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SYNTHESIS OF α-ALKYLIDENE-β-ETHOXYCARBONYL CYCLOPENTANONES AND -γ-BUTYROLACTONES

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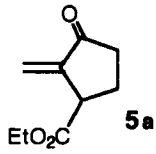
Abstract: *Synthesis of (E,Z)-α-Alkylidene-β-ethoxycarbonyl cyclopentanones* ***5*** *and (E,Z)-α-alkylidene-γ-butyrolactones* ***7*** *by condensing phosphonates* ***3*** *or* ***6*** *with a variety of aldehydes in the presence of aqueous potassium carbonate (6-10M) as base is reported.*

The biological importance and the structural diversity of cyclopentanoid products have made these compounds important synthetic targets[1]. Sarkomycin ester **5a** for example, has attracted considerable attention. A large-scale synthesis of this compound was described[2]. In this approach, the 2-diethoxyphosphonyl-3-carboethoxycyclopentanone **3** served as a key intermediate for the introduction of the *exo* methylene moiety which was effected by means of the Wittig-Horner reaction in the presence of (30%) aqueous formaldehyde using (6-10 M) potassium carbonate solution[3,4] as base in THF as solvent.



5a

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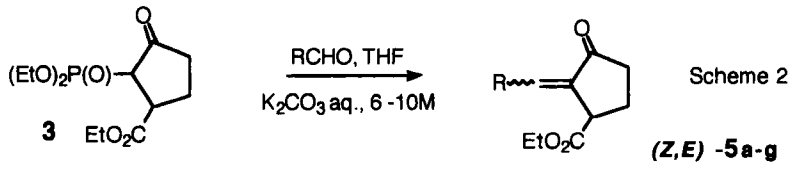
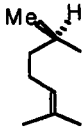
In continuation of our interest in the synthesis of cyclopentanoid polyfonctionalized compounds, we suggest here that the Wittig-Horner reaction can be extended to other aldehydes. Indeed, the condensation of various RCHO with the phosphonate **3** under the same mild conditions of Wittig-Horner reaction gives, with good yields, γ-ketoesters **5a-g** as a mixture of *Z* and *E* isomers according to the known tandem of the monohydroxyalkylation-elimination mechanism. The different unsaturated γ-ketoesters **5a-g** obtained with satisfactory yields (60-96%) are listed in Table 1.



Scheme 2

***(Z,E)* -5a-g**

Table 1: *α-Alkylidene-γ-ethoxycarbonylcyclopentanones* ***5b-g*** *synthesized.*

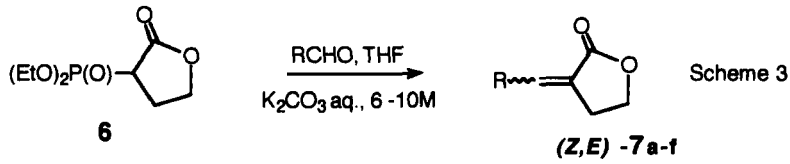
Entry	Product	R	Time (min)	*(Z/E)* %*	Yield (%)
1	**5a**	H	20	-	83
2	**5b**	CH_3	20	53/47	96
3	**5c**	C_2H_5	20	52/48	94
4	**5d**	C_3H_7	20	70/30	80
5	**5e**	i-C_4H_9	30	76/24	86
6	**5f**	C_5H_{11}	30	60/40	60
7	**5g**		30	63/37	70

(*) Ratio has been determined by ^1H NMR

Stereochemical assignment of each vinylic proton of compounds **5b-g** was in good agreement with the experimental ones calculated by Pascual's formula[5].

The α-methylene-γ-butyrolactone structural unit plays an important role in the mechanism of action of many physiologically active compounds[6-8]. In connection with our works, we have shown that the Wittig-Horner reaction can also be performed under the same mild conditions in the absence of any phase transfer

reagent[9,10] with the α-phosphonolactone **6** obtained in the Arbusov-reaction[11], leading to the stereoisomeric mixture of *(E,Z)* -α-alkylidene-γ-butyrolactones **7a-f** in good yields (Table 2).



