Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Organometallic Chemistry 691 (2006) 3151–3156
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Cyclodehydration of *cis*–2-butene-1,4-diol with active methylene compounds catalyzed by a diphosphinidenecyclobutene-coordinated palladium complex

Hiromi Murakami [a], Yukio Matsui [a], Fumiyuki Ozawa [a,*], Masaaki Yoshifuji [b,1]

[a] *International Research Center for Elements Science (IRCELS), Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*
[b] *Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan*

Received 29 December 2005; received in revised form 3 March 2006; accepted 4 March 2006
Available online 14 March 2006

Abstract

(π-Allyl)palladium triflate coordinated with 1,2-bis(4-methoxyphenyl)-3,4-bis(2,4,6-tri-*t*-butylphenylphosphinidene)cyclobutene (DPCB–OMe), [Pd(η^3-C_3H_5)(DPCB–OMe)]OTf, efficiently catalyzes cyclodehydration of *cis*–2-butene-1,4-diol with active methylene compounds such as acetylacetone and ethyl acetoacetate in toluene in the presence of pyridine. The reactions can be performed in air, giving 2-vinyl-2,3-dihydrofurans in good to high yields.

Keywords: Palladium catalyst; Low-coordinated phosphorus ligand; Cyclodehydration

1. Introduction

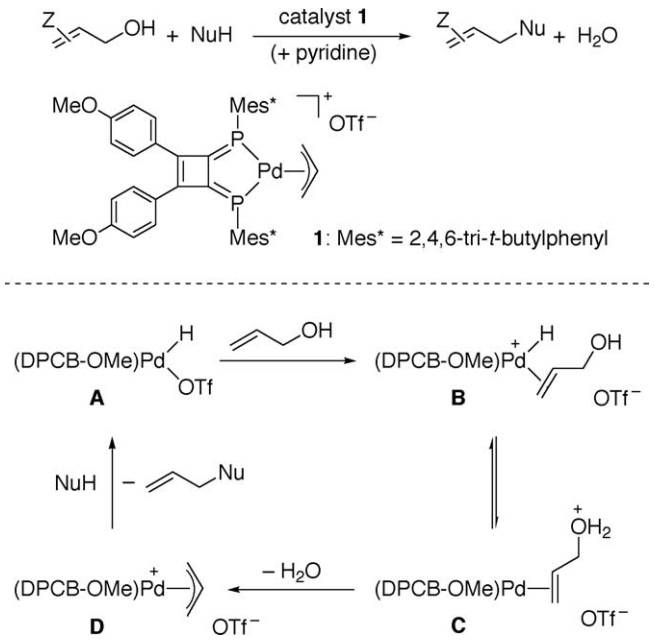
The palladium-catalyzed allylation is a useful synthetic means of constructing C–C, C–N, and C–O bonds [1]. While the reaction is generally conducted with allylic esters derived from allylic alcohols as allylation agents, there has been continuous research interest in developing the catalysts that enable direct conversion of allylic alcohols into allylation products. Thus, such reactions form water as the only co-product, possibly serving as an environmentally benign process with high atom efficiency [2]. However, due to the poor leaving ability of the OH group, most of the catalysts so far examined could be applied only to rather simple allylic alcohols [3], most of the catalytic reactions have been accomplished with the aid of in situ activation of the OH group using stoichiometric amounts of additives such as Lewis acids [4].

We recently found that π-allyl complex **1** bearing 1,2-bis(4-methoxyphenyl)-3,4-bis(2,4,6-tri-*t*-butylphenylphosphinidene)cyclobutene (DPCB–OMe) efficiently catalyzes direct conversion of allylic alcohols into N- and C-allylation products in the absence of Lewis acids (Scheme 1) [5a]. Several lines of evidences have suggested a novel C–O bond cleavage process of allylic alcohols promoted by an acidic hydride species **A** [5b]. Coordination of allyl alcohol to **A**, followed by proton-transfer from Pd to the OH group in **B**, forms **C** bearing an allyloxonium ligand. Elimination of water from **C** gives a π-allyl complex **D**, which subsequently undergoes external attack of nucleophiles to afford the allylation products, along with regeneration of **A**. We reasoned that the strong π-accepting ability of the DPCB–OMe ligand as a low-coordinated phosphorus compound [6] effectively stabilizes **C** as a Pd(0) species by π bonding to facilitate the proton-transfer in **B**.

