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# OPTICALLY ACTIVE FIVE-MEMBERED OXYGEN-CONTAINING RINGS. A SYNTHESIS OF (+)-ELDANOLIDE

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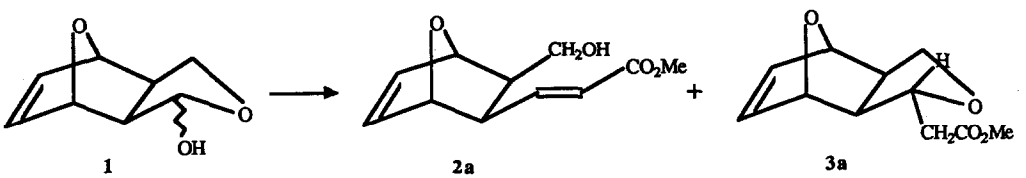
**Abstract :** Stereoselective tandem Wittig-Horner - intramolecular Michael reactions followed by a retro Diels-Alder cleavage convert the optically active tricyclic lactol 1 into 2-substituted 2,5-dihydrofurans of high enantiomeric purities. These compounds are useful synthons for the obtention of natural butenolides and butanolides as illustrated by the synthesis of the pheromone (+)-eldanolide.

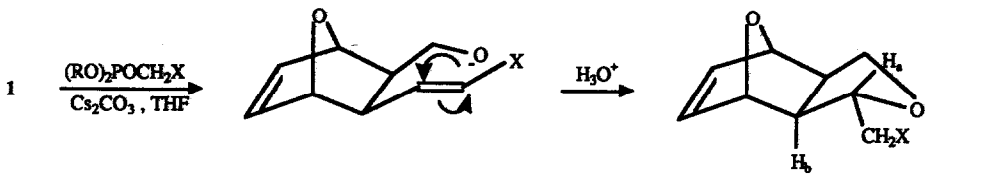
Optically active five-membered oxygen-containing rings are important structural moieties found in a number of natural products [1,2] and furthermore they are useful and versatile chiral templates for the synthesis of biologically interesting acyclic compounds [3]. We report in this paper an efficient and simple method for the synthesis of optically pure 2-substituted-2,5-dihydrofurans, their oxydation to 4-substituted butenolides and an application to the synthesis of (+)-eldanolide, the sex pheromone of "Eldana Saccharina".

In the course of our work directed towards the synthesis of (E,Z)-conjugated hydroxydienes, which are important intermediates for the synthesis of biologically active lipids [4], we have found that the tricyclic lactol 1, submitted to a Wittig-Horner reaction [$(MeO)_2POCH_2CO_2CH_3$/*n*BuLi, -78°C → RT, 15 h] gave rise to a mixture of the two products 2a and 3a.




Interestingly the tricyclic compound 3a, arising from a tandem Wittig-Horner - intramolecular Michael reaction, was produced as a single diastereoisomer [5] as shown by $^1H$ NMR at 250 MHz. The stereoselectivity of this reaction was probably due to the steric bulk of the oxanorbornenyl group which favored the formation of the most stable ether 3a where the methoxycarbonylméthyl substituent was in an exo position (vide infra).

Simple changes of the Wittig-Horner reaction conditions allowed the obtention of either one or the other compound 2a or 3a : the olefinic compound 2a was exclusively formed when the reaction was carried out with the aluminum alkoxide of the lactol 1, coming from the DIBAH reduction of the corresponding lactone [6] ; the tricyclic ether 3a was the only product when the lactol 1 was reacted with methyl dimethoxyphosphonoacetate in the presence of cesium carbonate in refluxing tetrahydrofuran [7]. This last reaction was found to be quite general and highly stereoselective and led to the synthesis of the tricyclic esters 3 as well as the nitrile 4 or the methylketone 5 (Table 1).




