvent was removed and unreacted starting materials were removed under reduced pressure (oil pump) to leave an oil which was chromatographed (silica gel, ether/light petroleum, 1:1). Cycloadduct **15** was isolated as a yellow oil, 0.13 g (39%). IR (CCl_4, cm^{-1}) 3030 (w), 2980 (m), 2960 (m), 2880 (m), 1740 (s), 1720 (vs), 1650 (w), 1630 (w), 1440 (m), 1260 (s), 1120 (s); 200 MHz ^1H NMR ($CDCl_3$) δ 0.87 (s, 3H-9), 1.33 (s, 3H-8), 1.4 (d, J = 10 Hz, *endo* H-7), 2.08 (m, H-5), 2.2 (bd, J = 15 Hz, H-4c), 2.48 (m, *exo* H-7), 2.7 - 2.9 (m, H-1, H-4t), 2.78 and 2.83 (s, 2 MeO), 5.51 (d, J = 2 Hz, H-11), 6.54 (d, J = 2 Hz, H-10); 50 MHz ^{13}C NMR ($CDCl_3$) δ 21.27 (q, C-9), 24.70 (t), 26.14 (q, C-8), 28.56 (t), 40.08 (d), 42.63 (s, C-6), 43.65 (d), 52.06 and 52.03 (q, 2 MeO), 83.02 (d, C-11), 91.14 (s, C-3), 130.6 (d, C-10), 151.7 (s), 157.1 (s), 162.4 (s), 163.1 (s, ester), 165.54 (s, ester); mass spectrum (70 eV, r.t.), *m/z* (relative intensity) 304 (1.7, M^+), 275 (9), 244 (23), 243 (100), 220 (35), 201 (33), 173 (29), 115 (27), 91 (43), 96 (46), 41 (59). Exact mass calcd. for $C_{17}H_{22}O_5$, 304.1310. Found 304.1311.

4,10,10-Trimethyl-12-oxatetracyclo[7.1.1.1.$^{4,7}0^{2,7}$]dodeca-2(3),5-diene-5,6-dicarboxylic Acid, Dimethyl Ester (**16**). Methylpinofuran (**2**) (50 mg, 0.28 mmol) and dimethyl acetylenedicarboxylate (40 mg, 0.28 mmol) were dissolved in CH_2Cl_2 (0.5 mL) and heated at 50°C. After 5.5 h (TLC) the solvent was evaporated and volatile components were removed under reduced pressure (oil pump). The crude product was purified by chromatography (silica gel, ether/-light petroleum, 1:1) to give **16**, yellow oil, 20 mg (22% yield), one isomer. IR (CCl_4, cm^{-1}) 2920 (s), 1725 (s), 1715 (vs), 1645 (w), 1620 (m), 1430 (s), 1315 (s), 1245 (s), 1130 (m); 200 MHz ^1H NMR ($CDCl_3$) δ 0.89 (s, 3H-9), 1.32 (s, 3H-8), 1.35 (d, obscured, *endo* H-7), 1.78 (s, 3H-14), 2.0 - 2.23 (m,

H-4c, H-5), 2.56 (m, *exo* H-7), 2.72 (dd, $J_{1/5} = J_{1/exo\text{-}7} = 5$ Hz, H-1), 2.97 (dd, J = 15 Hz, J = 4 Hz, H-4t), 3.80 (s, 2 MeO), 6.32 (s, H-10); 50 MHz ^{13}C NMR ($CDCl_3$) δ 15.90 (q, C-4), 21.25 (q, C-9), 24.69 (t), 26.08 (q, C-8), 28.20 (t), 40.09 (d, C-5), 42.49 (s, C-6), 43.56 (d, C-1), 51.92 (q) and 52.06 (q) (2 MeO), 89.22 (s) and 91.92 (s) (C-11 and C-3), 133.4 (d, C-10), 155.0 (s) and 155.2 (s) (C-12 and C-13), 163.6 (s, C-2), 164.5 (s) and 164.8 (s) (ester C=O); mass spectrum (70 eV, r.t.), m/z (relative intensity) 318 (1, M^+), 317 (2), 286 (4), 275 (6), 243 (100), 234 (38), 202 (69), 201 (44), 172 (41), 133 (19), 129 (19), 115 (27), 105 (19), 91 (23), 77 (22), 44 (59). Exact mass calcd. for $C_{18}H_{22}O_5$, 318.1467. Found 318.1467.

