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Studies on Pd^{II}-catalyzed cyclization of 4′-hydroxy-2′-alkenyl 2-alkynoates

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Abstract

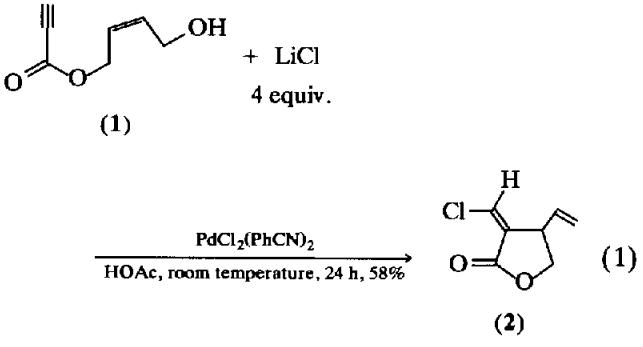
α-(*Z*)-Halomethylene-β-vinyl-γ-butyrolactones and α-(*Z*)-halomethylene-β-(2′-alkanonyl)-γ-butyrolactones were obtained highly stereoselectively from Pd^{II}-catalyzed cyclization of 4′-hydroxy-2′-alkenyl 2-alkynoates. A mechanism involving halopalladation, intramolecular insertion, β-OH elimination or β-H elimination is discussed.

1. Introduction

The α-methylene-γ-butyrolactone ring is regarded as a building block of many natural products with important biological activities, such as cytotoxicity, antitumor activity, *etc*. Recently we have developed a new method for stereoselective synthesis of α-(*Z*)-halomethylene-γ-butyrolactone derivatives by Pd^{II}-catalyzed cyclization of acyclic haloallylic 2-alkynoates [1,2]. In this reaction, the γ-butyrolactone ring is constructed by C–C bond formation, which is quite different from the methods previously reported [3,4]. In our continuing effort to develop more efficient catalytic systems for the synthesis of α-methylene-γ-butyrolactone derivatives, we now report our recent results on the Pd^{II}-catalyzed cyclization of 4′-hydroxy-2′-alkenyl 2-alkynoates.

2. Results and discussion

We first tried the reaction of 4′-hydroxy-2′(*Z*)-butenyl 2-propynoates (**1**) under the catalysis of $PdCl_2(PhCN)_2$ (5 mol%) in HOAc for 24 h. The reaction afforded α-(*Z*)-chloromethylene-β-vinyl-γ-butyrolactone (**2**), the same product of Pd^{II}-catalyzed cyclization of 4′-chloro-2′-butenyl 2-alkynoate [1,2] (eqn. (1)).



Some further examples of this reaction, given in Table 1 (eqn. (2)), show that in addition to the product similar to **2**, *i.e.*, compound **4**, α-(*Z*)-halomethylene-β-(2′-alkanonyl)-γ-butyrolactone (**5**) was isolated (entries 5–7, 9–12). The configuration of the *exo* double bonds in **4** and **5** were determined by comparing the chemical shift of the vinylic proton of the *exo* C=C bond with their analogues [2]. Although **3** was used as a diasteromeric mixture, *Z*-**3** afforded the β,γ-*trans*-substituted product (**4A**) highly stereoselectively (entries 2, 4, 6, 8, 10 and 12), while in the case of *E*-**3**, only when the R group becomes bulkier, was the *trans* product **4a** obtained highly stereoselectively (comparing entries 1, 3, 5, 7, 9 and 11). The relative stereo-chemistry of the

