

Highly Stereoselective Facile Synthesis of 2-Acetoxy-1,3(*E*)-alkadienes via a Rh(I)-Catalyzed Isomerization of 2,3-Allenyl Carboxylates

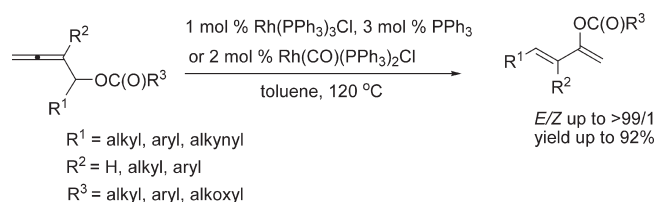
Xiaobing Zhang, Chunling Fu, and Shengming Ma*

Laboratory of Molecular Recognition and Synthesis, Department of Chemistry,
Zhejiang University, Hangzhou 310027, Zhejiang, People's Republic of China

masm@sioc.ac.cn

Received January 22, 2011

ABSTRACT



A highly stereoselective Rh(I)-catalyzed 1,3-acetoxy rearrangement of 1,2-allen-3-yl carboxylates leading to 2-acetoxy-1,3(*E*)-alkadienes has been developed. In addition to the high catalytic efficiency and the scope, the excellent *E*-selectivity of the double bond is remarkable.

1,3-Alkadien-2-yl carboxylates are important synthetic building blocks in organic synthesis since they may readily undergo the Diels–Alder reaction,¹ asymmetric hydrogenation,² and hydrolysis to afford the functionalized α,β -unsaturated enones.³ In the classical synthesis of 1,3-alkadien-2-yl carboxylate, 1-buten-3-yne⁴ and 2-enones^{1c,3b,5} have been used as starting materials; however, Hg(II)

(25 mol %)^{4a} or H₂SO₄ (40 mol %)^{1c} is required. Recently, transition metals such as Ag(I) (5 mol %),⁶ Au(I) (1–5 mol %),^{6a,7} Cu(I) (5 mol %),⁸ Hg(II) (5 mol %),⁹

(1) For examples, see: (a) Kropf, H.; Schröder, R.; Fölsing, R. *Synthesis* **1977**, 12, 894. (b) Shea, K. J.; Wada, E. *J. Am. Chem. Soc.* **1982**, 104, 5715. (c) Potman, R. P.; Kleef, F. J.; Scheeren, H. W. *J. Org. Chem.* **1985**, 50, 1955. (d) Shea, K. J.; Fruscella, W. M.; Carr, R. C.; Burke, L. D.; Cooper, D. K. *J. Am. Chem. Soc.* **1987**, 109, 447. (e) Hansen, D. W.; Pappo, R.; Garland, R. B. *J. Org. Chem.* **1988**, 53, 4244. (f) Philippot, K.; Devanne, D.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1990**, 17, 1199. (g) Stoodley, R. J.; Yuen, W.-H. *Chem. Commun.* **1997**, 15, 1371. (h) Areces, P.; Jiménez, J. L.; Pozo, M. C.; Román, E.; Serrano, J. A. *J. Chem. Soc., Perkin Trans. 1* **2001**, 754. (i) Roversi, E.; Vogel, P. *Helv. Chim. Acta* **2002**, 85, 761. (j) Pollini, G. P.; Bianchi, A.; Casolari, A.; Risi, C.; Zanirato, V.; Bertolasi, V. *Tetrahedron: Asymmetry* **2004**, 15, 3223.

(2) Boaz, N. W. *Tetrahedron Lett.* **1998**, 39, 5505. (3) (a) Bennett, G. J.; Lee, H.-H. *J. Chem. Soc., Perkin Trans. 1* **1986**, 633. (b) Seltzer, S. J. *J. Org. Chem.* **1995**, 60, 1189. (c) Tode, C.; Yamano, Y.; Ito, M. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1581.

(4) (a) Werntz, J. H. *J. Am. Chem. Soc.* **1935**, 57, 204. (b) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *J. Org. Chem.* **1987**, 52, 2230.

(5) Kalita, B.; Bezbarua, M. S.; Barua, N. C. *Synth. Commun.* **2002**, 32, 3181.