5,7,11,11-Tetramethyl-13-oxatetracyclo[8.1.1.1.^{4,8}0^{2,8}]tridec-2(3)-en-6-one (19). A mixture of NaI (1.23 g, 8.23 mmol), copper powder (0.39 g, 6.2 mmol) and abs. CH_3CN (10 mL) were stirred vigorously and a solution of pinofuran (1) (0.4 g, 2.47 mmol), α,α-dibromoketone **17** (0.5 g, 2.0 mmol) in abs. CH_3CN (4 mL) was dropped in under N_2 at r.t.. The mixture was stirred for 4.5 h and water (6 mL) and CH_2Cl_2 (12 mL) were added. Having been stirred further 10 min, the mixture was freed from solid by being suction-filtered through coarse silica gel. The organic phase of the filtrate was washed with dilute NH_3 solution (3 x 10 mL), saturated aqueous NaCl solution (2 x 20 mL) and dried ($MgSO_4$). After removal of the solvent the crude product was purified by flash column chromatography (silica gel, ether/light petroleum, 1:1), giving **19** (0.25 g, 50%) as a diastereomeric mixture (**19**αα : **19**ββ = 2:3). IR (CCl_4, cm^{-1}) 2940 (s), 1720 (vs), 1460 (m), 1090 (w), 980 (m), 930 (m); 200 MHz ^1H NMR ($CDCl_3$) δ (the first ppm values refer to the major **19**ββ isomer) 0.79/0.81 (s, 3H-9), 1.31/1.31 (s, 3H-8), 1.34/0.97 (d, $J_{ax} \sim 8$ Hz/$J_{eq} \sim 7$ Hz, methyl), 1.36/1.15 (d, $J_{ax} \sim 8$ Hz/$J_{eq} \sim 7$ Hz, methyl), 1.42/1.57 (d, obscured, J = 10 Hz, *endo* H-7), 4.62/4.78 (d/dd, J = 2 Hz/J = 5 Hz, J = 2 Hz,H-11), 5.72/5.78 (d, J = 2 Hz, H-10), 1.86 - 3.0 (series of m, remaining protons); 50 MHz ^{13}C NMR ($CDCl_3$) δ (the more intense signals were assigned to **19**ββ; these are given first) 14.55/10.35 (q, methyl), 17.96/12.48 (q, methyl), 21.92/21.57 (q, C-9), 25.89/25.89 (t), 25.97/26.19 (q, C-8), 31.32/ 34.05 (t), 41.15/-41.24 (d, C-5), 44.31/45.40 (s, C-6), 44.52/45.04 (d, C-1), 49.17/49.40 (d), 57.54/58.07 (d), 82.54/85.67 (s, C-3), 83.01/83.21 (d, C-11), 123.9/123.5 (d, C-10), 153.4/155.4 (s, C-2), 215.1/209.3 (s, C=O); mass spectrum (70 eV, r.t.), m/z (relative intensity) 246 (12, M^+), 231 (14), 203 (74), 189 (58), 175 (31), 160 (44), 147 (77), 121 (60), 114 (100), 109 (41), 91 (67), 85 (64), 69 (75), 41 (77). Exact mass calcd. for $C_{16}H_{22}O_2$, 246.1620. Found 246.1620.

5,5,7,7,11,11-Hexamethyl-13-oxatetracyclo[8.1.1.1.^{4,8}0^{2,8}]tridec-2(3)-en-6-one (20).[20] A 10 mL two-necked flask equipped with reflux condenser, gas inlet and septum was charged with a mixture of zinc powder (0.18 g, 2.78 mmol), CuCl (28 mg, 0.28 mmol) and pinofuran (1) (0.45 g, 2.78 mmol) under N_2. The flask was immersed optimally in an ultrasonic bath filled with ice water, and a solution of α,α'-dibromo ketone **18** (0.62 g, 2.32 mmol) in dioxan (1 mL) was dropped in within 10 min. After 2 h the dibromo ketone had disappeared (GC) and another portion of **18** (0.62 g, 2.32 mmol) in dioxan (1 mL) was added. After a reaction time of 3.5 h a further portion of zinc powder (0.18 g, 2.78 mmol) and catalytic CuCl were added. After sonication for 1 h the mixture was freed from solid by column filtration (silica gel, ether). The yellowish filtrate was washed with saturated aqueous NH_4Cl solution, saturated aqueous NaCl solution and dried. The solvent was removed and unreacted starting materials were pumped off at 50°C under reduced pressure (oil pump vacuum). Flash column chromatography (silica gel, ether/light petroleum, 1:1) gave **20** (0.31 g, 40%). IR (CCl_4, cm^{-1}) 2940 (s), 1710 (vs), 1475 (m), 1390 (m), 1050 (m); 200 MHz ^1H NMR ($CDCl_3$) δ 0.83 (s, 3 H-9), 0.95 (s, CH_3), 1.11 (s, CH_3), 1.32 (s, 3H-8 and CH_3), 1.38 (s, CH_3), 1.73 (d, J = 10 Hz, *endo* H-7), 2.0 (m, H-4c, H-5), 2.21 (dd, J = 16 Hz, J = 4 Hz, H-4t), 2.31 (dtd, $J_{gem} = 10$ Hz, $J_t = 5$ Hz, $J_{7/4} = 2$ Hz, *exo* H-7), 2.67 (dd, $J_{1/exo\text{-}7} = J_{1/5} = 5$ Hz, H-1), 4.38 (d, J = 3 Hz, H-11), 5.86 (d, J = 3 Hz, H-10); 50 MHz ^{13}C NMR ($CDCl_3$) δ 21.66 (q), 21.77 (q), 23.28 (q), 24.82 (q), 26.44 (q), 27.15 (q, 6 CH_3), 25.77 (t) and 31.69 (t) (C-4 and C-7), 41.50 (d), 46.06 (s, C-6), 46.18 (d), 50.03 (s) and 56.74 (s) (C-12 and C-14), 86.05 (s, C-3), 86.91 (d, C-11), 125.8 (d, C-10), 155.3 (s, C-2), 218.2 (s, C=O); mass spectrum (70 eV, r.t.), m/z (relative intensity) 274 (2.5, M^+), 259 (2), 231 (15), 213 (52), 188 (64), 156 (100), 131 (47), 129 (48), 77 (48), 56 (86), 42 (66). Exact mass calcd. for $C_{18}H_{26}O_2$, 274.1932. Found 274.1933.