3a X = $CO_2CH_3$ 4 X = CN
3b X = $CO_2C_2H_5$ 5 X = $COCH_3$

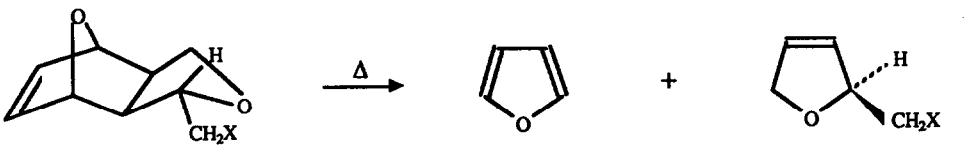
Table 1 - Stereoselectivity of the tandem Wittig-Horner - Michael reactions

| Reagent | Product | Yield % [a] | de % [b] |
|---|---|---|---|
| $(CH_3O)_2POCH_2CO_2CH_3$ | 3a | 76 | ⩾94 [c] |
| $(C_2H_5O)_2POCH_2CO_2C_2H_5$ | 3b | 61 | ⩾98 |
| $(C_2H_5O)_2POCH_2CN$ | 4 | 97 | ⩾98 |
| $(CH_3O)_2POCH_2COCH_3$ | 5 | 81 | 80 |

a) Yields are given for pure isolated compounds.
b) The diastereoisomeric excesses were determined by 250 MHz $^1H$ NMR of the crude mixture.
c) In some reactions, up to 3% of an isomer of 3a could be observed.

The most probable exo configuration of the fonctionnal chain in 3, 4 and 5 could not be assigned at this stage on the basis of spectroscopic data. Effectively, due to the conformational mobility of the tetrahydrofuran rings, the values of the coupling constants $J_{HaHb}$ could not be used : for example in the case of 5, the two diastereoisomers were available and the coupling constants found for each diastereomer were quite similar : $J_{HaHb}$ = 6.5 Hz for the major isomer and $J_{HaHb}$ = 5.6 Hz for the minor one.

We then took advantage of the stereoselectivity of this reaction to develop a simple and efficient synthesis of optically pure dihydrofurans through a transfer of chirality. The easily available optically active lactol 1 [8] gave tricyclic ethers 3a, 4 and 5 of high optical purities and a simple retro Diels-Alder reaction under flash thermolysis conditions (500°C, contact time ≃ 50 ms) led with excellent yields to the 2-substituted-2,5-dihydrofurans 6, 7 and 8 of high enantiomeric purities (Table 2).




3 - 5

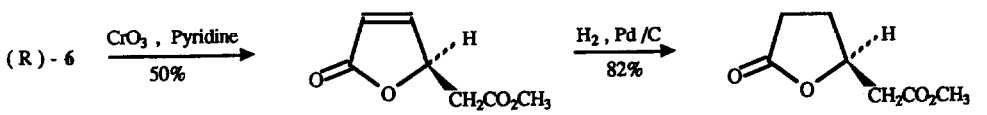
6 $X = CO_2CH_3$
7 $X = CN$
8 $X = COCH_3$

Table 2. Synthesis of optically active dihydrofurans

| Substrate | Product | Yield % [a] | $[\alpha]_D^{20}$ | ee % [b] |
|---|---|---|---|---|
| 3a | 6 | 93 | -76° ($CHCl_3$, c 1) | 94 |
| 4 | 7 | 80 | -164° ($CHCl_3$, c 1) | ≥95 |
| 5 | 8 | 82 | -64° (MeOH, c 0.4) | ≥95 |

a) Yields are given for pure isolated compounds.
b) Enantiomeric excesses were determined by $^1H$ NMR in the presence of chiral $Eu(hfc)_3$.

The (R) absolute configuration of the asymmetric center, which follows from the mode of formation, has been confirmed in the case of 6 by a chemical correlation with a known compound.