(6) (a) Zhang, L. *J. Am. Chem. Soc.* **2005**, 127, 16804. (b) Zhang, L.; Wang, S. *J. Am. Chem. Soc.* **2006**, 128, 1442. (c) Zhao, J.; Hughes, C. O.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, 128, 7436.

(7) (a) Wang, S.; Zhang, L. *J. Am. Chem. Soc.* **2006**, 128, 8414. (b) Witham, C. A.; Mauleón, P.; Shapiro, N. D.; Sherry, B. D.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, 129, 5838. (c) Lemiére, G.; Gandon, V.; Cariou, K.; Fukuyama, T.; Dhiman, A.-L.; Fensterbank, L.; Malacria, M. *Org. Lett.* **2007**, 9, 2207. (d) Yu, M.; Li, G.; Wang, S.; Zhang, L. *Adv. Synth. Catal.* **2007**, 349, 871. (e) Shapiro, N. D.; Toste, F. D. *J. Am. Chem. Soc.* **2008**, 130, 9244. (f) Correa, A.; Marion, N.; Fensterbank, L.; Malacria, M.; Nolan, S. P.; Cavallo, L. *Angew. Chem., Int. Ed.* **2008**, 47, 718. (g) Davies, P. W.; Albrecht, S. J.-C. *Chem. Commun.* **2008**, 238. (h) Dudnik, A. S.; Schwieter, T.; Gevorgyan, V. *Org. Lett.* **2008**, 10, 1465. (i) Mauleón, P.; Krinsky, J. L.; Toste, F. D. *J. Am. Chem. Soc.* **2009**, 131, 4513. (j) Pérez, A. G.; López, G. S.; Marco-Contelles, J.; Faza, O. N.; Soriano, E.; Lera, A. R. *J. Org. Chem.* **2009**, 74, 2982. (k) Yu, M.; Zhang, G.; Zhang, L. *Tetrahedron* **2009**, 65, 1846. (l) Dudnik, A. S.; Schwieter, T.; Gevorgyan, V. *Tetrahedron* **2009**, 65, 1859. (m) Dudnik, A. S.; Schwieter, T.; Gevorgyan, V. *J. Organometallic Chem.* **2009**, 694, 482. (n) Garayalde, D.; Gómez-Bengoa, E.; Huang, X.; Goeke, A.; Nevado, C. *J. Am. Chem. Soc.* **2010**, 132, 4720.

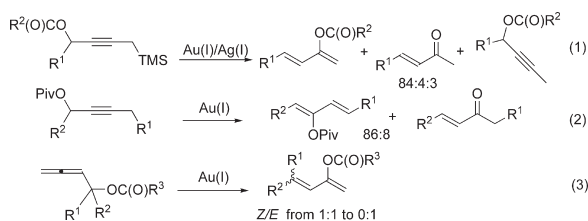
(8) (a) Barluenga, J.; Riesgo, L.; Vicente, R.; López, Z. A.; Tomás, M. *J. Am. Chem. Soc.* **2007**, 129, 7772. (b) Schwieter, T.; Sromek, A. W.; Yap, D. M. L.; Chernyak, D.; Gevorgyan, V. *J. Am. Chem. Soc.* **2007**, 129, 9868.

(9) Imagawa, H.; Asai, Y.; Takano, H.; Hamagaki, H.; Nishizawa, M. *Org. Lett.* **2006**, 8, 447.

(10) (a) Soriano, E.; Marco-Contelles, J. *J. Org. Chem.* **2007**, 72, 1443. (b) Ji, K.-G.; Shu, X.-Z.; Chen, J.; Zhao, S.-C.; Zheng, Z.-J.; Lu, L.; Liu, X.-Y.; Liang, Y.-M. *Org. Lett.* **2008**, 10, 3919. (c) Lu, L.; Liu, X.-Y.; Shu, X.-Z.; Yang, K.; Ji, K.-G.; Liang, Y.-M. *J. Org. Chem.* **2009**, 74, 474.