6 *(Z,E)* **-7a-f** Scheme 3

Table 2: *α-Alkylidene-γ-butyrolactones **7a-f** synthesized.*

Entry	Product	R	Time (h)	*(Z/E)* %*	Yield (%)
1	**7a**	H	0.3	-	74
1	**7b**	CH_3	1	36/64	85
2	**7c**	n-C_3H_7	2	43/57	83
3	**7d**	i-C_4H_9	2	49/51	73
4	**7e**	C_5H_{11}	3	53/47	85
5	**7f**		5	45/55	69

(*) Ratio has been determined by ^1H NMR

In conclusion, we have developed a novel methodology for a facile synthesis of (*E,Z*)-α-alkylidene-β-ethoxycarbonylcyclopenanones and α-alkylidene-γ-butyrolactones based on widely available reagents. Furthermore, this strategy could be successfully used for the synthesis of both natural and unatural products via the wittig-Horner reaction in aqueous media.

EXPERIMENTAL SECTION

Reaction progress was monitored by an Intersmat 20M gas chromatograph using a 3mx3mm column packed with 10% SE 30 and by TLC on silica gel plates (Fluka kieselgel 60 F_{254}). ^1H and ^{13}C NMR spectra were recorded on Jeol C-HL 60MHz and Bruker AC 300MHz spectrophotometers using TMS as the internal

standard. Mass spectra (GC-MS) were run on a Varian Mat 112 (EI mode at 70eV). Infrared spectra were recorded with a Perkin-Elmer Paragon 1000 PC. Phosphonates **3** and **6** were prepared in high yield according to reference 2.

Synthesis of 2-alkylidene-3-ethoxycarbonyl cyclopentanones 5a-g

Typical procedure

To a solution of 2-diethoxyphosphinyl-3-ethoxycarbonyl cyclopentanone **3** (5 mmol) in THF (5 mL), aldehyde RCHO (5 mmol) was added. The mixture was cooled to -10°C with simultaneous slow addition of the potassium carbonate solution (6-10M). The solution was stirred for the time indicated in Table 1 at room temperature (monitored by GLC) then extracted with diethyl ether (5x30ml). The organic layer is washed with brine and dried over $MgSO_4$, filtered and concentrated in vacuo. The remaining oil was purified on Merck silica gel using EtOAc/hexane as eluent to give the compounds **5a-g**.

α-Methylene-β-ethoxycarbonyl cyclopentanone **5a**
IR($CHCl_3$,νcm^{-1}) : 1680(C=C) ; 1715 ; 1735(C=O). ^{1}H NMR(300MHz $CDCl_3$) : 6.08(d, 1H, J = 2.6 Hz) ; 5.36(d, 1H, J = 2.6 Hz) ; 4.16(q, 2H, J = 7.0 Hz) ; 3.7(m, 1H) ; 2.33(m, 4H) ; 1.26(t, 3H, J = 7.0 Hz). ^{13}C NMR(75MHz, $CDCl_3$) : 204.5(C=O) ; 172.2($CO_2CH_2CH_3$) ; 142.5(CH_2=C) ; 119.9(CH_2=C) ; 61.3(CH_2CH_3) ; 46.2(CHCO$_2$Et) ; 36.8(CH_2C=O) ; 31.9(CH_2CH_2C=O) ; 14.3(CH_3CH_2). MS (EI, m/z) : 168(M^+·, 3) ; 149(10) ; 97(26) 83(32) ; 57(100) ; 43(84).

(E,Z)-α-Ethylidene-β-ethoxycarbonyl cyclopentanone **5b**
IR($CHCl_3$,νcm^{-1}) : 1649(C=C) ; 1727 ; 1730(C=O). ^{1}H NMR(300MHz $CDCl_3$) : 6.75(dq, 1H, J = 2.0 Hz, J = 7.3 Hz, *E*) ; 6.33(dq, 1H, J = 2.0 Hz, J = 7.3 Hz, Z) ; 4.08(m, 2H) ; 3.76(m, 1H, *E*) ; 3.55(m, 1H, *Z*) ; 1.95-2.57(m, 4H) ; 1.84(d, 3H, J = 7.3 Hz, *E*) ; 1.83(d, 3H, J = 7.3 Hz, *Z*) ; 1.19(m, 3H). ^{13}C NMR(75MHz, $CDCl_3$) : 206.4(C=O, *E*) ; 204.6(C=O, *Z*) ; 173.0($CO_2CH_2CH_3$) ; 137.8(CH=C, *E*) ; 136.4(CH=C,*Z*) ; 135.1(CH=C, *E*) ; 133.0(CH=C, *Z*) ; 60.9(CH_2CH_3, *E*) ; 60.8(CH_2CH_3, *Z*) ; 47.2(CHCO$_2$Et, *E*) ; 43.7(CHCO$_2$Et, *Z*) ; 36.6(CH_2CO) ; 23.5(CH_2CH_2CO, *E*) ; 23.2(CH_2CH_2CO, *Z*) ; 15.2(CH_3CH=C, *E*) ; 14.0(CH_3CH=C, *Z*) ; 13.9(CH_3CH_2). MS (EI, m/z) : 182(M^+·, 24) ; 126(13) ; 109(100) ; 98(21) ; 81(33) ; 41(20).