We herein describe application of this novel catalysis to the synthesis of 2-vinyl-2,3-dihydrofurans, starting from *cis*–2-butene-1,4-diol and active methylene compounds. Catalytic conversion of *cis*–2-butene-1,4-diol and its esters has been extensively studied as a cheap and short-step

* Corresponding author. Tel.: +81 774 76 3035; fax: +81 774 76 3039.
E-mail address: ozawa@scl.kyoto-u.ac.jp (F. Ozawa).
[1] Present address: Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487-0336, USA.

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.03.011



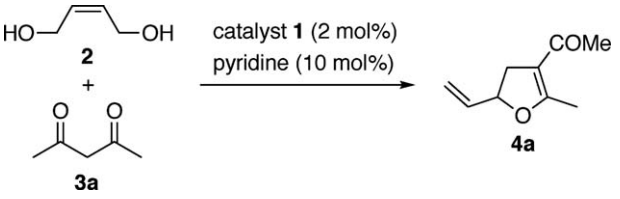
Scheme 1. Palladium-catalyzed allylation using DPCB–OMe ligand.

approach to N- and O-heterocyclic compounds such as vinylquinoxalines [7], vinylbenzoxazines [8], vinylpiperadines [9], vinylmorpholines [9,10], vinylbenzodioxanes [11], vinyloxazolidones [12], vinylpyrroles [13], and vinyldihydofurans [14]. Although the reactions of diol are generally carried out with in situ activation of the OH groups by Lewis acids, the present catalyst **1** successfully promotes the cyclodehydration of *cis*–2-butene-1,4-diol with active methylene compounds in the absence of such activators. Since the catalyst is fairly stable toward air and water, all manipulations can be conducted in air without special care to environmental conditions for the reactions.

2. Results and discussion

2.1. Cyclodehydration of cis–2-butene-1,4-diol with acetylacetone

First, of all, reaction conditions were optimized for acetylacetone (**3a**) as an active methylene compound (Eq. (1) and Table 1). A 1:1 mixture of *cis*–2-butene-1,4-diol (**2**) and **3a** was heated at 100 °C in toluene in the presence of catalytic amounts of **1** (2 mol%) and pyridine (10 mol%) (entry 1); pyridine was added to generate an enolate from **3a**. Compound **2** was consumed in 8 h, and 2-vinyl-4-acetyl-5-methyl-2,3-dihydrofuran (**4a**) was formed in 55% yield as confirmed by GLC using anisole as an internal standard. The yield of **4a** was improved to 92% when 2 molar quantity of **3a** was employed (entry 2), while further increase of **3a** caused a drop in the product yield (entry 3). The yield of **4a** was sensitive to the concentration of substrates as well (entries 4 and 5). Especially, decomposition of the catalyst took place in a dilute solution, where the reaction was not completed in 20 h (entry 5). The catalytic reaction proceeded smoothly in toluene and THF, but was clearly slower in DMSO, DMF, and 1,4-dioxane (entries 6–9). A similar solvent effect has been observed for the catalytic allylation of aniline with allylic alcohols [5a].



(1)

Fig. 1 shows time-course of the reaction of entry 2 in Table 1. Initially, **2** and **3a** were combined into 3-(4-hydroxy-2-butenyl)-2,4-pentanedione (**5**) as a C-allylation product. The amount of **5** reached the maximum after 1 h, and then gradually decreased with the formation of **4a**. The resulting **4a** was still reactive in the reaction system to be converted to an oligomeric compound ($M_n = 600$) upon prolonged heating. The degradation of **4a** was completely suppressed by addition of Et_3N to the system causing decomposition of the catalyst. As seen from Fig. 1, the decrease of **3a** almost stopped as **2** disappeared. Thus, although the yield of **4a** was notably improved by using 2 molar quantity of **3a** against **2** (entry 2, Table 1), a half of **3a** remained unreacted in the reaction solution.

The necessity of excess **3a** was found to be due to the occurrence of a competitive reaction leading to dehydration condensation of **2**. Thus, treatment of **2** with catalytic amounts of **1** and pyridine in toluene under heating pro-

Table 1
Cyclodehydration of *cis*–2-butene-1,4-diol (**2**) with acetylacetone (**3a**) catalyzed by **1** and pyridine[a]

Entry	Initial concentration (M)		Solvent	Time (h)	Yield of **4a** (%)
	2	**3a**			
1	0.5	0.5	Toluene	8	55
2	0.5	1.0	Toluene	4.5	92
3	0.5	5.0	Toluene	3	74
4	1.0	2.0	Toluene	3	42
5	0.1	0.2	Toluene	20	29
6	0.5	1.0	THF	4.5	73
7	0.5	1.0	DMSO	10	65
8	0.5	1.0	DMF	8.5	55
9	0.5	1.0	Dioxane	9.5	32

[a] All reactions were carried out at 100 °C using 2 mol% of **1** and 10 mol% of pyridine, except for entry 6, which was performed under reflux condition.