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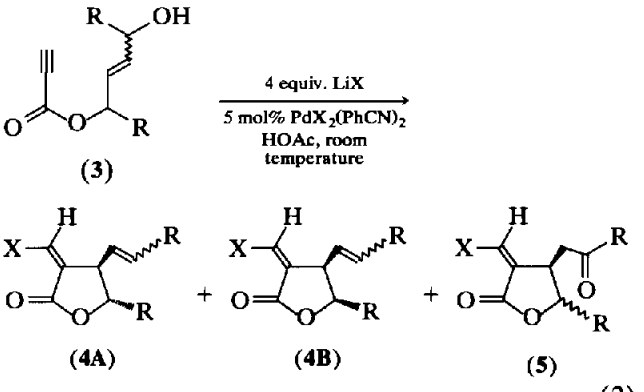
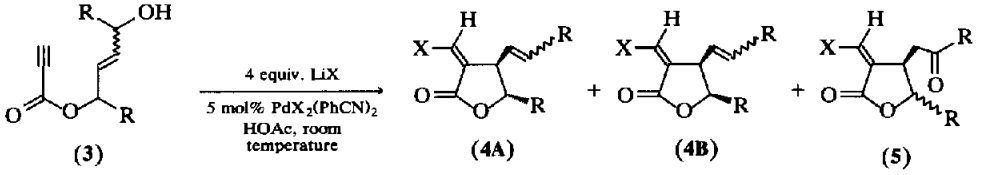
substituents at the β and γ positions in the product was determined by NOE difference spectra or ^{1}H 2D NOESY spectra, *i.e.*, the two hydrogen atoms at the β, γ carbons of the *cis* isomer show a stronger NOE correlation signal than that of the *trans* isomer. Upon irradiation at the methyl group (for compounds **4Aa, 4Ba, 4Aa'** and **4Ba'**) or the methylene group (for compounds **4Ab, 4Bb, 4Ab'** and **4Bb'**) adjacent to the C=C bond at the side chain in **4**, the coupling constants of the two vinylic protons at this C=C bond (8 Hz for the *Z* isomer, 15 Hz for the *E* isomer) were observed, implying that mixtures of *Z* and *E* isomers referred to the C=C bond at the side chain were obtained. Thus, two sets of ^{1}H NMR signals with similar splitting patterns for certain protons were observed (see Experimental section). But in the case of entries 9–12, the C=C bond was formed in the *E* configuration highly stereoselectively.



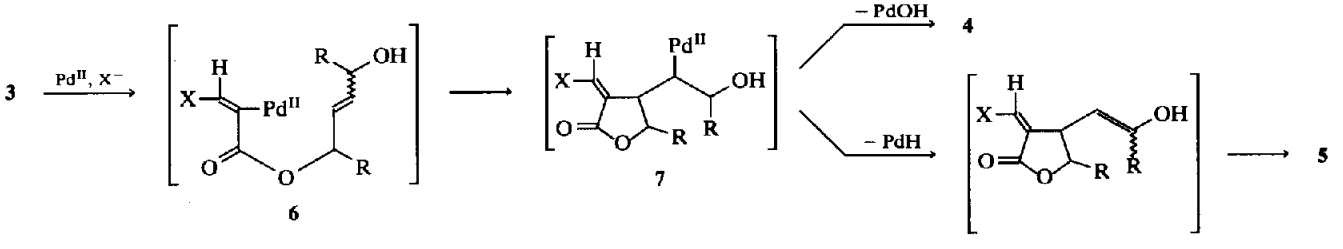
(2)

TABLE 1. $PdX_2(PhCN)_2$-catalyzed cyclization of 4'-hydroxy-1',4'-disubstituted-2'-alkenyl 2-propynoates



