

Cationic palladium complex-catalyzed cyclocarbonylation of 3-butyn-1-ols

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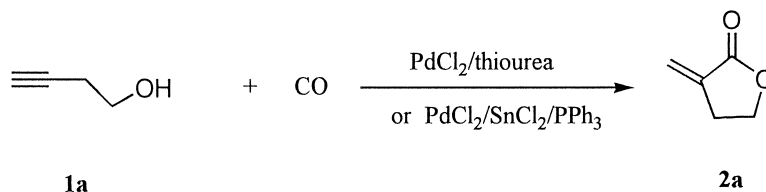
Abstract

Cyclocarbonylation of 3-butyn-1-ols catalyzed by cationic palladium complexes has been studied. Six-membered ring lactones were produced preferentially in acetonitrile using cationic complexes coordinated by certain chelating diphosphines as catalyst. A triphenylphosphine-coordinated cationic palladium complex, on the other hand, effected the formation of five-membered α -alkylidene lactones exclusively in *N,N*-dimethylformamide. A mechanism involving a palladium hydride as active species has been presumed for the formation of six-membered ring lactones. © 1998 Elsevier Science B.V.

Keywords: Cyclocarbonylation; 3-Butyn-1-ol; Palladium; Lactone

1. Introduction

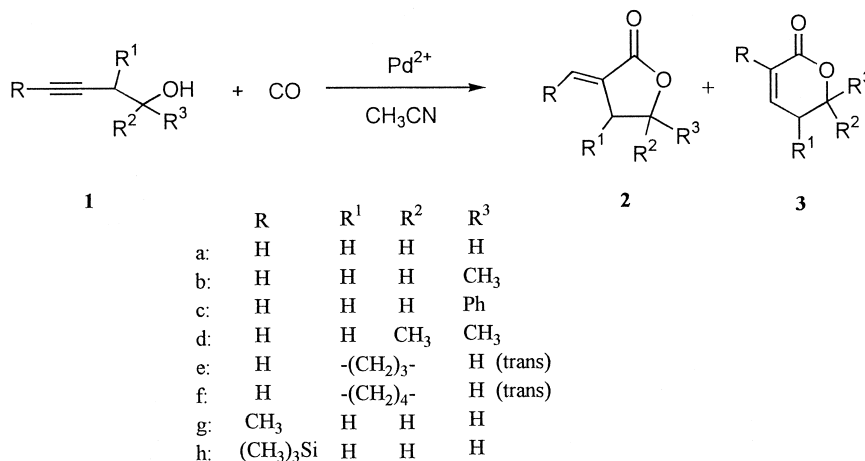
The palladium catalyzed hydroesterification of alkynes using carbon monoxide and alcohols has been the subject of many investigations [1,2]. This reaction normally gives α,β -unsaturated carboxylic esters. The cyclocarbonylation of 3-butyn-1-ols is the intramolecular version of this chemistry. The system composed of PdCl_2 -thiourea [3] or PdCl_2 - SnCl_2 - PPh_3 [4] was demonstrated to catalyze the cyclocarbonylation of 3-butyn-1-ol (**1a**) to afford a five-membered ring lactone, 2-methylenebutan-4-olide (**2a**) selectively.



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This type of reaction was shown to be also catalyzed by a platinum hydride complex [5]. Oxidative dicarbonylation of **1a** catalyzed by palladium(II) complexes was reported as well [6,7]. An α -silylmethylene lactone was obtained selectively with the aid of $\text{Rh}_4(\text{CO})_{12}$ in the carbonylation of a mixture of **1a**, triorganosilane, and triethylamine [8]. In these cases, the products obtained were generally five-membered alkylidene lactones.

During the studies directed toward the cyclocarbonylation of acetylenic alcohols [9], we found that certain palladium complexes promote the cyclocarbonylation of 3-butyn-1-ols **1** in acetonitrile to afford six-membered ring lactones **3** in preference to five-membered ring ones **2**. Straightforward synthesis of **3** is of considerable interest since the compound **3** represents an intermediate for the synthesis of verrucaric acid or α -pyrone [10].