Pt(II) (5–10 mol %),¹⁰ Pd(II) (5–10 mol %),¹¹ Ru(I) (5 mol %),¹² and Rh(I) (5 mol %)¹³ to catalyze the rearrangement of 2-alkynyl carboxylates have been extensively studied, some of which afforded 1,3-alkadien-2-yl carboxylates as the major products.¹⁴ For example Zhang et al. reported rearrangement–elimination of TMS-substituted propargylic carboxylates affording 1,3-alkadien-2-yl carboxylates as major products (84%) with the formation of minor products such as 3-alken-2-ones (4%) and propargylic carboxylates (3%) (Scheme 1, eq 1);^{14a} Zhang et al. also reported that 1,2-migration of propargylic pivalates gave the (1*Z*,3*E*)-2-pivaloxy-1,3-dienes (86%) together with the α,β -unsaturated enones (8%) (Scheme 1, eq 2).^{14b} As an alternative method for the synthesis of 1,3-alkadienes, allenols are regarded as effective starting materials.¹⁵ For the generation of 1,3-alkadien-2-yl carboxylates, the isomerization of 2,3-allenyl carboxylates catalyzed by Au(I) was recently reported (Scheme 1, eq 3).¹⁶ Although the reaction employed a set of mild conditions and excellent yields, there are several issues such as unsatisfactory stereoselectivity and the fact that substitutions can only be introduced to the 4-position of 1,3-alkadien-2-yl carboxylates. Thus, highly chemo- and stereoselective synthesis of 1,3-alkadien-2-yl carboxylates from 2,3-allenyl carboxylates is highly desirable.

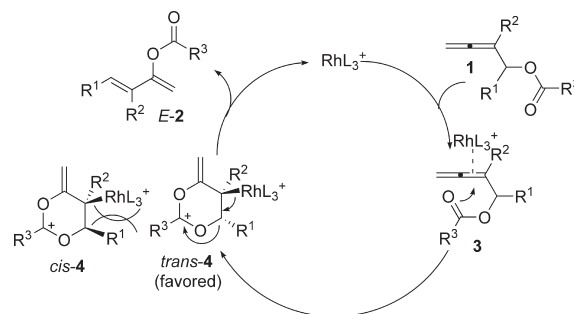
Scheme 1



By analogy with the proposed plausible mechanism for this 1,3-acetoxyl rearrangement of 2,3-allenyl carboxylates,^{6a,7a,10b,16} we believe that Rh^+ may undergo the following process: coordination with allenyl carboxylates would afford complex **3**. Subsequent oxametallation affords cyclic intermediate **4**, which undergoes

β -elimination to yield 1,3-butadien-2-yl carboxylates *E*-**2**. Predominant *E*-stereoselectivity would be realized by consideration of the more favorable cyclic intermediate *trans*-**4** since there is steric interaction between the R^1 and the Rh atom in *cis*-**4** (Scheme 2). RhL_3^+ may have a more remarkable steric effect by coordinating with three ligands and may be able to afford the product with a much better stereoselectivity than AuL^+ , which always coordinated with a single ligand. Here, we wish to present the realization of such a concept: Rh-catalyzed highly chemo- and stereoselective preparation of 3,4-disubstituted-1,3-(*E*)-alkadien-2-yl acetates from readily available 2,3-allenyl acetates, carbonate, or benzoates.

Scheme 2. Rationale for a Higher Stereoselectivity

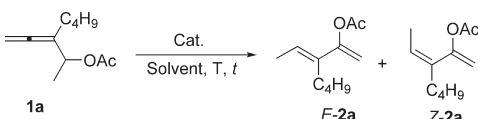


At the beginning, 3-butyl-3,4-pentadien-2-yl acetate **1a** was selected as the model substrate. A systematic study was undertaken to optimize the reaction conditions (Table 1). When 5 mol % of $\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ were used as the catalyst the reaction in toluene under reflux afforded 3-butyl-1,3(*E*)-pentadien-2-yl acetate *E*-**2a** in 74% yield with 14% recovery of starting material **1a**. However, we were happy to note that an excellent *E/Z* ratio ($\geq 98:2$) was observed (Table 1, entry 1), which encouraged us to conduct the reaction with other rhodium complexes: $[\text{Rh}(\text{COD})\text{Cl}]_2$ did not promote the reaction at all (Table 1, entry 2) while $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ gave a better result with a higher yield and stereoselectivity (Table 1, entry 3); although a ratio of $> 99:1$ was observed for the reaction in 1,4-dioxane, the yield was quite low (Table 1, entry 4); other solvents such as DMF or DMSO led to a low yield or no reaction at all (Table 1, entries 5 and 6). The loading of $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ could be reduced from 5 mol % to 2 mol % or even as low as 1 mol % with a higher concentration (Table 1, entries 8 and 9). To our delight, the addition of 3 mol % of PPh_3 would provide a little bit higher yield (81%) and a remarkable excellent stereoselectivity (*E/Z* ratio $> 99:1$) (Table 1, entry 10). We then defined the isomerization of **1** catalyzed by 1 mol % of $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ and 3 mol % of PPh_3 in toluene under reflux as conditions A. Additionally, $\text{Rh}(\text{PMe}_3)_3\text{Cl}$ gave a similar yield and slightly lower stereoselectivity as compared to $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (Table 1, entry 11).