(E,Z)-α-Propylidene-β-ethoxycarbonyl cyclopentanone **5c**

IR($CHCl_3$,νcm^{-1}) : 1625(C=C) ; 1723 ; 1730(C=O). ^1H NMR(300MHz $CDCl_3$) : 6.73(dt, 1H, J = 2.0 Hz, J = 7.3 Hz, *E)* ; 6.23(dt, 1H, J = 2.0 Hz, J = 7.3 Hz, *Z)* ; 4.15(m, 2H) ; 3.79(m, 1H, *E)* ; 3.55(m, 1H, *Z)* ; 2.62(m, 2H) ; 2.46-2.00(m, 4H) ; 1.10(m, 3H) ; 0.98(m, 3H). ^{13}C NMR(75MHz, $CDCl_3$) : 206.2(C=O, *E)* ; 204.4(C=O, *Z)* ; 173.1(CO_2, *E)* ; 173.0(CO_2, *Z)* ; 143.1(C=CH, *E)* ; 141.2(C=CH, *Z)* ; 135.2(C=CH, *E)* ; 133.6(C=CH, *Z)* ; 60.8($CO_2CH_2CH_3$, *E)* ; 60.7($CO_2CH_2CH_3$, *Z)* ; 47.4($CHCO_2$, *E)* ; 44.5($CHCO_2$, *Z)* ; 38.4(CH_2CH=, *E)* 36.8(CH_2CH=, *Z)* ; 36.6(CH_2CO) ; 23.7($COCH_2CH_2$, *E)* ; 23.1($COCH_2CH_2$, *Z)* 14.0(C=$CHCH_2CH_3$) ; 13.8($CO_2CH_2CH_3$). MS (EI, m/z) : 196($M^{+\cdot}$, 13) ; 131(21) ; 127(19) ; 123(63) ; 82(14) ; 57(100) ; 55(10) ; 29(16).

(E,Z)-α-Butylidene-β-ethoxycarbonyl cyclopentanone **5d**

IR($CHCl_3$,νcm^{-1}) : 1636(C=C) ; 1720 ; 1732(C=O). ^1H NMR(300MHz $CDCl_3$) : 6.75(dt, 1H, J = 2.0 Hz, J = 7.3 Hz, *E)* ; 6.22(dt, 1H, J = 2.0 Hz, J = 7.3 Hz, *Z)* ; 4.17(m, 2H) ; 3.82(m, 1H, *E)* ; 3.65(m, 1H, *Z)* ; 2.69(m, 2H) ; 2.65-2.00(m, 4H) ; 1.46(m, 2H) ; 1.27(t, 3H, J = 7.1 Hz, *E)* ; 1.26(t, 3H, J = 7.1 Hz, *Z)* ; 0.93(m, 3H). ^{13}C NMR(75MHz, $CDCl_3$) : 206.1(C=O, *E)* ; 204.2(C=O, *Z)* ; 173.2(CO_2, *E)* ; 173.0(CO_2, *Z)* ; 144.3(C=CH, *E)* ; 140.1(C=CH, *Z)* ; 135.3(C=CH, *E)* ; 133.3(C=CH, *Z)* ; 60.8($CO_2CH_2CH_3$, *E)* ; 60.6($CO_2CH_2CH_3$, *Z)* ; 47.1($CHCO_2$, *E)* ; 45.4($CHCO_2$, *Z)* ; 38.2(CH_2CH=, *E)* ; 36.8(CH_2CH=, *Z)* ; 36.5(CH_2CO) ; 29.5($CH_3CH_2CH_2$) ; 23.6($COCH_2CH_2$, *E)* ; 23.0($COCH_2CH_2$, *Z)* ; 13.8($CO_2CH_2CH_3$) ; 13.3(C=$CHCH_2CH_2CH_3$). MS (EI, m/z) : 210($M^{+\cdot}$, 1) ; 196(4) ; 151(100) ; 133(25) ; 109(95) ; 93(49) ; 55(20) ; 41(38) ; 29(41).