2. Results and discussion

The effects of various reaction conditions on the cyclocarbonylation of 3-butyn-1-ol (**1a**) catalyzed by several cationic palladium complexes are given in Table 1. Treatment of **1a** with carbon monoxide in acetonitrile in the presence of a cationic complex, $[\text{Pd}(\text{dppb})(\text{PhCN})_2](\text{BF}_4)_2$ [dppb = 1,4-

Table 1
Cyclocarbonylation of 3-butyn-1-ol (**1a**)^a

Entry	Catalyst	Solvent (ml)	Yield (%)	2a:3a
1	$[\text{Pd}(\text{dppb})(\text{PhCN})_2](\text{BF}_4)_2$	CH ₃ CN(2)	36	17:83
2 ^b	$[\text{Pd}(\text{dppb})(\text{PhCN})_2](\text{BF}_4)_2$	CH ₃ CN(8)	77	26:74
3	$[\text{Pd}(\text{dppb})(\text{PhCN})_2](\text{BF}_4)_2$	DMF(2)	40	88:12
4	$\text{PdCl}_2(\text{dppb})$	CH ₃ CN(2)	0	—
5	$[\text{Pd}(\text{dppf})(\text{PhCN})_2](\text{BF}_4)_2$	CH ₃ CN(2)	35	16:84
6	$[\text{Pd}(\text{dppp})(\text{PhCN})_2](\text{BF}_4)_2$	CH ₃ CN(2)	24	29:71
7	$[\text{Pd}(\text{dppe})(\text{PhCN})_2](\text{BF}_4)_2$	CH ₃ CN(2)	3	—
8	$[\text{Pd}(\text{PPh}_3)_2(\text{PhCN})_2](\text{BF}_4)_2$	CH ₃ CN(2)	44	73:27
9	$[\text{Pd}(\text{PPh}_3)_2(\text{PhCN})_2](\text{BF}_4)_2$	DMF(2)	48	100:0
10	$\text{PdCl}_2(\text{PPh}_3)_2$	CH ₃ CN(2)	60	96:4

^a2 mmol **1a**; 10 atm CO; 0.04 mmol catalyst; 80°C; 3 h.

^b100°C; 20 atm CO.

bis(diphenylphosphino)butane], for 3 h at 10 atm pressure and 80°C, afforded **2a** and 2-penten-5-olide (**3a**) with a ratio of 17:83 in a combined yield of 36% (entry 1). The yield increased to 77% with 74% selectivity to **3a** when the reaction was effected at an elevated temperature of 100°C under 20 atm pressure (entry 2). The reaction in *N,N*-dimethylformamide (DMF) gave the five-membered methylene lactone **2a** as the main product (entry 3). A neutral complex PdCl₂(dppb) did not exhibit the catalytic activity in acetonitrile leaving the starting material **1a** intact (entry 4). Cationic palladium complexes coordinated by bidentate diphosphines such as 1,1'-bis(diphenylphosphino)ferrocene (dppf) and 1,3-bis(diphenylphosphino)propane (dppp) were also effective for six-membered ring lactone formation (entry 5, 6). The cationic complex coordinated by 1,2-bis(diphenylphosphino)ethane, [Pd(dppe)(PhCN)₂](BF₄)₂, was almost ineffective for this carbonylation process (entry 7). On the other hand, the reaction using a triphenylphosphine-coordinated complex, [Pd(PPh₃)₂(PhCN)₂](BF₄)₂, afforded **2a** as the main product in acetonitrile (entry 8). The complete selectivity to **2a** was observed with this complex, when the reaction was performed in DMF (entry 9). A neutral complex PdCl₂(PPh₃)₂ was active enough in acetonitrile to afford **2a** and **3a** with a ratio of 96:4 in a combined yield of 60%.

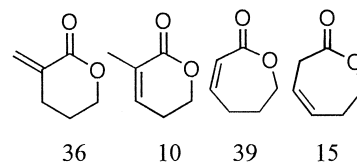
These preliminary findings indicate that the selectivity between the five- (**2a**) and six-membered ring lactone (**3a**) depends on phosphine ligand, solvent, and the electronic nature of the palladium catalyst. The suitable conditions for the formation of **3a** appear to be the combined employment of a bulky chelating diphosphine such as dppb or dppf as ligand, acetonitrile as solvent, and a cationic complex as catalyst precursor.