Under this set of optimized reaction conditions, the scope and the limitations for this reaction were explored. When R^2 is *n*-butyl and R^1 is *n*-hexyl, *i*-butyl, or *n*-hexynyl, the reaction provided the corresponding products

- (11) Caruana, P. A.; Frontier, A. J. *Tetrahedron* **2007**, *63*, 10646.
 (12) Bray, C. V.-L.; Dérien, S.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2009**, *48*, 1439.
 (13) Shibata, Y.; Noguchi, K.; Tanaka, K. *J. Am. Chem. Soc.* **2010**, *132*, 7896.
 (14) (a) Wang, S.; Zhang, L. *Org. Lett.* **2006**, *8*, 4585. (b) Li, G.; Zhang, G.; Zhang, L. *J. Am. Chem. Soc.* **2008**, *130*, 3740.
 (15) For examples of stereoselectivity synthesis of 1,3-alkadienes from allenols, see: (a) Shen, Q.; Hammond, G. B. *Org. Lett.* **2001**, *3*, 2213. (b) Horváth, A.; Bäckvall, J.-E. *J. Org. Chem.* **2001**, *66*, 8120. (c) Ma, S.; Wang, G. *Tetrahedron Lett.* **2002**, *43*, 5723. (d) Alcaide, B.; Almendros, P.; Aragoncillo, C.; Redondo, M. C. *Eur. J. Org. Chem.* **2005**, 98. (e) Deng, Y.; Jin, X.; Ma, S. *J. Org. Chem.* **2007**, *72*, 5901. (f) Deng, Y.; Yu, Y.; Ma, S. *J. Org. Chem.* **2008**, *73*, 585. (g) Alcaide, B.; Almendros, P.; Campo, T. M.; Carrascosa, R. *Chem.-Asian J.* **2008**, *3*, 1140. (h) Deng, Y.; Li, J.; Ma, S. *Chem.-Eur. J.* **2008**, *14*, 4263. (i) Deng, Y.; Jin, X.; Fu, C.; Ma, S. *Org. Lett.* **2009**, *11*, 2169. (j) Durán-Galván, M.; Connell, B. T. *Eur. J. Org. Chem.* **2010**, 2445.
 (16) Buzas, A. K.; Istrate, F. M.; Gagosz, F. *Org. Lett.* **2007**, *9*, 985.

Table 1. Effects of Catalyst, Solvent, Temperature, and Ligand on the Rh-Catalyzed 1,3-Rearrangement Reaction of **1a**^a



entry	cat. (mol %)	solvent/temp (°C) ^b	t (h)	NMR yield of 2a ^c (E/Z)	1a ^d
1	Rh(CO)(PPh ₃) ₂ Cl (5)	toluene/120	8	74 (>98/2)	14
2	[Rh(COD)Cl] ₂ (2.5)	toluene/120	6	0	99
3	Rh(PPh ₃) ₃ Cl (5)	toluene/120	4	84 (>98/2)	0
4	Rh(PPh ₃) ₃ Cl (5)	dioxane/120	6	44 (>99/1)	0
5	Rh(PPh ₃) ₃ Cl (5)	DMF/120	6	0	93
6	Rh(PPh ₃) ₃ Cl (5)	DMSO/120	6	2	66
7	Rh(PPh ₃) ₃ Cl (5)	toluene/80	6	18 (99/1)	75
8	Rh(PPh ₃) ₃ Cl (2)	toluene/120	6	88 (98/2)	0
9 ^e	Rh(PPh ₃) ₃ Cl (1)	toluene/120	10	85 (98/2)	0
10 ^{e,f}	Rh(PPh₃)₂Cl (1)	toluene/120	10	89 (>99/1)^g	0
11 ^{e,h}	Rh(PMe ₃) ₃ Cl (1)	toluene/120	10	84 (>98/2)	0