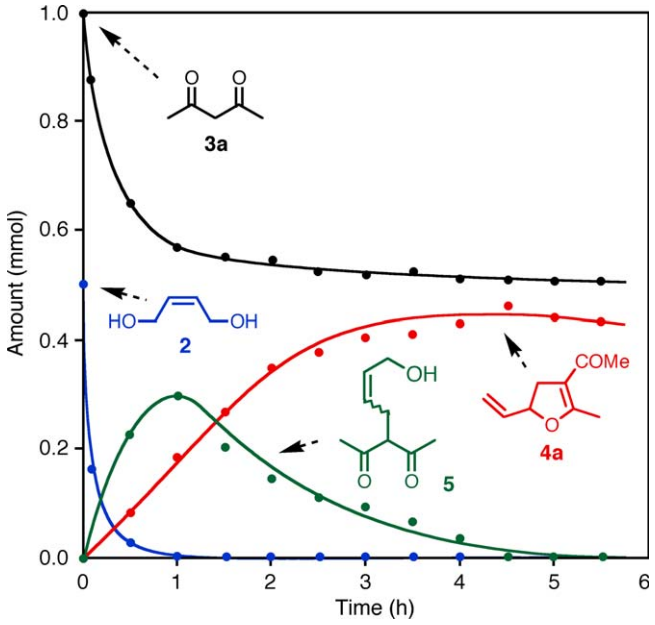
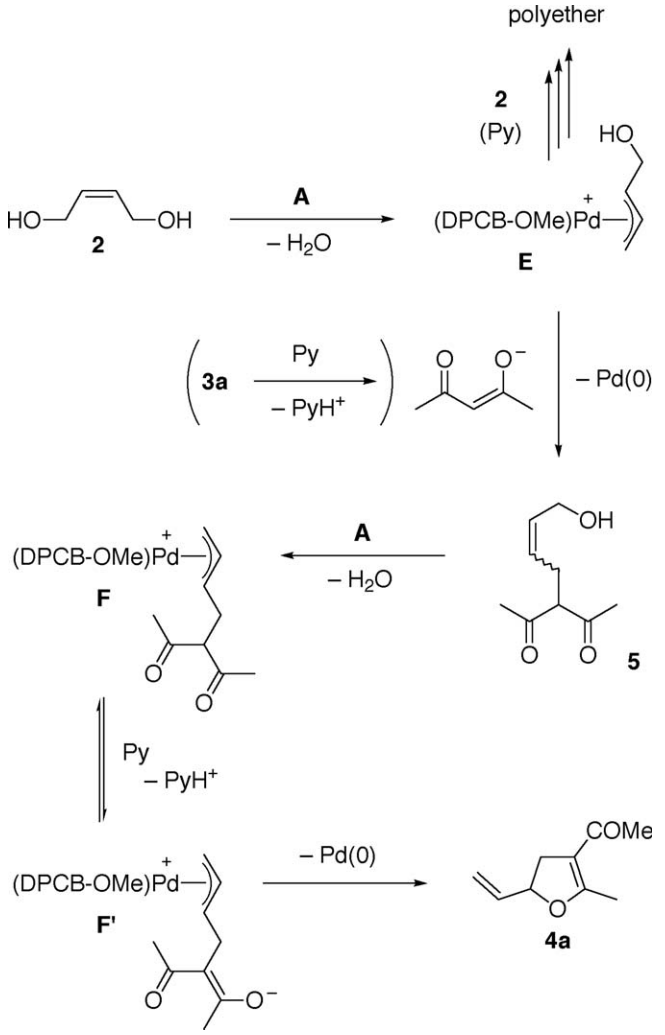


Fig. 1. Time-course of the reaction of entry 2 in Table 1.

vided a sticky material. Although this product showed complicated ^{1}H NMR signals and could not be identified, it was considered to be a polyether derived from **2**, because allyl alcohol was rapidly dimerized to diallyl ether in the same catalytic system. It was also confirmed that isolated **5** is converted exclusively to **4a** by the treatment with **1** (2 mol%) and pyridine (10 mol%) in toluene at 100 °C for 1 h.