(R) - 9 (S) - 10

Oxidation of the dihydrofuran 6 with Collins reagent led to the corresponding butenolide 9, $[\alpha]_D^{20}$ -78° ($CHCl_3$, c 1), which is a cytotoxic natural compound recently isolated from a marine sponge [9]. The (R) configuration had been tentatively assigned by the authors to the asymmetric carbon of the natural product $[\alpha]_D^{20}$ +80°($CHCl_3$, c 0.27) on the basis of an empirical correlation. If this assignment were true, an (S) configuration, the opposite of the one we had expected, had to be given to the asymmetric carbon of the dihydrofuran 6. In order to find more reliable arguments, the butenolide 9 was hydrogenated to give the butanolide 10 $[\alpha]_D^{20}$ +39° (EtOH, c 1). An (S) absolute configuration could be assigned to the asymmetric center of 10 by comparison of the signs of optical rotation of our product and of the known (S)-10 [10a], $[\alpha]_D^{20}$ +29° (EtOH, c 0.4) and (R)-10 [10b], $[\alpha]_D^{25}$ -36° (EtOH, c 1). This result entailed an (R) configuration of the asymmetric carbon of the butenolide 9 and of the dihydrofuran 6 and confirmed the exo position of the methoxycarbonylmethyl chain in 3a. It also showed that the natural product possesses a (S) configuration.

With these results in hand, we developped an easy and efficient synthesis of (+)-eldanolide. (3S,4R)-3,7-Dimethyl-6-octen-4-olide **16** or eldanolide, a long-range sex attractant pheromone, has been isolated from the male wing glands of the African sugar cane borer "Eldana Saccharina" [11] and its structure and absolute configuration have been recently reported [12]. Since then, eldanolide has been synthetized several times either in racemic [13] or in optically active form [14]. Our synthesis of (+)-eldanolide **16** is shown in Scheme 1.

Reduction of the tricyclic ester **3a** (ee $\geq$ 95%) gave the alcohol **11**, $[\alpha]_D^{20}$ +25.5° ($CHCl_3$, c 1) which after Swern oxidation [15] led to the aldehyde **12**, $[\alpha]_D^{20}$ -3.2° ($CHCl_3$, c 2) of high enantiomeric purity as shown by $^1H$ NMR in the presence of optically active Eu(hfc)$_3$ (ee $\geq$95%). Wittig olefination followed by flash thermolysis at 500°C afforded the dihydrofuran **14** $[\alpha]_D^{20}$ -145° ($CHCl_3$, c 1) which was oxidized to the known (R)-(-)-butenolide **15** $[\alpha]_D^{20}$ -135° (MeOH, c 1) ; lit. [14h] $[\alpha]_D^{20}$ -133° (MeOH, c 1.56). Obtention of (+)-eldanolide **16** by a Michael addition of lithiumdimethylcuprate to butenolide **15** has already been described [12].

In conclusion we described here an efficient synthesis of optically active dihydrofurans which are useful intermediates for the obtention of natural butenolides of high enantiomeric purities.

## Experimental section

General : IR spectra were recorded on a Perkin Elmer 682 spectrophotometer. $^1H$ NMR were recorded in $CDCl_3$ on a Brucker AM250 spectrometer with tetramethylsilane as an internal standard. Mass spectra were obtained with a GC/MS R10-10 spectrometer. Optical rotations were measured on a Perkin Elmer 241 polarimeter. Flash thermolyses were carried out with an apparatus similar to the one described previously [16]. All reactions were carried out under an inert atmosphere of argon and were monitored by thin-layer chromatography (TLC). TLC was performed on Merck silica gel 60F-254 precoated on glass.