(E,Z)-α-(3-Methylbutylidene)-β-ethoxycarbonyl cyclopentanone **5e**

IR($CHCl_3$,νcm^{-1}) : 1636(C=C) ; 1720 ; 1730(C=O). ^1H NMR(300MHz $CDCl_3$) : 6.68(dt, 1H, J = 2.0 Hz, J = 7.3 Hz, *E)* ; 6.17(dt, 1H, J = 2.0 Hz, J = 7.3 Hz, *Z)* ; 4.08(m, 2H) ; 3.78(m, 1H, *E)* ; 3.55(m, 1H, *Z)* ; 2.55(m, 2H) ; 2.35-1.96(m, 4H) ; 1.65(m, 1H) ; 1.21(m, 3H) ; 0.86(m, 6H). ^{13}C NMR(75MHz, $CDCl_3$) : 206.3(C=O, *E)* ; 205.2(C=O, *Z)* ; 173.4(CO_2, *E)* ; 173.3(CO_2, *Z)* ; 143.8(C=CH, *E)* ; 139.5(C=CH, *Z)* ; 136.0(C=CH, *E)* ; 133.8(C=CH, *Z)* ; 60.9($CO_2CH_2CH_3$, *E)* ; 60.8($CO_2CH_2CH_3$, *Z)* ; 47.5($CHCO_2$, *E)* ; 44.1($CHCO_2$, *Z)* ; 38.5(CH_2CH=, *E)* ; 36.7(CH_2CH=, *Z)* ; 36.5(CH_2CO) ; 28.8($CH(CH_3)_2$, *E)* ; 28.1($CH(CH_3)_2$, *Z)* ; 23.9($COCH_2CH_2$, *E)* ; 23.3($COCH_2CH_2$, *Z)* ; 22.3(CH_3CH) ; 22.2(CH_3CH) ;

14.1($CO_2CH_2\underline{C}H_3$). MS (EI, m/z): 224($M^{+}\cdot$, 5) ; 151(100) ; 109(95) ; 93(49) ; 109(95) ; 79(42) ; 55(20) ; 41(38) ; 29(41).

(E,Z)-α-Hexylidene-β-ethoxycarbonyl cyclopentanone **5f**

IR($CHCl_3$,νcm^{-1}) : 1641(C=C) ; 1721 ; 1730(C=O). ^1H NMR(300MHz $CDCl_3$) : 6.65(dt, 1H, J = 2.0 Hz, J = 7.3 Hz, *E)* ; 6.14(dt, 1H, J = 2.0 Hz, J = 7.3 Hz, *Z);* 4.12(m, 2H) ; 3.75(m, 1H, *E)* ; 3.55(m, 1H, *Z)* ; 2.64(m, 2H) ; 2.52-1.92(m, 4H) 1.50-1.10(m, 9H) ; 0.82(m, 3H). ^{13}C NMR(75MHz, $CDCl_3$) : 206.0($\underline{C}O$, *E)* ; 204.9($\underline{C}O$, *Z)* ; 173.1($\underline{C}O_2$, *E)* ; 173.0($\underline{C}O_2$, *Z)* ; 144.6($\underline{C}$=CH, *E)* ; 140.4($\underline{C}$=CH, *Z)* ; 135.0(C=$\underline{C}$H, *E)* ; 133.0(C=$\underline{C}$H, *Z)* ; 60.7($CO_2\underline{C}H_2CH_3$, *E)* ; 60.6($CO_2\underline{C}H_2CH_3$, *Z)* ; 47.1($\underline{C}HCO_2$, *E)* ; 43.8($\underline{C}HCO_2$, *Z)* ; 38.2($\underline{C}H_2CH$=, *E)* 36.5($\underline{C}H_2CH$=, *Z)* ; 31.7($\underline{C}H_2CO$) ; 28.4($\underline{C}H_2CH_2CH$=) ; 27.6($\underline{C}H_2(CH_2)_2CH$=) ; 23.1($COCH_2\underline{C}H_2$, *E)* ; 22.6($COCH_2\underline{C}H_2$, *Z)* ; 22.1($CH_3\underline{C}H_2CH_2$) ; 13.8($CO_2CH_2\underline{C}H_3$) ; 13.7(C=CH$(CH)_4\underline{C}H_3$). MS (EI, m/z) : 238($M^{+}\cdot$, 37) ; 165(100) ; 147(26) ; 109(25) ; 79(26) ; 41(18) ; 29(21).