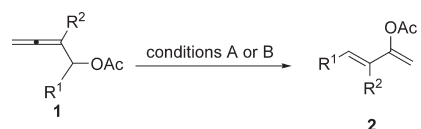
^aThe reaction was conducted by using 0.25 mmol of **1a** and corresponding catalyst in 6 mL of solvent. ^bTemperature of the oil bath. ^cNMR yield determined by using 1,3,5-trimethylbenzene as the internal standard. ^d**1a** recovered after the reaction. ^e0.5 mmol of **1a** in 3 mL of solvent was used. ^f3 mol % of PPh₃ were added. ^gIsolated yield was 81%. ^h3 mol % of PMe₃ were added.

E-2b–2d in 76%–89% yields under conditions A (Table 2, entries 2–4); the formation of the *Z*-isomer was not serious. For 2-butyl-1-phenyl-2,3-butadien-1-yl acetate **1e**, an unsatisfactory *E/Z* ratio (92/8) was observed, but the Rh(CO)(PPh₃)₂Cl-catalyzed reaction showed an excellent stereoselectivity with 2 mol % of the catalyst (Table 2, entries 5 and 6). We then defined **1** catalyzed by 2 mol % of Rh(CO)(PPh₃)₂Cl in toluene under reflux as conditions B. Furthermore, we may easily conduct the reaction of 0.9701 g (4 mmol) of **1e** to provide 0.8535 g of **E-2e** (88%), and the loading of catalyst may also be reduced to 1 mol % (Table 2, entry 7). Under conditions B, R¹ may be alkyl and aryl groups; R² may be allyl and aryl groups generating the products in 65–80% yields with *E/Z* ratios ranging from 96/4 to 99/1 (Table 2, entries 8–10). In addition, an excellent stereoselectivity (*E/Z* ratio > 99/1) with moderate yields was observed when the reaction of the substrates with R¹ being aryl groups and R² being H was performed (Table 2, entries 11 and 12).

Compared to the reaction catalyzed by Au(I) (conditions: 0.5 mmol of **1**, 1 mol % of Au(X-Phos)NTf₂ in 2 mL of CH₂Cl₂),¹⁶ Rh(I) provided a notably higher stereoselectivity and higher yield with an R² substituent (Scheme 2, **1a** and **1e**), while Au(I) gave a higher yield but Rh(I) provided a better stereoselectivity with R² being H (Scheme 3, **1i**). A slightly higher *E-2e/Z-2e* ratio was observed after heating the *E/Z* mixture (59:41) at 120 °C in toluene with 2 mol % of Rh(CO)(PPh₃)₂Cl for 5 h, indicating that the thermodynamic process of isomerizing the *Z*-isomer into the *E*-isomer is not obvious (Scheme 3, eq 4).

Further studies showed that not only acetate but also *p*-nitrobenzoate and carbonate could be used in the

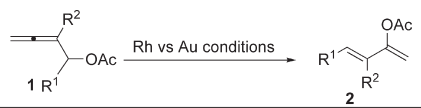
Table 2. Substrate Scope of the Rh-Catalyzed 1,3-Rearrangement Reaction of 2,3-Allenyl Carboxylates **1**