Entry	R	3 C=C	LiX	Time (h)	Yield of 4 (%) [a]	Ratio 4A	Ratio 4B	Yield of 5 (%) [a,b]
1	Me	*E*-**3a**	Cl	72	48	67 (**4Aa**)	33 (**4Ba**)	– [c]
2	Me	*Z*-**3a**	Cl	21	54	100 (**4Aa**)	0 (**4Ba**)	– [c]
3	Me	*E*-**3a**	Br	72	47	64 (**4Aa'**) [d]	36 (**4Ba'**) [d]	– [c]
4	Me	*Z*-**3a**	Br	25	50	100 (**4Aa'**) [d]	0 (**4Ba'**) [d]	– [c]
5	Et	*E*-**3b**	Cl	41	30	91 (**4Ab**)	9 (**4Bb**)	21 (**5b**) (83:17)
6	Et	*Z*-**3b**	Cl	49	28	100 (**4Ab**)	0	35 (**5b**) (100:0)
7	Et	*E*-**3b**	Br	41	26	86 (**4Ab'**) [d]	14 (**4Bb'**) [d]	21 (**5b'**) [d] (80:20)
8	Et	*Z*-**3b**	Br	48	30	100 (**4Ab'**) [d]	0	– [e]
9	^{i}Pr	*E*-**3c**	Cl	28	17	100 (**4Ac**)	0	35 (**5c**) (100:0)
10	^{i}Pr	*Z*-**3c**	Cl	48	25	100 (**4Ac**)	0	51 (**5c**) (100:0)
11	^{i}Pr	*E*-**3c**	Br	40	25	100 (**4Ac'**) [d]	0	34 (**5c'**) [d] (100:0)
12	^{i}Pr	*Z*-**3c**	Br	25	14	100 (**4Ac'**) [d]	0	47 (**5c'**) [d] (100:0)

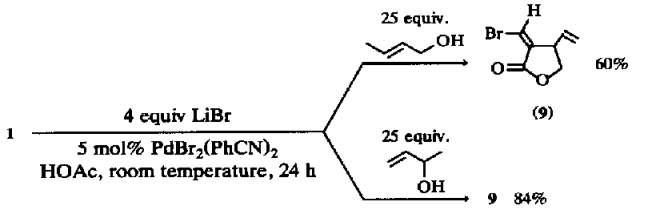
[a] The ratio of *E*/*Z* referred to the *exo* C=C bonds is 0:100. [b] The numbers in parentheses are the ratios of *trans*/*cis* (referred to the β,γ-substituents in products **5**) determined by 200 MHz ^{1}H NMR spectroscopy. [c] Product **5** was not detected by 200 MHz ^{1}H NMR spectroscopy. [d] The compounds with the prime at the upright corner represent the bromo-analogues. [e] 14% of the stereospecific hydrobromination product of the carbon–carbon triple bond, i.e., 4'-hydroxy-1'-ethyl-2'-hexenyl (*Z*)-3-bromo-2-propenoate, is obtained instead of **5c'** [10–12].



Scheme 1.

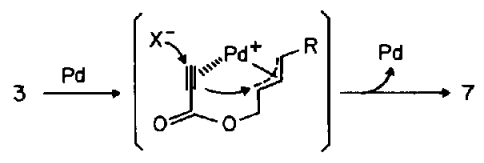
The present reaction might occur through a similar mechanism [2] as shown in Scheme 1, *i.e.*, the Pd intermediate **7** was formed by intramolecular insertion of the C=C bond to the C–Pd bond in the vinyl palladium intermediate **6**, which might be first formed through the highly stereoselective *trans*-halopalladation. Through β-OH elimination, the intermediate **7** might afford the product **2** or **4**. Although only a few examples of β-OH elimination involving transition metals have been reported [5,6], recently several authors have reported such a β-OH elimination reaction involving Pd [7–9].

Alternatively, the reaction might also occur through a mechanism (Scheme 2) in which the allylic alcohol moiety might first react with the palladium complex to form a π-allyl palladium intermediate **8**, which might be captured by a carbanion generated *in situ* by the nucleophilic addition of the halide anion to the electron-deficient carbon–carbon triple bond to afford **4** [10–12]. But even when 25 equiv. of 2-butenol or 3-buten-2-ol were added to the system of $PdBr_2(PhCN)_2$, LiBr and **1**, the reaction afforded α-(*Z*)-bromomethylene-β-vinyl-γ-butyrolactone (**9**) as the sole product (eqn. (3)).



(3)

Furthermore, the yields of the preparation of π-allyl palladium complexes by the reaction of an allylic alcohol and $PdCl_2$ [13,14] are low. The oxidative addition of Pd^{II} with allylic alcohol to form a π-allyl Pd^{IV} complex was proved to be impossible by Henry *et al.* [7]. Thus, instead of the mechanism shown in Scheme 2, the reaction probably occurred through a β-OH elimination (or dehydroxypalladation) mechanism as shown in Scheme 1. Products **5** might be formed by β-H elimination [15,16] of intermediate **7** in competition with β-OH elimination. It is unclear why the β-H elimination products **5** of *E*- and *Z*-**3a** were not detected.