(E,Z)-α-(3,7-Dimethyloct-6-enylidene)-β-ethoxycarbonyl cyclopentanone **5g**

IR($CHCl_3$,νcm^{-1}) : 1624(C=C) ; 1719 ; 1732(C=O). ^1H NMR(300MHz $CDCl_3$) : 6.70(m, 1H, *E)* ; 6.17(m, 1H, *Z)* ; 5.01(m, 1H) ; 4.08(m, 2H) ; 3.72(m, 1H, *E)* ; 3.56(m, 1H, *Z)* ; 2.62(m, 2H) ; 2.35-1.98(m, 4H) ; 1.91(m, 2H) ; 1.60(s, 3H) ; 1.52(s, 3H) ; 1.21(m, 6H) ; 0.82(m, 3H). ^{13}C NMR(75MHz, $CDCl_3$) : 205.9($\underline{C}$=O, *E)* ; 204.1($\underline{C}$=O, *Z)* ; 173.2($\underline{C}O_2CH_2CH_3$, *E)* ; 173.1($\underline{C}O_2CH_2CH_3$, *Z)* ; 143.6($\underline{C}$=$CHCH_2$, *E)* ; 138.5($\underline{C}$=$CHCH_2$, *Z)* ; 130.9($(CH_3)_2\underline{C}$=$CHCH_2$, *E)* ; 130.8($(CH_3)_2\underline{C}$=$CHCH_2$, *Z)* ; 124.4($(CH_3)_2C$=$\underline{C}HCH_2$) ; 124.2(C=$\underline{C}HCH_2$, *E)* ; 124.1(C=$\underline{C}HCH_2$, *Z)* ; 60.7($CO_2\underline{C}H_2CH_3$) ; 47.3($CO_2\underline{C}H$, *E)* ; 44.1($CO_2\underline{C}H$, *Z)* ; 38.4(C=$CH\underline{C}H_2$, *E)* ; 36.8(C=$CH\underline{C}H_2$, *Z)* ; 36.6($CO\underline{C}H_2CH_2$) ; 36.0($\underline{C}H_2CH(CH_3)_2$) ; 32.9($\underline{C}HCH_3$, *E)* ; 31.2($\underline{C}HCH_3$, *Z)* ; 25.5($\underline{C}H_3C$=) ; 25.3($\underline{C}H_2CHCH_3$) ; 23.1($COCH_2\underline{C}H_2$, *E)* ; 22.0($COCH_2\underline{C}H_2$, *Z)* ; 19.2($\underline{C}H_3CH$) ; 17.4($\underline{C}H_3C$=) ; 13.9($CO_2CH_2\underline{C}H_3$). MS (EI, m/z) : 292($M^{+}\cdot$, 3) ; 219(100) ; 206(28) ; 135(26) ; 121(22) ; 109(51) ; 55(33) ; 41(55) ; 29(22).

α-Methylene-γ-butyrolactone **7a**

IR($CHCl_3$,νcm^{-1}) : 1765(C=O) ; 1668(C=C) ; 810(C=CH_2). ^1H NMR(300MHz, $CDCl_3$) : 6.17(t, 1H, J = 3 Hz) ; 5.64(t, 1H, J = 3 Hz) ; 4.37(t, 2H, J = 7 Hz) ; 2.98(m, 2H). MS (EI, m/z) : 98($M^{+}\cdot$, 79) ; 68(M-CH_2O, 100).