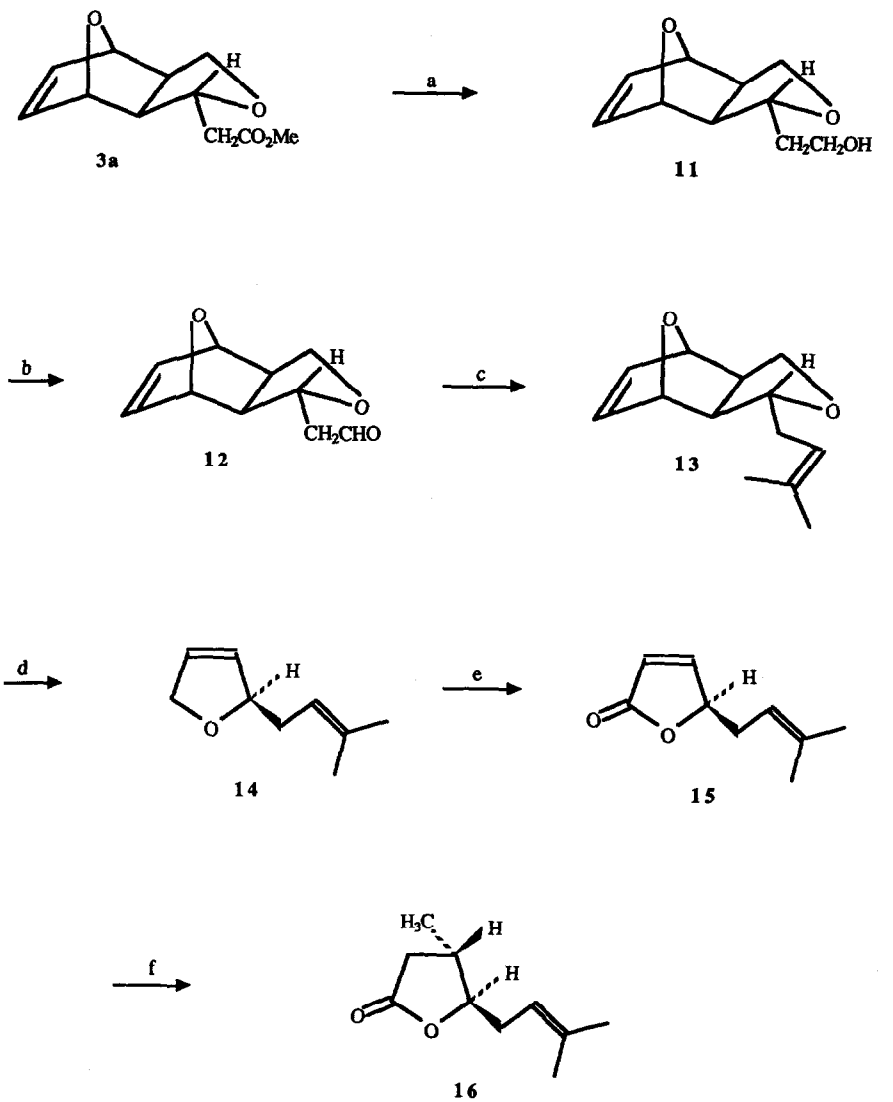
General procedure for the preparation of compounds **3 - 5**

To a stirred solution of lactol **1** (154 mg, 1 mmol) in dry tetrahydrofuran (10 mL) was added the Wittig-Horner reagent (1.5 mmol) and cesium carbonate (293 mg, 1 mmol) and the resulting mixture was refluxed for 24 h (3 h for the nitrile **4**). After cooling to room temperature, water was added (10 mL) and after separation of the organic layer, the aqueous phase was extracted with $CH_2Cl_2$ (3 x 10 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, concentrated in vacuo and the residue was purified by column chromatography (ether) on silica gel to afford the tricyclic ethers **3** to **5**.

(1R,2S,5R,6S,7S)-5-Methoxycarbonylmethyl-4,10-dioxatricyclo [5.2.1.0$^{2,6}$]-dec-8-ene **3a**

Yield 76%. $[\alpha]_D^{20}$ -6° ($CHCl_3$, c 1). IR (film) : 1740, 1050 cm$^{-1}$. CIMS ($NH_3$), m/e (relative intensity) : 228 ($MNH_4^+$, 100) ; 211 ($MH^+$, 55). $^1H$ NMR $\delta$ 2.15 (1H, dd, J = 8 and 6.5 Hz) ; 2.52 (1H, dd, J = 15 and 7 Hz) ; 2.55 (1H, m) ; 2.67 (1H, dd, J = 15 and 6.5 Hz) ; 3.45 (1H, dd, J = 9 and 7 Hz) ; 3.68 (3H, s) ; 3.94 (1H, dt, J = 6.5 and 6 Hz) ; 4.01 (1H, dd, J = 9 and 8 Hz) ; 4.68 (1H, s) ; 4.85 (1H, s) ; 6.35