These observations suggest the catalytic processes depicted in Scheme 2. First, one of the C–O bond of **2** is cleaved by the hydridopalladium species **A** to give π-allyl complex **E**, which reacts either with the enolate of **3a** or the alkoxide of **2**. Thus, the nucleophilic attack of the enolate affords the *C*-allylation product **5**, whereas the reaction with the alkoxide causes dehydration condensation of **2**. Compound **5** thus formed again reacts with **A** to give another π-allyl complex **F**, which undergoes intramolecular *O*-allylation with the aid of the pyridine base to give the final product **4a**.

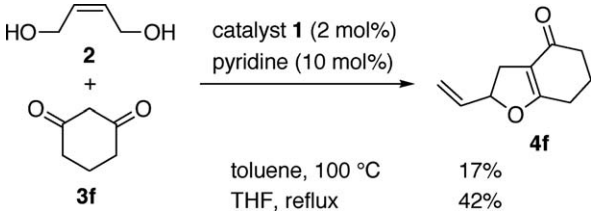


Scheme 2. Reaction processes for formation of **4a**.

2.2. Scope and limitation of the cyclodehydration

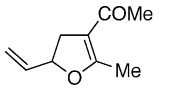
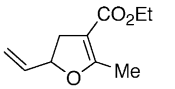
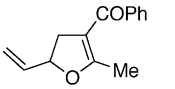
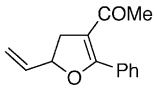
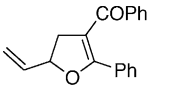
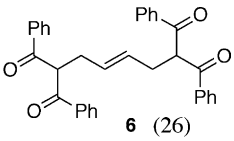
Next, several active methylene compounds were subjected to cyclodehydration with **2** under optimized conditions. Table 2 summarizes the results including that for acetylacetone (**3a**) (entry 1). The reaction with ethyl acetoacetate (**3b**) was completed in 6 h to give **4b** in 80% yield (entry 2). The reaction with benzoylacetone (**3c**) provided two isomers of vinyl dihydrofuran (**4ca** and **4cb**) in 52% and 26% yields, respectively (entry 3). The major product **4ca** is formed by O-allylation with the methyl-substituted enolate, whereas the minor isomer **4cb** is afforded by nucleophilic attack of the phenyl-substituted enolate; the product selectivity reflects the bulkiness of the enolates. Dibenzoylmethane (**3d**) successfully reacted with **2** to give vinyldihydrofuran **4d** in 51% yield, while the reaction also formed a considerable amount of acyclic compound **6** (entry 4). Diethyl malonate (**3e**) with the least acidity was unreactive (entry 5).

As another entry, the reaction with 1,3-cyclohexanedione (**3f**) was examined (Eq. (2)). Because **3f** was sparingly soluble in toluene, the yield of the desired compound **4f** was low (17%) in this solvent, but improved to 42% in reflux THF. Similar attempts using 1,3-cyclopentadione, 1,3-indandione, 5,5-dimethyl-1,3-cyclohexanedione, and 2,2-dimethyl-1,3-dioxane-4,6-dione were unsuccessful due to hardly soluble nature of these active methylene compounds.



(2)

Table 2
Cyclodehydration of *cis*–2-butene-1,4-diol (**2**) with active methylene compounds (**3a**–**e**) catalyzed by **1** and pyridine[a]

Entry	$R^1COCH_2COR^2$			Time (h)	Products and yields (%)[b]
	R^1	R^2			
1	Me	Me	(**3a**)	4.5	 **4a** 92 (91)
2	Me	OEt	(**3b**)	6	 **4b** 80 (74)
3	Me	Ph	(**3c**)	3	 **4ca** 52 (50)  **4cb** 26 (25)
4	Ph	Ph	(**3d**)	2.5	 **4d** 51 (47)  **6** (26)
5	OEt	OEt	(**3e**)	25	No reaction

[a] All reactions were carried out in toluene at 100 °C using **2** (0.5 mmol), **3** (1.0 mmol), **1** (2 mol%) and pyridine (10 mol%).
[b] The values in parentheses are isolated yields after silica gel column chromatography.