Scheme 2.

3. Experimental section

^1H NMR spectra were recorded on a Varian XL-200 or JEOL FX-90Q spectrometer. Chemical shifts are reported as δ values by using Me_4Si as an internal standard. NOE difference spectra and 2D NOESY spectra were taken on an AMX-600 spectrometer. IR spectra were taken with an IR-440 instrument. MS spectral data were obtained with a Finnigan GC-MS-4021 spectrometer.

LiX was dried over P_2O_5 under vacuum. $PdX_2(PhCN)_2$ (X = Cl [17], X = Br [17,18]) was prepared according to the literature method. Oct-4-(*Z*)- or (*E*)-en-3,6-diol and 2,7-dimethyloct-4(*Z*)- or (*E*)-3,6-diol were prepared by catalytic hydrogenation (P–2Ni, H_2) [19] or reduction with $LiAlH_4$ [20] of oct-4-yn-3,6-diol and 2,7-dimethyloct-4-yn-3,6-diol, respectively, which were prepared via the reaction of acetylene dimagnesium bromide with the corresponding aldehydes in THF [21]. 4'-Hydroxy-2'(*Z*)- or (*E*)-alkenyl 2-propynoates were prepared according to the literature method [22].

3.1. $PdCl(PhCN)_2$ catalyzed cyclization of 2-propynoate complexes

3.1.1. General procedure

To a mixture of 2-propynoate (1 mmol), LiX (4 mmol) and HOAc (5 ml) was added $PdCl_2(PhCN)_2$ (5 mol%). The reaction was carried out at room temperature and monitored by TLC. After the reaction was over, ethyl acetate (10 ml) and water (5 ml) were added. The mixture was carefully neutralized with solid Na_2CO_3 in portions, and extracted with ethyl acetate (3 × 10 ml). After drying ($MgSO_4$) and evaporating, the crude product was submitted to preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate 5 : 1) to afford products **4** and **5**.

*3.1.2. trans β-(1'-Propenyl)-γ-methyl-α-(Z)-chloromethylene-γ-butyrolactone (**4Aa**).*

B.p. 145–147°C (bath temperature)/7 mmHg. IR (neat): 2950, 1760, 1620, 1180 cm^{-1}. MS: *m/e* 189 ($M^+(^{37}Cl)$ + 1)/187 ($M^+(^{35}Cl)$ + 1), 171/169, 151, 144/142, 116/114, 107, 79, 78, 77. ^1H NMR ($CDCl_3$/200 MHz): 6.44, 6.21 (d, J = 2.89 Hz, 1H, CHCl=); 6.00–5.82, 5.82–5.60 (m, 1H, CH=); 5.40–5.20 (m, 1H, CH=); 4.30–4.10 (m, 1H, OCH); 3.65, 3.23 (dt, J = 2.89 Hz, J = 8.40 Hz, 1H, CH–C=); 1.84–1.70 (m, 3H, CH_3); 1.45, 1.43 (d, J = 4.00 Hz, 3H, CH_3) ppm. Anal. Found: C, 57.80; H, 5.83. $C_9H_{11}ClO_2$ calc.: C, 57.92; H, 5.94%.