entry	R ¹ /R ²	conditions ^a	t (h)	yield of E-2 (E/Z) ^{b,c}
1	Me/ <i>n</i> -C ₄ H ₉ (1a)	A	10	81 (2a) (>99/1)
2	<i>n</i> -C ₆ H ₁₃ / <i>n</i> -C ₄ H ₉ (1b)	A	10	89 (2b) (99/1)
3	<i>i</i> -C ₄ H ₉ / <i>n</i> -C ₄ H ₉ (1c)	A	4.5	88 (2c) (>99/1)
4	<i>n</i> -hexynyl/ <i>n</i> -C ₄ H ₉ (1d)	A	6	76 (2d) (97/3)
5	Ph/ <i>n</i> -C ₄ H ₉ (1e)	A	9	74 (2e) (92/8)
6	Ph/ <i>n</i> -C ₄ H ₉ (1e)	B	8	92 (2e) (>99/1)
7 ^d	Ph/ <i>n</i> -C ₄ H ₉ (1e)	B	9	88 (2e) (>99/1)
8	Ph/Allyl (1f)	B	4.5	65 (2f) (99/1)
9	Me/Ph (1g)	B	12	75 (2g) (98/2)
10	<i>p</i> -MeOC ₆ H ₄ /Ph (1h)	B	12	80 (2h) (96/4)
11	Ph/H (1i)	B	2.5	53 (2i) (>99/1)
12	<i>p</i> -ClC ₆ H ₄ /H (1j)	B	1.5	49 (2j) (>99/1)

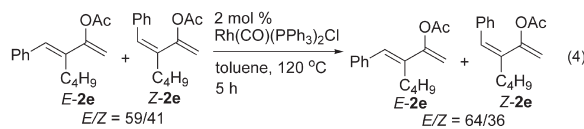
^aConditions A: The reaction was conducted by using 0.5 mmol of **1**, 1 mol % of Rh(PPh₃)₃Cl, and 3 mol % of PPh₃ in 3 mL of toluene under 120 °C. Conditions B: The reaction was conducted by using 1 mmol of **1** and 2 mol % of Rh(CO)(PPh₃)₂Cl in 6 mL of toluene under 120 °C. ^bIsolated yields. ^c*E/Z* ratio was confirmed by ¹H NMR analysis before chromatography on silica gel. ^d4 mmol of **1e** and 1 mol % of Rh(CO)(PPh₃)₂Cl were applied.

Scheme 3



R ¹	R ²	Rh protocol		Au protocol ^{ref. 16}	
		t (h)	yield (%) (E/Z)	t (h)	yield (%) (E/Z) recovery (%)
Me	<i>n</i> -C ₄ H ₉ (1a)	10	81 (2a) >99/1	24	63 (2a) 96/4 28
Ph	<i>n</i> -C ₄ H ₉ (1e)	8	92 (2e) >99/1	19	30 (2e) 58/42 70
Ph	H (1i)	2.5	53 (2i) >99/1	5	91 (2i) 95/5 0

Au protocol: 0.5 mmol of **1**, 1 mol % of Au(X-Phos)NTf₂ in 2 mL of CH₂Cl₂ at rt
Rh protocol: see the corresponding conditions listed above.



reaction to afford the corresponding products in good yields with an excellent stereoselectivity (Scheme 4, eqs 5 and 6) and the structure including the configuration of the C=C bond in **E-2k** was unambiguously determined by single crystal X-ray diffraction analysis (Figure 1).¹⁷

(17) Crystal data for **E-2k**: C₂₁H₂₁NO₄, MW = 351.39, monoclinic, space group P2(1)/c, final *R* indices [*I* > 2σ(*I*)], *R*₁ = 0.0608, *wR*₂ = 0.1451, *R* indices (all data) *R*₁ = 0.0694, *wR*₂ = 0.1500, *a* = 7.7254(7) Å, *b* = 8.2025(7) Å, *c* = 29.583(3) Å, α = 90°, β = 96.638(3)°, γ = 90°, *V* = 1862(3) Å³, *T* = 173 K, *Z* = 4, reflections collected/unique: 20256/3269 (*R*_{int} = 0.0364), number of observations [*I* > 2σ(*I*)] 2783, parameters: 243. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC 805894).

Scheme 4

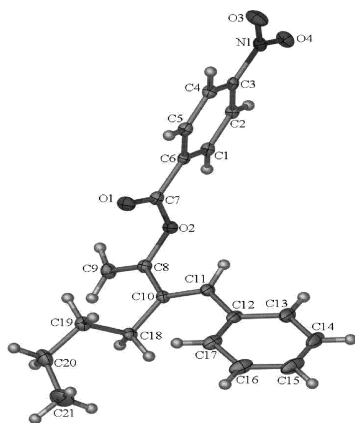
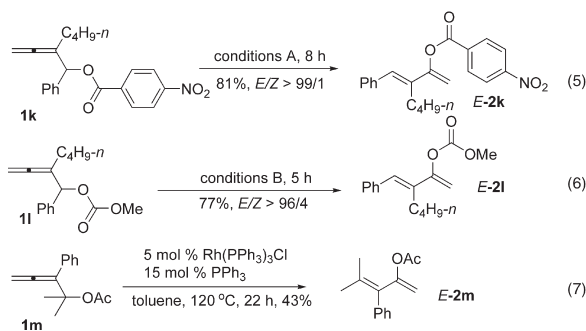