3. Experimental

3.1. General considerations

All manipulations were carried out in air unless otherwise noted. NMR spectra were recorded on a Varian Mercury 300 spectrometer (300.08 MHz for ^1H and 75.46 MHz for ^{13}C). Chemical shifts are reported in δ (ppm), referred to the signals of $CDCl_3$ (δ 7.26 for ^1H and δ 77.0 for ^{13}C). GLC analysis was performed on a Shimadzu GC-8A instrument (PEG-20 M, 5 mm$\phi \times$ 1 m). IR spectra were recorded on a JASCO FT/IR-410 spectrometer. HRMS was obtained using a JEOL JMS-700 spectrometer. The catalyst Pd(η^3-C_3H_5)(DPCB–OMe) (**1**) was prepared as previously reported [5b]. All other chemicals were obtained from commercial suppliers and used without purification.

3.2. Synthesis of 3-(4-hydroxy-2-butenyl)-2,4-pentadione (5) [14c]

To a 20 mL Schlenk tube were successively added $Pd(PPh_3)_4$ (92 mg, 0.080 mmol), ethyl 4-hydroxy-2-butyl carbonate (640 mg, 4.00 mmol), THF (4 mL), and acetylacetone (800 mg, 7.99 mmol) under a nitrogen atmosphere, and the mixture was stirred at 30 °C for 0.5 h. The reaction solution was diluted with Et_2O, extracted with an aqueous NaOH solution (1 N), washed with brine, and dried over $MgSO_4$. Silica gel column chromatography purification (hexane:AcOEt = 2:1, 1:1, and then 1:2) gave **5** as colorless oil in 51% yield. ^1H NMR ($CDCl_3$, 20 °C): [*cis*, keto form] δ 2.17 (s, 6H), 2.19 (s, 1H), 2.58 (dddt, J = 7.2, 5.4, 1.2 and 1.2 Hz, 2H), 3.68 (t, J = 7.2 Hz, 1H), 4.07 (ddt, J = 5.4, 1.2 and 1.2 Hz, 2H), 5.51–5.75 (m, 2H); [*cis*, enol form] δ 2.03 (s, 1H), 2.10 (s, 6H), 2.12 (s, 1H), 2.98 (ddt, J = 5.0, 1.2 and 1.2 Hz, 2H), 4.13 (ddt, J = 5.0, 1.2 and 1.2 Hz, 2H), 5.51–5.75 (m, 2H); [*trans*, keto form] δ 2.19 (s, 6H), 2.19 (s, 1H), 2.61 (ddd, J = 7.2, 6.9 and 1.2 Hz, 2H), 3.72 (t, J = 7.2 Hz, 1H), 4.20 (dd, J = 6.9 and 1.2 Hz, 2H), 5.51–5.75 (m, 2H); [*trans*, enol form] δ 2.03 (s, 1H), 2.10 (s, 6H), 2.11 (s, 1H), 3.11 (ddt, J = 6.6, 1.2 and 0.9 Hz, 2H), 4.28 (ddt, J = 6.9, 1.2 and 0.9 Hz, 2H), 5.51–5.75 (m, 2H).

3.3. Cyclodehydration of cis–2-butene-1,4-diol (2) with active methylene compounds (3)

Compound **2** (44.1 mg, 0.50 mmol), active methylene compound (1.00 mmol), complex **1** (11.1 mg, 0.010 mmol), and anisole (3.96 mg, 0.050 mmol, GLC standard) were placed in a 10 mL Schlenk tube and dissolved in toluene (1 mL). Pyridine (10.8 mg, 0.10 mmol) was added, and the solution was stirred at 100 °C. After **2** was consumed, the reaction was quenched with Et_3N (0.1 mL) and the

product purified by silica gel column chromatography (CH_2Cl_2) to give 2-vinyl-2,3-dihydrofuran derivatives (**4**) as listed in Table 2.

*2-Vinyl-4-acetyl-5-methyl-2,3-dihydrofuran (**4a**) [14c]:* pale yellow oil. ^{1}H NMR ($CDCl_3$, 20 °C): δ 2.18 (s, 3H), 2.21 (dd, $J = 1.5$ and 1.5 Hz, 3H), 2.73 (ddd, $J = 14.1$, 8.0 and 1.5 Hz, 1H), 3.12 (ddd, $J = 14.1$, 10.5 and 1.5 Hz, 1H), 5.02 (ddddd, $J = 10.5$, 8.0, 6.6, 1.2 and 0.9 Hz, 1H), 5.22 (ddd, $J = 10.2$, 1.2 and 0.9 Hz, 1H), 5.30 (ddd, $J = 17.4$, 0.9 and 0.9 Hz, 1H), 5.92 (ddd, $J = 17.4$, 10.2 and 6.6 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ 15.0, 29.4, 36.3, 82.6, 111.9, 116.9, 136.6, 167.3, 194.4. IR (neat): ν 2989, 2928, 1715, 1671, 1599, 1227, 989, 934, 625 cm^{-1}. HRMS. calc. for $C_9H_{12}O_2$: 152.0837. Found: 152.0832.