(E,Z)-α-Ethylidene-γ-butyrolactone **7b**

IR($CHCl_3$,νcm^{-1}) : 1745(C=O) ; 1681(C=C). ^1H NMR(300MHz, $CDCl_3$): 6.79(m, 1H, *E*) ; 6.39(m, 1H, *Z*) ; 4.36(t, 2H, J = 7.2 Hz, *E*) ; 4.31(t, 2H, J = 7.3 Hz, *Z*) ; 2.98(m, 2H) ; 2.17(m, 3H, *E*) ; 1.88(m, 3H, *Z*). ^{13}C NMR(75MHz, $CDCl_3$) : 171.0(CO, *E*) ; 170.2(CO, *Z*) ; 138.5(C=CH, *E*) ; 135.5(C=CH, *Z*) ; 126.2(C=CH, *E*) ; 124.1(C=CH, *Z*) ; 65.3(CH_2O, *E*) ; 65.1(CH_2O, *Z*) ; ,28.8(CH_2C=, *E*) ; 24.7(CH_2C=, *Z*) ; 15.5(CH_3CH=, *E*) ; 13.7(CH_3CH=, *Z*). MS (EI, m/z) : 112($M^+\cdot$, 100) ; 97(7) ; 83(19) ; 67(47) ; 65(13) ; 54(61) ; 51(17).

(E,Z)-α-Butylidene-γ-butyrolactone **7c**

IR($CHCl_3$,νcm^{-1}) : 1750(C=O) ; 1679(C=C). ^1H NMR(300MHz, $CDCl_3$) : 6.73(m, 1H, *E*) ; 6.24(m, 1H, *Z*) ; 4.38(t, 2H, J = 7.3 Hz, *E*) ; 4.31(t, 2H, J = 7.5 Hz, *Z*) ; 2.98(m, 2H) ; 2.7(m, 2H, *E*) ; 2.2(m, 2H, *Z*) ; 1.4(m, 2H) ; 0.98(m, 3H). ^{13}C NMR(75MHz, $CDCl_3$) : 171.2(CO, *E*) ; 170.0(CO, *Z*) ; 143.8(C=CH, *E*) ; 140.5(C=CH, *Z*) ; 125.2(C=CH, *E*) ; 124.4(C=CH, *Z*) ; 65.2(CH_2O, *E*) ; 65.0(CH_2O, *Z*) ; 31.9(CH_2CH=, *E*) ; 29.1(CH_2CH=, *Z*) ; 28.8(CH_2C=, *E*) ; 24.8(CH_2C=, *Z*) ; 21.2(CH_3CH_2) ; 13.5(CH_3CH_2). MS (EI, m/z) : 140($M^+\cdot$, 26) ; 125(35) ; 99(100) ; 81(66) ; 79(32) ; 67(75) ; 53(57).

(E,Z)-α-(3-Methylbutylidene)-γ-butyrolactone **7d**

IR($CHCl_3$,νcm^{-1}) : 1750(C=O) ; 1679(C=C). ^1H NMR(300MHz, $CDCl_3$) : 6.75(m, 1H, *E*) ; 6.26(m, 1H, *Z*) ; 4.38(t, 2H, J = 7.3 Hz, *E*) ; 4.31(t, 2H, J = 7.5 Hz, *Z*) ; 2.94(m, 2H, *E*) ; 2.88(m, 2H, *Z*) ; 2.6(m, 2H, *E*) ; 2.16(m, 2H, *Z*) ; 1.82(m, 1H, *E*) ; 1.73(m, 1H, *Z*) ; 0.95(m, 6H). ^{13}C NMR(75MHz, $CDCl_3$) : 171.0(CO, *E*) ; 169.9(CO, *Z*) ; 142.8(C=CH, *E*) ; 139.4(C=CH, *Z*) ; 125.7(C=CH, *E*) ; 123.8(C=CH, *Z*) ; 65.1(CH_2O, *E*) ; 65.0(CH_2O, *Z*) ; 39.0(CH_2CH=, *E*) ; 35.8(CH_2CH=, *Z*) ; 28.9($CHCH_2CH$=, *E*) ; 28.3($CHCH_2CH$=, *Z*) ; 27.8(CH_2C=, *E*) ; 24.9(CH_2C=, *Z*) ; 22.1(($CH_3)_2CHCH_2$, *E*) ; 22.0(($CH_3)_2CHCH_2$, *Z*). MS (EI, m/z) : 154($M^+\cdot$, 4) ; 112(100) ; 99(50) ; 94(9) ; 83(16) ; 67(36) ; 53(28).