The lactonization process in acetonitrile employing [Pd(dppb)(PhCN)₂](BF₄)₂ is applicable to a variety of 3-butyne-1-ols **1** containing alkyl and aryl groups attached to the hydroxy-bearing carbon, yielding the corresponding six-membered ring lactones **3** preferentially as shown in Table 2 (entry 1–4). *Trans*-3-butyne-1-ols having five- (**1e**) and six- (**1f**) membered ring structure gave fused-ring lactones of the corresponding stereochemistry (entry 5, 6). The declined yield of 10% in entry 5 was ascribed to the occurrence of intermolecular reactions giving rise to higher boiling products.

The course of cyclocarbonylation of **1** with the internal C–C triple bond depended on the substituent R on the triple bond decidedly. Nearly equal amounts of five- and six-membered ring lactones were formed in a modest yield of 30% when the substituent R is methyl group (entry 7). The

Table 2
Cyclocarbonylation of 3-butyne-1-ols **1** in CH₃CN^a

Entry	1	Time (h)	Yield (%)	2:3	
1	1a	3	77	2a3a	26:74
2	1b	3	65	2b3b	34:66
3	1c	10	73	2c3c	25:75
4	1d	10	61	2d3d	36:64
5	1e	10	10	2e3e	14:86
6	1f	10	63	2f3f	22:78
7	1g	10	30	2g3g	53:47
8	1h	30	62	2h3h	100:0
9	4-pentyne-1-ol	10	11		



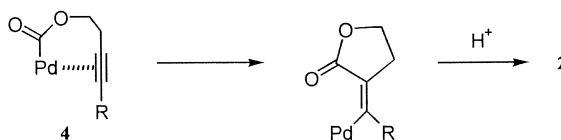
^a 2 mmol substrate; 20 atm CO; 0.04 mmol [Pd(dppb)(PhCN)₂](BF₄)₂; 8 ml CH₃CN; 100°C.

E stereochemistry in **2g** was determined by comparison of the $^1\text{H-NMR}$ data with the reported one [11]. Specifically, five-membered alkylidene lactone **2h** was generated exclusively from **1h** bearing a trimethylsilyl (TMS) substituent (entry 8). Cyclocarbonylation of a longer carbon chain substrate, 4-pentyn-1-ol, gave a mixture of six- and seven-membered ring lactones in a modest yield (entry 9).

In order to obtain further scope, cyclocarbonylation of **1** catalyzed by $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ was studied in DMF. The results are given in Table 3. The reactions of **1a–f** with carbon monoxide took place with good selectivity to give five-membered methylene lactones **2a–f** in moderate yields (entry 1–6). Although the yield of 38% for significantly strained fused lactone **2e** is unsatisfactory (entry 5), it is still an improved value compared to the reported one [4], indicating the usefulness of the present procedure.

It is reported that cyclocarbonylation of methyl-substituted 3-butyn-1-ol **1g** with the internal triple bond is unsuccessful [4]. Our reaction with **1g** proceeded sluggishly to give the ethylidene lactone **2g** in a reduced yield of 11% (entry 7). On the other hand, trimethylsilyl-substituted butynol **1h** exhibited fair reactivity giving rise to five-membered ring lactone **2h** selectively in 61% yield (entry 8). 4-Pentyn-1-ol was converted selectively to six-membered 2-methylenepentan-5-olide although the yield was declined (entry 9).

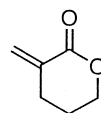
The mechanism for the synthesis of methylene lactone **2** catalyzed by PdCl_2 /monodentate phosphine was studied carefully [12,13]. It involves the initial formation of a carboalkoxy species **4** from PdCl_2 , carbon monoxide, and the substrate alcohol **1**, followed by intramolecular *cis* addition to the triple bond. Cleavage of the resulting vinyl–palladium bond by the proton generated initially eliminates the product **2** and regenerates the initial palladium(II) species.