*2-Vinyl-4-ethoxycarbonyl-5-methyl-2,3-dihydrofuran (**4b**) [15]:* pale yellow oil. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.27 (t, $J = 7.1$ Hz, 3H), 2.20 (dd, $J = 1.5$ and 1.5 Hz, 3H), 2.67 (ddd, $J = 14.1$, 8.0 and 1.5 Hz, 1H), 3.06 (ddd, $J = 14.1$, 10.5 and 1.5 Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 5.02 (ddddd, $J = 10.5$, 8.0, 6.6, 1.2 and 0.9 Hz, 1H), 5.24 (ddd, $J = 10.2$, 1.2 and 0.9 Hz, 1H), 5.30 (ddd, $J = 17.4$, 0.9 and 0.9 Hz, 1H), 5.92 (ddd, $J = 17.4$, 10.2 and 6.6 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ 14.1, 14.4, 35.6, 59.5, 82.5, 101.7, 116.6, 136.9, 166.1, 167.5. IR (neat): ν 2982, 2871, 1704, 1651, 1257, 1224, 1082, 990, 968, 762 cm^{-1}. HRMS. calc. for $C_{10}H_{14}O_3$: 182.0943. Found: 182.0939.

*2-Vinyl-4-benzoyl-5-methyl-2,3-dihydrofuran (**4ca**) [16]:* pale yellow oil. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.83 (t, $J = 1.5$ Hz, 3H), 2.90 (ddd, $J = 14.4$, 8.3 and 1.5 Hz, 1H), 3.24 (ddd, $J = 14.4$, 10.1 and 1.5 Hz, 1H), 5.09 (ddddd, $J = 10.5$, 8.0, 6.6, 1.2 and 0.9 Hz, 1H), 5.24 (ddd, $J = 10.2$, 1.2 and 0.9 Hz, 1H), 5.30 (ddd, $J = 17.4$, 0.9 and 0.9 Hz, 1H), 5.92 (ddd, $J = 17.4$, 10.2 and 6.6 Hz, 1H), 7.35–7.60 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ 15.4, 36.9, 82.6, 112.2, 117.0, 127.7, 128.2, 129.1, 130.9, 136.5, 168.4, 193.0. IR (neat): ν 2926, 1718, 1623, 1591, 1239, 1117, 1071, 989, 918, 699 cm^{-1}. HRMS calc. for $C_{14}H_{14}O_2$: 214.0994. Found: 214.0989.

*2-Vinyl-4-acetyl-5-phenyl-2,3-dihydrofuran (**4cb**):* pale yellow oil. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.96 (s, 3H), 2.94 (dd, $J = 14.8$ and 8.2 Hz, 1H), 3.30 (dd, $J = 14.8$ and 10.3 Hz, 1H), 5.10–5.20 (m, 1H), 5.26 (ddd, $J = 10.4$, 1.3 and 0.9 Hz, 1H), 5.38 (ddd, $J = 16.9$, 0.9 and 0.9 Hz, 1H), 6.00 (ddd, $J = 17.0$, 10.4 and 6.6 Hz, 1H), 7.40–7.60 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ 28.8, 37.1, 82.6, 114.5, 117.1, 128.3, 129.2, 130.6, 130.8, 136.6, 194.6. IR (neat): ν 2924, 1717, 1608, 1386, 1222, 1102, 975, 901, 703 cm^{-1}. HRMS calc. for $C_{14}H_{14}O_2$: 214.0994. Found: 214.0999.

*2-Vinyl-4-benzoyl-5-phenyl-2,3-dihydrofuran (**4d**) [17]:* pale yellow oil. ^{1}H NMR ($CDCl_3$, 20 °C): δ 3.14 (dd, $J = 15.0$ and 8.4 Hz, 1H), 3.45 (dd, $J = 15.0$ and 10.0 Hz, 1H), 5.25–5.27 (m, 1H), 5.31 (ddd, $J = 11.5$, 1.3 and 1.3 Hz, 1H), 5.46 (ddd, $J = 17.0$, 1.3 and 1.3 Hz, 1H), 6.10 (ddd, $J = 17.4$, 10.2 and 6.6 Hz, 1H), 7.00–7.50 (m, 5H), 7.00–7.50 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ 38.7, 82.5, 111.8, 117.2, 127.6, 128.6, 128.9, 129.4, 129.9, 130.0, 131.1, 136.6, 165.6, 193.5. IR (neat): ν 3060, 1610, 1574, 1491, 1446, 1367, 1238, 1115, 992, 927, 886, 696 cm^{-1}. HRMS calc. for $C_{19}H_{16}O_2$: 276.1150. Found: 276.1145.