Scheme 1




Reagents : a $LiAlH_4$ , ether ,91% ; b $(COCl)_2$ / DMSO , $CH_2Cl_2$ then $NEt_3$ , 84% ;. c $Ph_3P^+CH(CH_3)_2$ , $Br^-$ / n-BuLi , THF , 76% ; d 500°C , 88% ; e $CrO_3$ / Pyridine , $CH_2Cl_2$ , 41% ; f ref 12 .

(2H, m). Anal. Calcd for $C_{11}H_{14}O_4$ : C, 62.83 ; H, 6.72. Found : C, 62.84 ; H, 6.52.

(±)-5-Ethoxycarbonylmethyl-4,10-dioxatricyclo [5.2.1.0$^{2,6}$]-dec-8-ene **3b**

Yield 61%. IR (film) : 1735, 1050 cm$^{-1}$. CIMS ($NH_3$), m/e (relative intensity) : 242 ($MNH_4^+$, 66) ; 225 ($MH^+$, 100) ; 155 (25). $^1$H NMR $\delta$ 1.28 (3H, t, J = 7 Hz) ; 2.20 (1H, dd, J = 8 and 6.5 Hz) ; 2.50 (1H, dd, J = 15 and 7.5 Hz) ; 2.59 (1H, m) ; 2.70 (1H, dd, J = 15 and 6.5 Hz) ; 3.50 (1H, dd, J = 9 and 7 Hz) ; 3.99 (1H, dt, J = 7 and 6.5 Hz) ; 4.06 (1H, dd, J = 9 and 7.5 Hz) ; 4.16 (2H, q, J = 7 Hz) ; 4.7 (1H, s); 4.85 (1H, s) ; 6.38 (2H, m). Anal. Calcd for $C_{12}H_{16}O_4$ : C, 64.25 ; H, 7.20. Found : C, 64.05 ; H, 7.42.

(1R,2S,5R,6S,7S)-5-Cyanomethyl-4,10-dioxatricyclo [5.2.1.0$^{2,6}$]dec-8-ene **4**

Yield 97%. $[\alpha]_D^{20}$ +6.7° ($CHCl_3$, c 1). IR (film) : 2260 cm$^{-1}$. CIMS ($NH_3$), m/e (relative intensity) : 195 ($MNH_4^+$, 100) ; 178 ($MH^+$, 0.4). $^1$H NMR $\delta$ 2.34 (1H, dd, J = 8 and 6 Hz) ; 2.66 (3H, m) ; 3.52 (1H, dd, J = 9 and 7.5 Hz) ; 3.88 (1H, dt, J = 6 and 6.5 Hz) ; 4.17 (1H, dd, J = 9 and 8.5 Hz) ; 4.73 (1H, s) ; 4.83 (1H, s) ; 6.42 (2H, m). Anal. Calcd for $C_{10}H_{11}O_2N$ : C, 67.76 ; H, 6.26 ; N, 7.91. Found : C, 68.00 ; H, 6.20 ; N, 7.64.

(1R,2S,5R,6S,7S)-5-(2'-oxo-1'-propyl)-4,10-dioxatricyclo [5.2.1.0$^{2,6}$]-dec-8-ene **5**