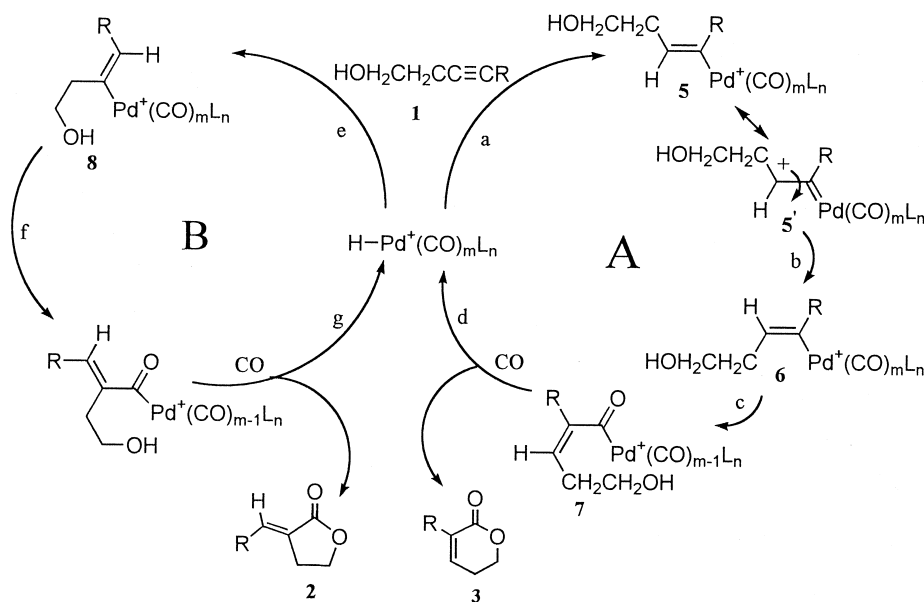
In our cationic palladium(II)-catalyzed reaction, the reaction in DMF is **2**-selective while the reaction in acetonitrile is controlled by both the phosphine ligand employed and the substituent on the

Table 3
Cyclocarbonylation of 3-butyn-1-ols **1** in DMF^a

Entry	1	Time (h)	Yield (%)	2:3
1	1a	3	49	2a3a 100:0
2	1b	10	66	2b3b 96:4
3	1c	20	50	2c3c 100:0
4	1d	20	45	2d3d 99:1
5	1e	10	38	2e3e 100:0
6	1f	10	53	2f3f 81:19
7	1g	10	11	2g3g 100:0
8	1h	30	61	2h3h 100:0
9	4-pentyn-1-ol	10	28	



^a 2 mmol substrate; 20 atm CO; 0.04 mmol $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$; 2 ml DMF; 80°C.



Scheme 1.

triple bond in **1**. The results obtained in DMF could be explained in terms of the carboalkoxy mechanism mentioned above. However this mechanism cannot explain the formation of six-membered ring lactone **3** in acetonitrile. Because the formation of **3** requires opposite direction of addition to the triple bond which proceeds in a *cis* fashion and would result in the formation of a highly strained lactone containing a *trans* double bond [12]. Consequently the mechanism must be different. An alternative mechanism involving a metal hydride may be proposed to explain the results obtained in acetonitrile as illustrated in Scheme 1.

This mechanism begins with *cis* addition of a palladium hydride to the acetylenic bond in **1**¹. Obviously, the regiochemistry of addition reaction should be influenced by the steric and electronic nature of the substrate **1** and the complex. In the present reaction, however, this process appears to be controlled decidedly by steric factors. Thus, in the case where the ligand is a bulky chelating diphosphine and the substituent R in **1** is H, palladium would preferentially combine with the less hindered terminal position remote from the methylene group to give **5** (cycle A; step a). The existence of intermediate **5** was confirmed by trapping it with CO and methanol. Thus, the reaction of **1a** with carbon monoxide in methanol at 100°C in the presence of [Pd(dppb)(PhCN)₂](BF₄)₂ afforded methyl *trans*-5-hydroxy-2-pentenoate regio- and stereoselectively as the major product in addition to **2a** and **3a**. Then, *trans*-*cis* isomerization of the double bond in the alkenylpalladium species **5** would take place via a route involving a possible carbocation species **5'** (step b). Carbonylation (step c) followed by intramolecular alcoholysis (step d) affords the six-membered ring lactone **3** and regenerates the metal hydride. A metal hydride is known to be a double-bond isomerization catalyst. The occurrence of the double bond-isomerized products in the reaction of 4-pentyn-1-ol also suggests the presence of such a species (Table 2, entry 9). When the substituent R is a bulky trimethylsilyl group, on the other hand, palladium would combine exclusively with the internal carbon of the triple bond to minimize

¹ Several *trans* addition reactions were also reported [14].

steric interaction affording **8** (cycle B; step e). Carbonylation (step f) followed by intramolecular alcoholysis (step g) affords the five-membered alkylidene lactone **2** of E stereochemistry. In the case where the substituent R is methyl group, which is not so bulky, both the cycles A and B may be operative to give **2** and **3** in a comparable yield. In the case where the ligand L is monodentate triphenylphosphine, the steric repulsion may be relieved to some extent because the triple bond may displace a phosphine ligand prior to insertion. Consequently, the selectivity to **3** will be declined in the reaction using monodentate phosphine as ligand compared to that using a bulky chelating diphosphine as ligand.