*1,1,6,6-Tetrabenzoyl-3-hexene (**6**):* white powder. ^{1}H NMR ($CDCl_3$, 20 °C): δ 2.74 (m, 4H), 5.16 (t, $J = 6.6$ Hz, 2H), 5.57–5.62 (m, 2H), 7.42 (ddd, $J = 8.4$, 7.5 and 1.8 Hz, 8H), 7.55 (tt, $J = 7.5$ and 1.8 Hz, 4H), 7.88 (ddd, $J = 8.4$, 1.8 and 1.2 Hz, 8H). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ 32.3, 56.8, 128.5, 128.9, 129.7, 133.5, 135.8, 195.5. IR (KBr): ν 3038, 3031, 2963, 2917, 1685, 1667, 1596, 1448, 1357, 1342, 1180, 1007, 924, 701 cm^{-1}. HRMS calc. for $C_{34}H_{28}O_4$: 500.1988. Found: 500.1979.

3.4. Cyclodehydration of cis–2-butene-1,4-diol (**2**) with 1,3-cyclohexanedione (**3f**)

The reaction of Eq. (2) was conducted similarly to Section 3.3, using **2** (43.85 mg, 0.50 mmol), **3f** (111.94 mg, 1.00 mmol), **1** (11.1 mg, 0.010 mmol), pyridine (10.81 mg, 0.10 mmol), and THF (1 mL) as the solvent. The reaction mixture was stirred for 0.5 h under reflux, quenched with Et_3N (0.1 mL), and purified by silica gel column chromatography (hexane:AcOEt = 4:1 and then 2:1) to afford **4f** as a pale yellow oily material (34 mg, 42%). ^{1}H NMR ($CDCl_3$, 20 °C): δ 2.04 (qui, $J = 6.3$ Hz, 2H), 2.35 (t, $J = 6.3$ Hz, 2H), 2.44 (ddt, $J = 6.3$, 1.2 and 1.2 Hz, 2H), 2.61 (ddt, $J = 14.4$, 7.5 and 1.2 Hz, 1H), 3.01 (ddt, $J = 14.4$, 10.2 and 1.2 Hz, 1H), 5.15–5.24 (m, 1H), 5.24 (ddd, $J = 10.5$, 1.2 and 0.9 Hz, 1H), 5.32 (ddd, $J = 17.1$, 1.2 and 1.2 Hz, 1H), 5.93 (ddd, $J = 17.1$, 10.5 and 6.6 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ 21.6, 23.9, 31.8, 36.4, 85.7, 112.9, 117.4, 136.2, 177.1, 195.5. IR (neat): ν 2952, 2896, 2827, 2252, 1624, 1403, 1230, 987, 909, 649 cm^{-1}. HRMS calc. for $C_{10}H_{12}O_2$: 164.0829. Found: 164.0837.

References

[1] (a) J. Tsuji, Transition Metal Reagents and Catalysts, Wiley, New York, 2000;
(b) J.A. Davis, in: E.W. Able, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 9, Pergamon Press, Oxford, 1995, p. 291;
(c) S.A. Godleski, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 3, Pergamon Press, New York, 1991, p. 585.

[2] (a) B.M. Trost, Angew. Chem. Int. Ed. 34 (1995) 259;
(b) B.M. Trost, Science 254 (1991) 1471.

[3] (a) H. Kinoshita, H. Shinokubo, K. Oshima, Org. Lett. 6 (2004) 4085;
(b) Y. Kayaki, T. Koda, T. Ikariya, Eur. J. Org. Chem. (2004) 4989;
(c) N. Komine, A. Sako, S. Hirahara, M. Hirano, S. Komiya, Chem. Lett. 34 (2005) 246;
(d) H. Bricout, J.-F. Carpentier, A.J. Mortreux, Mol. Catal. A 136 (1998) 243, and references cited therein.