*3.1.3. cis β-(1'-Propenyl)-γ-methyl-α-(Z)-chloromethylene-γ-butyrolactone (**4Ba**)*

Oil. IR (neat): 2950, 1760, 1620, 1180 cm^{-1}. MS: *m/e* 189 (M^+ (^{37}Cl) + 1)/187 ($M^+(^{35}Cl)$ + 1), 144/142,

116/114, 107, 79, 78, 77. ^{1}H NMR($CDCl_3$/200 MHz): 6.48, 6.44 (d, J = 2.86 Hz, 1H, CHCl=); 6.00–5.82, 5.82–5.60 (m, 1H, CH=); 5.44–5.20 (m, 1H, CH=); 4.70 (quintet, J = 6.50 Hz, 1H, OCH); 4.18, 3.76 (dt, J = 2.86 Hz, J = 8.4 Hz, 1H, CH–C=); 1.78, 1.72 (dd, J = 1.38 Hz, J = 6.50 Hz, 3H, CH_3); 1.29, 1.27 (d, J = 6.50 Hz, 3H, CH_3) ppm. HRMS: Found: 142.0198 (^{35}Cl), 144.0155 (^{37}Cl). C_7H_7ClO ($M^+ - OCHCH_3$) calc.: 142.0185 (^{35}Cl), 144.0154 (^{37}Cl).

3.1.4. trans β-(1'-Propenyl)-γ-methyl-α-(Z)-bromomethylene-γ-butyyrolactone (4Aa')

B.p. 140–142°C (bath temperature)/4 mmHg. IR (neat): 2950, 1760, 1640, 1180 cm^{-1}, MS: m/e 233 (M^+(^{81}Br) + 1)/231 (M^+(^{79}Br) + 1), 188/186, 160/158, 151, 107, 79, 77. ^{1}H NMR ($CDCl_3$/200 MHz): 6.70, 6.65 (d, J = 2.90 Hz, 1H, CHBr=); 6.00–5.64 (m, 1H, CH=); 5.36–5.18 (m, 1H, CH=); 4.28–4.10 (m, 1H, OCH); 3.57, 3.14 (dt, J = 2.90 Hz, J = 8.60 Hz, 1H, CH–C=); 1.76, 1.72 (dd, J = 1.60 Hz, J = 6.50 Hz, 3H, CH_3); 1.44, 1.42 (d, J = 6.50 Hz, 3H, CH_3) ppm. Anal. Found: C, 46.89; H, 4.95. $C_9H_{11}BrO_2$ calc.: C, 46.78; H, 4.80%.

3.1.5 cis β-(1'-Propenyl)-γ-methyl-α-(Z)-bromomethylene-γ-butyrolactone (4Ba')

Oil. IR (neat): 2950, 1760, 1630, 1170 cm^{-1}, MS: m/e 233 (M^+(^{37}Cl) + 1)/231 (M^+(^{35}Cl) + 1), 215/213, 188/186, 160/158, 151, 107, 79, 77. ^{1}H NMR ($CDCl_3$/200 MHz): 6.73, 6.68 (d, J = 2.80 Hz, 1H, CHBr–); 6.00–5.60 (m, 1H, CH=); 5.42–5.18 (m, 1H, CH=); 4.68 (quintet, J = 6.5 Hz, 1H, OCH); 4.10, 3.70 (dt, J = 2.80 Hz, J = 6.50 Hz, 1H, CH–C=); 1.76, 1.70 (dd, J = 1.30 Hz, J = 6.50 Hz, 3H, CH_3); 1.27, 1.24 (d, J = 6.50 Hz, 3H, CH_3) ppm. HRMS: Found: 185.9715 (^{79}Br), 187.9687 (^{81}Br). C_7H_7BrO ($M^+ - OCHCH_3$) calc.: 185.9680 (^{79}Br), 187.9660 (^{81}Br).

3.1.6. trans β-(1'-Butenyl)-γ-ethyl-α-(Z)-chloromethylene-γ-butyrolactone (4Ab)

B.p. 130–132°C (bath temperature)/1 mmHg. IR (neat): 2950, 1770, 1640, 1180 cm^{-1}. MS: m/e 217 (M^+(^{37}Cl) + 1)/215 (M^+(^{35}Cl) + 1), 199/197, 179, 158/156, 135, 130/128, 121, 93, 91. ^{1}H NMR ($CDCl_3$/200 MHz): 6.47, 6.41 (d, J = 2.60 Hz, 1H, CHCl–); 5.86–5.66 (m, 1H, CH=); 5.36–5.14 (m, 1H, CH=); 4.14–3.98 (m, 1H, OCH); 3.70, 3.30 (dt, J = 2.60 Hz, J = 8.60 Hz, 1H, CH–C=); 2.12 (quintet, J = 8.0 Hz, 2H, CH_2C–); 1.90–1.60 (m, 2H, CH_2); 1.14–0.98 (m, 6H, $2CH_3$) ppm. Anal. Found: C, 61.56; H, 7.33. $C_{11}H_{15}ClO_2$ calc.: C, 61.54; H, 7.04%.