The observation that cationic $[\text{Pd}(\text{dppb})(\text{PhCN})_2](\text{BF}_4)_2$ is active for the cyclocarbonylation of **1a** while neutral $\text{PdCl}_2(\text{dppb})$ is inactive, suggests that the ready availability of two coordination sites [15] is crucial to this reaction. Another key to the formation of **3** may be the ability of dppb to coordinate to palladium through one or both phosphine atoms depending on the circumstances [16,17] inferring the result that $[\text{Pd}(\text{dppb})(\text{PhCN})_2](\text{BF}_4)_2$ is effective whereas $[\text{Pd}(\text{dpe})(\text{PhCN})_2](\text{BF}_4)_2$ is almost ineffective for this cyclocarbonylation process.

3. Experimental

3.1. Materials

Diphosphines, i.e., dppe, dppp, dppb, and dppf, were obtained commercially. The cationic palladium complexes were prepared according to the reported procedure [18]. Acetylenic alcohols were purchased (**1a**, **1b**, **1g**, 4-pentyn-1-ol) or prepared (**1c**, **1d**, **1e**, **1f**, **1h**) according to the literature method [19,20].

3.2. General methods

^1H - and ^{13}C -NMR spectra were recorded in CDCl_3 solution at 400 and 100 MHz, respectively, with Me_4Si as internal standard. IR spectra were run on a FT/IR 350 spectrometer. GLC analyses were performed with 3 mm \times 3 m columns packed with PEG-20M, 5%. Preparative GLCs were done with 6 mm \times 3 m columns packed with PEG-20M, 5%. Column chromatography was carried out on silica gel using hexane/ethyl acetate as eluent.

3.3. General procedure for the cyclocarbonylation of 3-butyn-1-ols **1**

3.3.1. Procedure for reactions of Table 2

Into a 50 ml stainless-steel autoclave were added 0.04 mmol of $[\text{Pd}(\text{dppb})(\text{PhCN})_2](\text{BF}_4)_2$, 8 ml of CH_3CN , and 2 mmol of **1** under nitrogen atmosphere. The reaction vessel was then pressurized with 20 atm of carbon monoxide. The reaction was allowed to proceed at 100°C. After the reaction, the resulting solution was taken up in diethyl ether and passed through a short florisil[®] column to remove palladium complexes. The products were isolated by either column chromatography (**2a**, **3a**, **2b**, **3b**, **2c**, **3c**, **2d**, **3d**, **2e**, **3e**, **2g**, **3g**, the products from 4-pentyn-1-ol) or Kugelrohr distillation (**2f**, **3f**, **3h**). Analytical samples were obtained by preparative GLC. Quantitative analyses by GLC were performed if necessary (**2a**, **3a**, **2b**, **3b**, **2f**, **3f**, **2g**, **3g**, products from 4-pentyn-1-ol).

3.3.2. Procedure for reactions of Table 3

In the same manner as above, 0.04 mmol of $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$, 2 ml of DMF, and 2 mmol of **1** were agitated under the pressure of 20 atm of carbon monoxide at 80°C. The products were isolated by column chromatography (**2a**, **2b**, **2c**, **2e**, **2f**, **3f**, **2g**, **2h**, 2-methylenepentan-5-olide) or by Kugelrohr distillation (**2d**). Quantitative analyses by GLC were performed if necessary (**2f**, **3f**, products from 4-pentyn-1-ol).

3.3.3. Lactones

The following lactones are known compounds and have spectral data in accord with the reported ones: **2a**, **2b**, **2c**, **2d**, **2e** [4], **2f** [21], **2g** [11], **2h** [22], **3a**, **3b**, **3d**, **3e** [23], **3g**, 2-methylenepentan-5-olide, 2-hexen-6-olide [24].