[4] (a) T. Satoh, M. Ikeda, M. Miura, M. Nomura, J. Org. Chem. 62 (1997) 4877;
(b) S.-C. Yang, Y.-C. Tsai, Organometallics 20 (2001) 763;
(c) I. Stray, I.G. Stará, P. Kocovsky, Tetrahedron 50 (1994) 529;

(d) Y. Masuyama, M. Kagawa, Y. Kurusu, Chem. Lett. (1995) 1121;
(e) Y. Tamaru, Eur. J. Org. Chem. (2005) 2647, and references cited therein.
[5] (a) F. Ozawa, H. Okamoto, S. Kawagishi, S. Yamamoto, T. Minami, M. Yoshifuji, J. Am. Chem. Soc. 124 (2002) 10968;
(b) F. Ozawa, T. Ishiyama, S. Yamamoto, S. Kawagishi, H. Murakami, M. Yoshifuji, Organometallics 23 (2004) 1698.
[6] (a) F. Mathey, Angew. Chem. Int. Ed. 42 (2003) 1578;
(b) F. Ozawa, M. Yoshifuji, C. R. Chimie 7 (2004) 747;
(c) M. Doux, A. Moores, N. Mezailles, L. Ricard, Y. Jean, P. Le Floch, J. Organomet. Chem. 690 (2005) 2407.
[7] (a) M. Massacret, P. Lhoste, D. Sinou, Eur. J. Org. Chem. (1999) 129;
(b) S.-C. Yang, Y.-J. Shue, P.-C. Liu, Organometallics 21 (2002) 2013;
(c) S.-C. Yang, P.-C. Liu, W.-H. Feng, Tetrahedron Lett. 45 (2004) 4951.
[8] (a) A. Yamazaki, I. Achiwa, K. Achiwa, Tetrahedron Asymm. 7 (1996) 403;
(b) M. Massacret, R. Lakhmiri, P. Lhoste, C. Nguefack, F.B.B. Abdelouahab, R. Fadel, D. Sinou, Tetrahedron Asymm. 11 (2000) 3561;
(c) S.-C. Yang, H.-C. Lai, Y.-C. Tsai, Tetrahedron Lett. 45 (2004) 2693.
[9] (a) T. Tsuda, T. Kiyoi, T. Saegusa, J. Org. Chem. 55 (1990) 3388;
(b) Y. Uozumi, A. Tanahashi, T. Hayashi, J. Org. Chem. 58 (1993) 6826;
(c) A. Yamazaki, K. Achiwa, Tetrahedron Asymm. 6 (1995) 1021.
[10] C. Thorey, J. Wilken, F. Hénin, J. Martens, T. Mehler, J. Muzart, Tetrahedron Lett. 36 (1995) 5527.
[11] M. Massacret, C. Goux, P. Lhoste, D. Sinou, Tetrahedron Lett. 35 (1994) 6093.
[12] (a) T. Hayashi, A. Yamamoto, Y. Ito, Tetrahedron Lett. 28 (1987) 4837;
(b) T. Hayashi, A. Yamamoto, Y. Ito, Tetrahedron Lett. 29 (1988) 99;
(c) M. Moreno-Mañas, L. Morral, R. Pleixats, S. Villarroya, Eur. J. Org. Chem. (1999) 181;
(d) S. Tanimori, M. Kirihata, Tetrahedron Lett. 41 (2000) 6785.
[13] S.-I. Murahashi, T. Shimamura, I. Moritani, J. Chem. Soc., Chem Commun. (1974) 931.
[14] (a) T. Hayashi, A. Yamamoto, Y. Ito, Tetrahedron Lett. 29 (1988) 669;
(b) T. Hayashi, A. Ohno, A.S.-J. Lu, Y. Matsumoto, E. Fukuyo, K. Yanagi, J. Am. Chem. Soc. 116 (1994) 4221;
(c) M. Sakamoto, I. Shimizu, A. Yamamoto, Bull. Chem. Soc. Jpn. 69 (1996) 1065;
(d) N. Nomura, K. Tsurugi, M. Okada, Angew. Chem. Int. Ed. 40 (2001) 1932.
[15] Y. Bahurel, F. Collonges, A. Manet, F. Pautet, A. Poncet, G. Descotes, Bull. Soc. Chim. Fr. (1971) 2203.
[16] L.S. Barinelli, K.M. Nicholas, J. Org. Chem. 53 (1988) 2114.
[17] H. Braun, G. Huber, Tetrahedron Lett. 25 (1976) 2121.