3.1.7. cis-β-(1'-Butenyl)-γ-ethyl-α-(Z)-chloromethylene-γ-butyrolactone (4Bb)

Oil. IR (neat): 2950, 1750, 1640, 1200 cm^{-1}. MS: m/e 217 (M^+(^{37}Cl) + 1)/215 (M^+(^{35}Cl) + 1), 199/197, 179, 171/169, 163/161, 158/156, 135, 130/128, 121. ^{1}H NMR ($CDCl_3$/200 MHz): 6.50, 6.45 (d, J = 2.60 Hz, 1H, CHCl–); 5.84–5.70 (m, 1H, CH=); 5.44–5.26 (m, 1H, CH=); 4.55–4.40 (m, 1H, OCH); 4.10, 3.80 (dt, J = 2.60 Hz, J = 8.60 Hz, 1H, CHC=); 2.12 (quintet, J = 8.0 Hz, 2H, CH_2C=); 1.80–1.50 (m, 2H, CH_2); 1.02 (t, J = 8.0 Hz, 6H, $2CH_3$) ppm. HRMS Found: 155.9940 (^{35}Cl), 158.0014(^{37}Cl). $C_7H_5ClO_2$ ($M^+ - 2Et$) calc.: 155.9978 (^{35}Cl), 157.9948 (^{37}Cl).

3.1.8. β-(2'-Butanonyl)-γ-ethyl-α-(Z)-chloromethylene-γ-butyrolactone (5b)

Oil. IR (neat): 2950, 1750, 1630, 1240, 1190 cm^{-1}. MS: m/e 233 (M^+(^{37}Cl) + 1)/231 (M^+(^{35}Cl) + 1), 215/213, 203/201, 195, 176/174, 160/158, 138, 137, 123, 58. ^{1}H NMR ($CDCl_3$/200 MHz): 6.71, 6.70 (d, J = 2.00 Hz, 1H, CHCl–); 4.30–4.00 (m, 1H, OCH); 3.55–3.24 (m, 1H, CH–C–CO); 2.78 (dd, J = 2.0 Hz, J = 8.0 Hz), 2.68 (d, J = 8.0 Hz) (2H, CH_2CO); 2.48 (q, J = 8.0 Hz, 2H, $COCH_2$); 1.82–1.60 (m, 2H, CH_2); 1.20–0.90 (m, 6H, $2CH_3$) ppm. HRMS: Found: 194.0934. $C_{11}H_{14}O_3$ ($M^+ - H - Cl$) calc.: 1.94.0943.

3.1.9. trans β-(1'Butenyl)-γ-ethyl-α-(Z)-bromomethylene-γ-butyrolactone (4Ab')

B.p. 160–162°C (bath temperature)/5 mmHg. IR (neat): 2950, 1770, 1630, 1180 cm^{-1}. MS: m/e 261 (M^+(^{81}Br) + 1)/259 (M^+(^{79}Br) + 1), 202/200, 179, 174/172. ^{1}H NMR ($CDCl_3$/200 MHz): 6.70, 6.64 (d, J = 2.60 Hz, 1H, CHBr=); 5.90–5.64 (m, 1H, CH=); 5.40–5.14 (m, 1H, CH=); 4.12–3.96 (m, 1H, OCH); 3.60, 3.22 (dt, J = 2.60 Hz, J = 8.0 Hz, 1H, CH–C=); 2.10 (quintet, J = 8.0 Hz, 2H, CH_2C=); 1.92–1.60 (m, 2H, CH_2); 1.12–0.98 (m, 6H, $2CH_3$) ppm. Anal. Found: C, 51.43; H, 5.99. $C_{11}H_{15}BrO_2$ calc.: C, 50.98; H, 5.83%.