5-Phenyl-2-penten-5-olide (**3c**): Mp 47–48°C. IR(neat), 1723, 1246, 1022 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3), δ 7.42–7.34 (5H, m), 6.97 (1H, ddd, $J = 9.7, 3.1, 5.4$ Hz), 6.13 (1H, ddd, $J = 9.7, 1.1, 2.4$ Hz), 5.44 (1H, dd, $J = 10.7, 5.3$ Hz), 2.70–2.57 (2H, m). $^{13}\text{C-NMR}$ (CDCl_3), δ 164.1, 145.0, 138.4, 128.7, 128.6, 126.0, 121.6, 79.2, 31.6. MS (70 eV), m/z 68, 174 (M^+). Calcd. for $\text{C}_{11}\text{H}_{10}\text{O}_2$: C: 75.83, H: 5.70. Found: C: 75.66, H: 5.85.

2-Oxabicyclo[4.4.0]-4-decen-3-one (**3f**): Mp 41–44°C. IR(neat), 1730, 1700, 1250, 1040 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3), δ 6.67 (1H, d, $J = 9.4$ Hz), 5.96 (1H, d, $J = 9.4$ Hz), 3.98 (1H, dt, $J = 4.0, 11.2$ Hz), 2.33–1.20 (9H, m). $^{13}\text{C-NMR}$ (CDCl_3), δ 164.6, 150.9, 120.9, 82.0, 39.6, 31.2, 28.9, 25.3, 23.9. MS (70 eV), m/z 67, 81, 152 (M^+). Calcd. for $\text{C}_9\text{H}_{12}\text{O}_2$: C: 71.03, H: 7.95. Found: C: 70.86, H: 7.96.

(*E*)-2-(Trimethylsilylmethylene)butan-4-olide (**2h**): IR(neat), 1758, 1636, 1251, 1174, 1020, 841 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3), δ 6.94 (1H, t, $J = 2.8$ Hz), 4.38 (2H, t, $J = 7.3$ Hz), 2.97 (2H, dt, $J = 2.8, 7.3$ Hz), 0.19 (9H, s). $^{13}\text{C-NMR}$ (CDCl_3), δ 170.5, 139.5, 138.9, 65.0, 27.3, –1.4. MS (70 eV), m/z 83, 155, 170 (M^+). Calcd. for $\text{C}_8\text{H}_{14}\text{O}_2\text{Si}$: C: 56.41, H: 8.30. Found: C: 56.23, H: 8.14.

3-Hexen-6-olide: IR(neat), 1730, 1660, 1150, 1060 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3), δ 5.74 (1H, dtt, $J = 11.3, 3.5, 1.7$ Hz), 5.56 (1H, dtt, $J = 11.3, 1.8, 5.5$ Hz), 4.44 (2H, t, $J = 5.4$), 3.40 (2H, ddt, $J = 1.5, 5.5, 1.7$ Hz), 2.58–2.46 (2H, m). MS (70 eV), m/z 39, 54, 67, 112 (M^+).

3.3.4. Carbonylation of **1a** in methanol

A mixture of 2 mmol of **1a** and 0.04 mmol of $[\text{Pd}(\text{dppb})(\text{PhCN})_2](\text{BF}_4)_2$ was dissolved in 8 ml of methanol and placed in a 50 ml autoclave. The autoclave was pressurized with 20 atm of carbon monoxide and heated for 3 h at 100°C. The reaction mixture was then cooled to room temperature and filtered through a short florisil[®] column. Column chromatography on silica gel eluting with hexane/ethyl acetate gave methyl *trans*-5-hydroxy-2-pentenoate in 44% yield together with **2a** and **3a** as minor products.

Methyl *trans*-5-hydroxy-2-pentenoate: IR(neat), 3442, 1724, 1660, 1283, 1210, 1047, 977 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3), δ 6.98 (1H, dt, $J = 15.1, 6.3$), 5.93 (1H, dt, $J = 15.1, 1.4$ Hz), 3.77 (2H, t, $J = 6.3$ Hz), 3.73 (3H, s), 2.45–2.50 (2H, m), 2.22 (1H, br). $^{13}\text{C-NMR}$ (CDCl_3), δ 166.9, 145.8, 123.0, 60.9, 51.6, 35.3. MS (70 eV), m/z 41, 69, 100.

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