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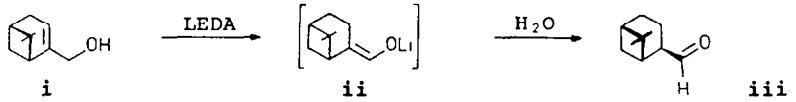
[8]This finding accords with the preferred protonation of the enolate **ii** generated from myrtenol **i**, which furnished syn-configurated aldehyde **iii**.[9]



i ii iii

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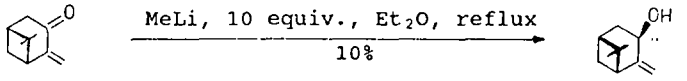
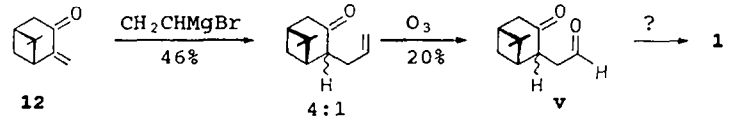
[10]Whereas Grignard reagents and pinocarvone (**12**) enter into 1,4-additions, we have found that refluxing of **12** with a massive excess of methyllithium in ether gives previously unknown tertiary allylic alcohol **iv** as a white crystalline solid, mp 39-40°C (one stereoisomer, new methyl group *anti* to the *gem*-dimethyl group).



12 iv

IR (CCl_4, cm^{-1}) 3620 (w), 3080 (w), 2920 (vs), 1645 (w), 900 (m); 200 MHz ^1H NMR ($CDCl_3$) δ 0.86 (s, 3H-9), 1.27 (s, 3H-8), 1.40 (d, J = 10 Hz, *endo* H-7), 1.53 (s, 3H-11), 2.02 (m, H-5), 2.12 (d and s, J = 3 Hz, 2H-4, OH), 2.34 (dtd, J = 10 Hz, $J_{7/1} = J_{7/5} = 6$ Hz, $J_{7/4c} = 1.5$ Hz, *exo* H-7), 2.53 (dd, 2xJ = 6 Hz, H-1), 4.78 (bs, H-10), 5.13 (d, J = 1 Hz, H-10); 50 MHz ^{13}C NMR ($CDCl_3$) δ 22.05 (q, C-9), 25.90 (q, C-8), 27.29 (t, C-7), 38.87 (q, C-11), 40.73 (d, C-5), 40.76 (s, C-6), 42.47 (t, C-4), 51.54 (d, C-1), 69.47 (s, C-3), 107.7 (t, C-10); mass spectrum (10 eV, r.t.), *m/z* (relative intensity) 166 (2, M^+), 148 (7), 133 (33), 106 (34), 105 (74), 97 (23), 91 (39), 79 (27), 69 (39), 55 (25), 43 (100), 41 (51). Exact mass calcd. for $C_{11}H_{18}O$, 166.1356. Found 166.1357.

[11]Analogously, the sensitive ketoaldehyde **v** was obtained by ozonolysis, however in low yield. Treatment of **v** with acid produced a mixture of several compounds, and it is clear that the route to **1** (Scheme 1) is very much superior. Apparently, the additional methyl group in **14** simplifies handling of this 1,4-dicarbonyl compound and also facilitates ring closure to **2**.



12 4:1 v

[12]Cf. also the Diels-Alder additions of nopadiene, which can be regarded as a less rigid, bicyclic analogue of pinofurans **1** and **2**. Selected references: (a) Ashkenazi, P.; Benn, R.; Ginsburg, D. Helv.Chim.Acta **1984**, *67*, 583; (b) Samuel, O.; Couffignal, R.; Lauer, M.; Zhang, S.Y.; Kagan, H.B. Nouv.Journal Chimie **1981**, *5*, 15; (c) Carr, R.V.C.; Williams, R.V.; Paquette, L.A. J.Org.Chem. **1983**, *48*, 4976; (d) Lange, W. Holz als Roh- und Werkstoff **1976**, *34*, 101.
Attempts to use nopadiene as a 4π component in oxyallyl cation cycloadditions were not successful.

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[20]Contribution of A. Weichert.