3.1.10. cis-β-(1'-Butenyl)-γ-ethyl-α-(Z)-bromomethylene-γ-butyrolactone (4Bb')

Oil. IR (neat): 2950, 1750, 1640, 1180 cm^{-1}, MS: m/e 261 (M^+(^{81}Br) + 1)/259 (M^+(^{79}Br) + 1), 202/200, 179, 174/172, 107/105, 93, 91, 77. ^{1}H NMR ($CDCl_3$/200 MHz): 6.73, 6.71 (d, J = 2.5 Hz, 1H, CHBr=); 5.80–5.60 (m, 1H, CH=); 5.36–5.23 (m, 1H, CH=); 4.10, 3.70 (dt, 1H, J = 2.5 Hz, J = 8.40 Hz, 1H, CH–C=); 2.10 (quintet, J = 8.0 Hz, 2H, CH_2C=); 1.90–1.50 (m, 2H, CH_2); 1.00 (t, J = 8.0 Hz, 6H, $2CH_3$) ppm. HRMS: Found: 199.9818 (^{79}Br), 201.9818 (^{81}Br). C_8H_9BrO ($M^+ - CO - C_2H_6$) calc.: 199.9837 (^{79}Br), 201.9816 (^{81}Br).

3.1.11. β-(2'-Butanonyl)-γ-ethyl-α-(Z)-bromomethylene-γ-butyrolactone (5b')

Oil. IR (neat): 2950, 1760, 1705, 1630, 1180 cm^{-1}. MS: m/e 277 (M^+(^{81}Br) + 1)/275 (M^+(^{79}Br) + 1),

204/202, 195, 161/159, 139/137, 123, 109, 58. ^{1}H NMR ($CDCl_3$/200 MHz): 6.96, 6.94 (d, J = 1.6 Hz, 1H); 4.30–4.00 (m, 1H, OCH); 3.60–3.24 (m, 1H, CH–C–O); 2.80, 2.70 (d, J = 6.0 Hz, 2H, CH_2C=O); 2.50 (q, J = 6.70 Hz, 2H, O=C–CH_2); 1.72 (q, J = 6.70 Hz, 2H, O–C–CH_2); 1.20–0.90 (m, 6H, $2CH_3$) ppm. HRMS Found: 217.9950 (^{79}Br), 219.9900 (^{81}Br). $C_8H_{11}BrO_2$ calc.: 217.9943 (^{79}Br), 219.9922 (^{81}Br).

3.1.12. trans β-(3'-Methyl-1'-butenyl)-γ-isopropyl-α-(Z)-chloromethylene-γ-butyrolactone (4Ac)

B.p. 155–157°C (bath temperature)/2 mmHg. IR (neat): 2950, 1760, 1640, 1180 cm^{-1}. MS: *m/e* 245 (M^+(^{37}Cl) + 1)/243 (M^+(^{35}Cl) + 1), 207, 189/187, 172/170, 135, 129, 128, 107, 91, 43. ^{1}H NMR ($CDCl_3$/90 MHz): 6.42 (d, J = 2.60 Hz, 1H, CHCl=); 5.60 (dd, J = 6.4 Hz, J = 15.6 Hz, 1H, CH=); 5.20 (dd, J = 8.0 Hz, J = 15.6 Hz, CH=); 3.96 (dd, J = 2.0 Hz, J = 5.2, 1H, O–CH); 3.40 (dt, J = 2.60 Hz, J = 5.2 Hz, 1H, O–C–CH); 2.48–2.20 (m, 1H, CH–C=); 2.04–1.60 (m, 1H, CH); 1.00 (d, J = 6.0 Hz, 12H, $4CH_3$) ppm. HRMS: Found: 207.1368. $C_{13}H_{19}O_2$ (M^+ − Cl) calc.: 207.1385.