Yield 70%. $[\alpha]_D^{20}$ +2° (MeOH, c 1). IR (film) : 1720, 1050 cm$^{-1}$. CIMS ($NH_3$), m/e (relative intensity) : 212 ($MNH_4^+$, 40) ; 195 ($MH^+$, 100) ; 126 (13). $^1$H NMR $\delta$ 2.08 (1H, dd, J = 8 and 6.5 Hz) ; 2.18 (3H, s) ; 2.55 (1H, dt, J = 8 and 7 Hz) ; 2.65 (1H, dd, J = 16 and 7 Hz) ; 2.86 (1H, dd, J = 16 and 6.5 Hz) ; 3.46 (1H, dd, J = 9 and 7 Hz) ; 3.96 (1H, dt, J = 6.5 and 6 Hz) ; 4.02 (1H, dd, J = 9 and 7 Hz) ; 4.67 (1H, s) ; 4.92 (1H, s) ; 6.36 (2H, m). Anal. Calcd for $C_{11}H_{14}O_3$ : C, 68.00 ; H, 7.27. Found : C, 68.33 ; H, 6.98.

General procedure for thermolyses

Small samples (100 mg to 1 g) of compounds **3** - **5** were evaporated through an horizontal mullite tube [16] (500°C, $10^{-2}$ torr) and the products were collected in a trap cooled to liquid nitrogen temperature. After warming to room temperature, the content of the trap was dissolved in ether and the resulting solution was concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, hexane/ether) to provide pure dihydrofurans.

(R)-2-Methoxycarbonylmethyl-2,5-dihydrofuran **6**

1 g of ester **3a** was thermolyzed to give 630 mg (93%) of dihydrofuran **6**, $[\alpha]_D^{20}$ -76.4° ($CHCl_3$, c 1). IR (film) : 1750 cm$^{-1}$. M.S., m/e (relative intensity) : 142 ($M^+$, 13) ; 110 (10) ; 81 (10) ; 74 (13) ; 69 (100) ; 59 (18). $^1$H NMR $\delta$ 2.51 (2H, m) ; 3.63 (3H, s) ; 4.58 (2H, m) ; 5.14 (1H, m) ; 5.78 (1H, m) ; 5.88 (1H, m).

(R)-2-Cyanomethyl-2,5-dihydrofuran **7**

170 mg of nitrile **4** gave 84 mg (80%) of dihydrofuran **7**, $[\alpha]_D^{20}$ -164° ($CHCl_3$, c 1). IR (film) :

2260 $cm^{-1}$. M.S., m/e (relative intensity) : 69 (100) ; 52 (15) ; 41 (40). $^1H$ NMR $\delta$ 2.62 (2H, m) ; 4.74 (2H, m) ; 5.07 (1H, m) ; 5.84 (1H, m) ; 6.14 (1H, m). Anal. calcd for $C_6H_7ON$ : C, 66.02 ; H, 6.47 ; N, 12.84. Found : C, 66.07 ; H, 6.58 ; N, 12.73.

(R)-2-(2'-Oxo-1'-propyl)-2,5-dihydrofuran **8**

Flash thermolysis of 195 mg of ketone **5** led to 104 mg (83%) of dihydrofuran **8**, $[\alpha]_D^{20}$ -64° ($CH_3OH$, c 0.4). IR (film) : 1715 $cm^{-1}$. M.S., m/e (relative intensity) : 126 ($M^+$, 5) ; 98 (13) ; 69 (50) ; 68 (25) ; 43 (100). $^1H$ NMR $\delta$ 2.19 (3H, s) ; 2.7 (2H, m) ; 4.65 (2H, m) ; 5.2 (1H, m) ; 5.83 (1H, m); 5.92 (1H, m).

(R)-5-Methoxycarbonylmethyl-2(5H)-furanone **9**

To a solution of chromic anhydride (1 g, 10 mmol) in dry dichloromethane (20 mL) was added pyridine (1.6 mL, 20 mmol) and the solution was stirred at room temperature for 20 min. The resulting mixture was cooled to 0°C and a solution of **6** (142 mg, 1 mmol) in dichlorométhane (2 mL) was added. After 30 min. at 0°C, the mixture was warmed to room temperature and was stirred for an additional 3 h. The solution was then quickly filtered on a small column of florisil and the column was washed with dichloromethane (2 x 10 mL). The combined organic phases were washed with a 10% HCl solution (20 mL), then with saturated sodium bicarbonate (20 mL) and were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (70:30 hexane-ether) to give 78 mg (50%) of the butenolide **9**, $[\alpha]_D^{20}$ -79° ($CHCl_3$, c 1). Lit. [9] $[\alpha]_D^{20}$ +80 ($CHCl_3$, c 0.27). Spectral data are in good agreement with the reported ones [9].