(E,Z)-α-Hexylidene-γ-butyrolactone **7e**

IR($CHCl_3$,νcm^{-1}) : 1746(C=O) ; 1678(C=C). ^1H NMR(300MHz, $CDCl_3$) : 6.72(m, 1H, *E*) ; 6.24(m, 1H, *Z*) ; 4.37(t, 2H, J = 7.3 Hz, *E*) ; 4.33(t, 2H, J = 7.5 Hz, *Z*) ; 2.89(m, 2H) ; 2.7(m, 2H, *E*) ; 2.2(m, 2H, *Z*) ; 1.47(m, 2H) ; 1.42(m,

2H) ; 1.34(m, 2H) ; 0.98(m, 3H). ^{13}C NMR(75MHz, $CDCl_3$) : 171.1(CO, *E*) ; 169.9(CO, *Z*) ; 144.0(C=CH, *E*) ; 140.6(C=CH, *Z*) ; 124.9(C=CH, *E*) ; 123.1(C=CH, *Z*) ; 65.2(CH_2O, *E*) ; 65.0(CH_2O, *Z*) ; 30.1(CH_2CH=C, *E*) ; 29.9(CH_2CH=C, *Z*) ; 28.8(CH_2C=, *E*) ; 28.7(CH_2C=, *Z*) ; 28.4(CH_2CH_2CH=C, *E*) ; 28.1(CH_2CH_2CH=C, *Z*) ; 27.5($CH_3CH_2CH_2$) ; 22.1($CH_3CH_2CH_2$) ; 13.6(CH_3CH_2). MS (EI, m/z) : 168($M^{+}\cdot$, 23) ; 125(100) ; 112(7) ; 99(10) ; 81(21) ; 79(21) ; 67(16) ; 53(15).

(E,Z)-α-(3,7-Dimethyloct-6-enylidene)-γ-butyrolactone **7f**

IR($CHCl_3$, νcm^{-1}) : 1747(C=O) ; 1678(C=C). ^{1}H NMR(300MHz, $CDCl_3$) : 6.70(m, 1H, *E*) ; 6.30(m, 1H, *Z*) ; 5.08(m, 1H) ; 4.34(t, 2H, *J* = 7.3 Hz, *E*) ; 4.29(t, 2H, *J* = 7.5 Hz, *Z*) ; 2.87(m, 2H) ; 2.64(m, 1H, *E*) ; 2.20(m, 1H, *Z*) ; 1.72-2.12(m, 2H, 1H) ; 1.71(s, 3H) ; 1.6(s, 3H) ; 1.2(m, 2H) ; 0.98(m, 3H). ^{13}C NMR(75MHz, $CDCl_3$) : 170.9(CO, *E*) ; 169.8(CO, Z) ; 142.7(C=CH, *E*) ; 139.4(C=CH, *Z*) ; 131.1($(CH_3)_2C$=CH, *E*) ; 130.8($(CH_3)_2C$=CH, *Z*) ; 125.8(C=$CHCH_2$, *E*) ; 124.8(C=$CHCH_2$, *Z*) ; 124.0($(CH_3)_2C$=CH) ; 65.1(CH_2O, *E*) ; 64.9(CH_2O, *Z*) ; 37.2(CH_2CH=C, *E*) ; 36.4(CH_2CH=C, *Z*) ; 34.1(CH_2CH=$C(CH_3)_2$) ; 32.6($CHCH_3$, *E*) ; 32.1($CHCH_3$, *Z*) ; 28.9(CH_2C=, *E*) ; 27.4(CH_2C=, *Z*) ; 25.5(CH_3C=) ; 25.1(CH_2CHCH_3) ; 19.1(CH_3CH, *E*) ; 18.9(CH_3CH, *Z*) ; 17.3(CH_3C=). MS (EI, m/z) : 222($M^{+}\cdot$, 10) ; 179(19) ; 166(12) ; 151(8) ; 139(91) ; 93(38) ; 81(29) ; 69(68) ; 53(39).

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