3.1.13. trans β-(3'-Methyl-2'-butanonyl)-γ-isopropyl-α-(Z)-chloromethylene-γ-butyrolactone (5c)

M.p. 54–56°C. IR (Nujol film): 2950, 1760, 1700, 1640, 1470, 1200, 1100 cm^{-1}. MS: *m/e* 261 (M^+(^{37}Cl) + 1/259 (M^+(^{35}Cl) + 1), 243/241, 175/173, 174/172, 71, 43. ^{1}H NMR ($CDCl_3$/90 MHz): 6.66 (d, J = 1.7 Hz, 1H, CHCl=); 3.90 (dd, J = 2.8 Hz, J = 5.7 Hz, 1H, O–CH); 3.52–3.28 (m, 1H, CH–C=); 2.80 (d, J = 7.5 Hz, 2H, CH_2–C=O); 2.76–2.40 (m, 1H, O=C–CH); 2.08–1.64 (m, 1H, CH); 1.20–0.90 (m, 12H, $4CH_3$) ppm. Anal. Found: C, 60.47; H, 7.38. $C_{13}H_{19}ClO_3$ calc.: C, 60.35; H, 7.40%.

3.1.14. trans β-(3'-Methyl-2'-butenyl)-γ-isopropyl-α-(Z)-bromomethylene-γ-butyrolactone (4Ac')

B.p. 160–162°C (bath temperature)/2 mmHg. IR (neat): 2950, 1750, 1630, 1150 cm^{-1}. MS: *m/e* 289 (M^+(^{81}Br) + 1)/287 (M^+(^{79}Br) + 1), 245/243, 233/231, 216/214, 207, 201/199, 189/187, 174/172, 135, 42. ^{1}H NMR ($CDCl_3$/200 MHz): 6.62 (d, J = 2.80 Hz, 1H, CHBr=); 5.58 (dd, J = 6.8 Hz, J = 15.2 Hz, 1H, CH=); 5.18 (ddd, J = 15.2 Hz, J = 8.4 Hz, J = 1.2 Hz, 1H, CH=); 3.88 (dd, J = 5.7 Hz, J = 7.5 Hz, 1H, O–CH); 3.28 (dt, J = 2.8 Hz, J = 7.5 Hz, 1H, O–C–CH); 2.40–2.20 (m, 1H, CH–C=); 2.00–1.80 (m, 1H, CH); 1.04–0.90 (m, 12H, $4CH_3$) ppm. HRMS: Found: 214.0010 (^{79}Br), 215.9983 (^{81}Br). $C_9H_{11}BrO$ calc.: 213.9993 (^{79}Br), 215.9973 (^{81}Br).

3.1.15. trans β-(3'-Methyl-2'-butanonyl)-γ-isopropyl-α-(Z)-bromomethylene-γ-butyrolactone (5c')

B.p. 170–172°C (bath temperature)/2 mmHg. IR (neat): 2950, 1760, 1710, 1630, 1170 cm^{-1}. MS: *m/e* 305 (M^+(^{81}Br) + 1)/303 (M^+(^{79}Br) + 1), 287/285, 261/259, 223, 218/216, 203/201, 137, 123, 43. ^{1}H NMR ($CDCl_3$/200 MHz): 6.93 (d, J = 1.60 Hz, 1H, CHBr=); 3.90 (dd, J = 2.90 Hz, J = 5.70 Hz, 1H, OCH); 3.50–3.30 (m, 1H, O–C–CH); 2.80 (d, J = 6.80 Hz, 2H, CH_2–C=O); 2.70–2.50 (m, 1H, O=C–CH); 2.00–1.80 (m, 1H, O–C–CH); 1.12 (dd, J = 2.2 Hz, J = 6.9 Hz, 6H, $2CH_3$); 0.96 (overlapped t, J = 6.70 Hz, 6H, $2CH_3$) ppm. Anal. Found: C, 52.09; H, 6.24. $C_{13}H_{19}BrO_3$ calc.: C, 51.50; H, 6.32%.

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