(S)-$\gamma$-Methoxycarbonylmethylbutanolide **10**

To a stirred suspension of 5 mg of 10% palladium on coal in ethanol (2 mL) under an hydrogen atmosphere was added 20 mg (0.13 mmol) of butenolide **9** in ethanol (1 mL). When the required amount of hydrogen had been taken up (2.9 mL), the catalyst was removed by filtration. The filtrate was concentrated in vacuo and the residue was purified by flash chromatography to give 16 mg (80%) of butanolide **10** $[\alpha]_D^{20}$ +39 (EtOH, c 1). Lit. [10a] $[\alpha]_D^{22}$ +29 (EtOH, c 0.4). IR and $^1H$ NMR spectra were identical with those reported [9].

(1R,2S,5R,,6S,7S)-5-(2'-Hydroxy-1'-ethyl)-4,10-dioxatricyclo [5.2.1.$0^{2,6}$]-dec-8-ene **11**

To a stirred suspension of lithium aluminum hydride (110 mg, 2.4 mmol) in ether (15 mL) cooled at -15°C was added dropwise a solution of the tricyclo ester **3a** (420 mg, 2 mmol) in ether (5 mL). The resulting mixture was allowed to warm to room temperature and was stirred for 2 h. Small ice chips were added until a white precipitate was formed. The solid was removed by vacuum filtration and washed with ether (2 x 10 mL). The combined filtrates were dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatogra-

phy on silica gel (ether) to give 327 mg (91%) of pure **11**, $[\alpha]_D^{20}$ +27.5° ($CHCl_3$, c 1). IR (film) : 3440, 1050 $cm^{-1}$. CIMS ($NH_3$), m/e (relative intensity) : 200 ($MNH_4^+$, 100) ; 183 ($MH^+$, 65). $^1H$ NMR $\delta$ 1.82 (2H, m) ; 2.13 (1H, dd, J = 8 and 7 Hz) ; 2.54 (1H, dt, J = 8.5 and 8 Hz) ; 2.71 (1H, br s) ; 3.45 (1H, dd, J = 9 and 7 Hz) ; 3.7 - 3.8 (3H, m) ; 4.15 (1H, dd, J = 9 and 8 Hz) ; 4.67 (1H, s) ; 4.72 (1H, s) ; 6.35 (2H, br s).

(1R,2S,5R,6S,7S)-5-(2'-Oxo-1'-ethyl)-4,10-dioxatricyclo [5.2.1.$0^{2,6}$]-dec-8-ene **12**

To a stirred solution of oxalyl chloride (0.2 mL, 2.2 mmol) in dichloromethane (4 mL) cooled to -60°C was added a solution of dimethylsulfoxide (0.34 mL, 4.4 mmol) in dichloromethane (0.5 mL) at -50° -60°C. The reaction mixture was stirred for 10 min., a solution of alcohol **11** (364 mg, 2 mmol) in dichloromethane (1 mL) was added at -50°C and stirring was continued for an additional 30 min. Then triethylamine (1.4 mL, 10 mmol) was added dropwise at -70°C, the reaction mixture was stirred for 5 min and then allowed to warm to room temperature. Water (10 mL) was added and the organic layer was separated. The aqueous layer was extracted with $CH_2Cl_2$ (3 x 10 mL) and the combined organic extracts were washed with brine and dried over magnesium sulfate. Evaporation of the solvent in vacuo and chromatography of the residue on silica gel (ether-hexane 80:20) gave 302 mg (84%) of aldehyde **12**, $[\alpha]_D^{20}$ -3.2° ($CHCl_3$, c 1). IR (film) : 1730, 1050 $cm^{-1}$. CIMS ($NH_3$), m/e (relative intensity) : 198 ($MNH_4^+$, 100) ; 181 ($MH^+$, 3). $^1H$ NMR $\delta$ 2.14 (1H, dd, J = 8 and 6 Hz) ; 2.6 (1H, dt, J = 8 and 7.5 Hz) ; 2.72 (2H, m) ; 3.46 (1H, dd, J = 9 and 8 Hz) ; 4.0 - 4.1 (2H, m) ; 4.6 (1H, s) ; 4.75 (1H, s) ; 6.35 (2H, br s) ; 9.68 (1H, t, J = 1.6 Hz). Anal. Calcd for $C_{10}H_{12}O_3$ : C, 66.63 ; H, 6.72. Found : C, 66.03 ; H, 6.60.

(1R,2S,5R,6S,7S)-5-(3'-Methyl-2'-butenyl)-4,10-dioxatricyclo [5.2.1.$0^{2,6}$]-dec-8-ene **13**

To a suspension of isopropyltriphenylphosphonium bromide (770 mg, 2 mmol) in dry tetrahydrofuran (8 mL) was added dropwise a 1.6M solution of n-BuLi in hexane (1.2 mL, 1.9 mmol). The resulting red solution was stirred for 3 h at room temperature and then cooled to -15°C. A solution of aldehyde **12** (180 mg, 1 mmol) in THF (2 mL) was added and the mixture was allowed to reach room temperature and was stirred for 3 h. Ether (10 mL) was added and the pale yellow solid formed was removed by vacuum filtration. The filtrate was dried over magnesium sulfate and concentrated. The residue was purified by flash chromatography (80:20 ether-hexane) to afford 155 mg (76%) of pure **13**, $[\alpha]_D^{20}$ -3.3° ($CHCl_3$, c 1). IR (film) : 1100 $cm^{-1}$. CIMS ($NH_3$), m/e (relative intensity) : 224 ($MNH_4^+$, 100) ; 207 ($MH^+$, 76). $^1H$ NMR $\delta$ 1.63 (3H, s) ; 1.72 (3H, s) ; 2.09 (1H, dd, J = 8 and 7 Hz) ; 2.32 (2H, m) ; 2.53 (1H, dt, J = 8.5 and 8 Hz) ; 3.46 (1H, dd, J = 8.5 and 8 Hz) ; 3.58 (1H, dt, J = 7 and 6.5 Hz) ; 4.06 (1H, dd, J = 8.5 and 8 Hz) ; 4.65 (2H, s) ; 5.2 (1H, m) ; 6.35 (2H, br s). Anal. Calcd for $C_{13}H_{18}O_2$ : C, 75.68 ; H, 8.80. Found : C, 75.81 ; H, 8.66.

(R)-2-(3-Methyl-2-butenyl)-2,5-dihydrofuran **14**

150 mg of **13** were thermolyzed at 500°C to give 88 mg (88%) of dihydrofuran **14**, $[\alpha]_D^{20}$ -145°

($CHCl_3$, c 1). IR (film) : 1080 $cm^{-1}$. M.S., m/e (relative intensity) : 138 ($M^+$, 0.5) ; 69 (100) ; 41 (38). $^1H$ NMR $\delta$ 1.64 (3H, s) ; 1.75 (3H, s) ; 2.25 (2H, m) ; 4.65 (2H, m) ; 4.84 (1H, m) ; 5.20 (1H, m) ; 5.80 (1H, m); 5.90 (1H, m).

(R)-5-(3-Methyl-2-butenyl)-2(5H)-furanone 15

Dihydrofuran **14** (52 mg was oxydized as described above for **8** to give 24 mg (41%) of the lactone **15**, $[\alpha]_D^{20}$ -135° (MeOH, c 0.5) Lit. [14h] $[\alpha]_D^{20}$ -133°(MeOH, c 1.56). The spectroscopic properties of **15** were in good agreement with the reported ones [14h].

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