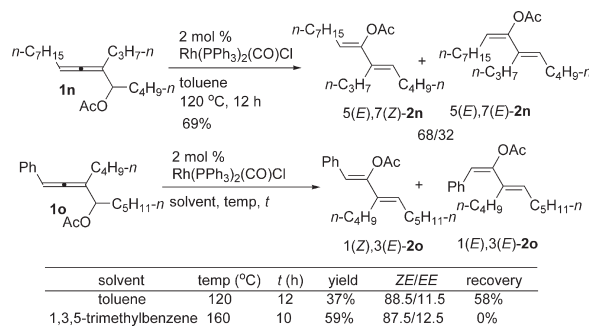
Figure 1. ORTEP drawing of *E*-2k.

However, due to the steric effect, remarkably more catalyst was needed with a longer reaction time when 2-methyl-3-phenylpenta-2-yl acetate **1m** was used in the reaction (Scheme 4, eq 7).

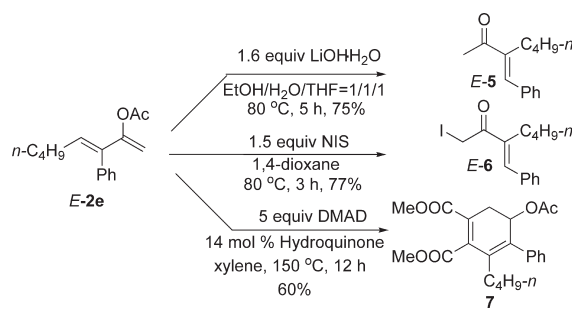
It is interesting to note that 2,4-disubstituted 2,3-allenyl carboxylates can also be used in the reaction: 6-propyl-6,7-pentadecadien-5-yl acetate **1n** undergoes the Rh-catalyzed 1,3-rearrangement to afford 6-propyl-5(*E*),7(*Z*)-pentadecadien-7-yl acetate **5(*E*),7(*Z*)-2n** and 6-propyl-5(*E*),7(*E*)-pentadecadien-7-yl acetate **5(*E*),7(*E*)-2n** in 69% yield with an *EZ/EE* ratio of 68/32; a better *EZ/EE* ratio of 87.5/12.5 was observed, but a higher temperature in 1,3,5-trimethylbenzene was needed when 3-butyl-1-phenyl-1,2-nonadien-4-yl acetate **1o** was applied (Scheme 5).

Treatment of 3-butyl-4-phenyl-1,3(*E*)-butadien-2-yl acetate **E-2e** with LiOH·H₂O or NIS generated the hydrolysis product α,β-unsaturated enone **E-5** and iodination product 3-butyl-1-iodo-4-phenyl-3(*E*)-buten-2-one **E-6** in 75% and 77% yields, respectively.^{18,19} Moreover, dimethyl

Scheme 5



Scheme 6. Synthetic Application of the 1,3(*E*)-Alkadien-2-ol Acetates



5-acetoxy-3-butyl-4-phenylcyclohexa-1,3-diene-1,2-dicarboxylate **7** was formed directly from a Diels–Alder reaction between **E-2e** and DMAD in xylene (Scheme 6).²⁰

In summary, we have achieved a highly stereoselective Rh(I)-catalyzed 1,3-rearrangement of 2,3-allenyl carboxylates affording 3,4-disubstituted-1,3(*E*)-butadien-2-yl carboxylates in good to excellent yields. The products readily undergo the hydrolysis, iodination, and Diels–Alder reactions to afford synthetically useful compounds. Due to the easy availability of the starting materials, excellent stereoselectivity, and potential of the products, this reaction will be useful in organic chemistry. Further studies in this area are ongoing in our laboratory.

Acknowledgment. We greatly acknowledge the financial support from the NSF of China (20732005) and the National Basic Research Program of China (2011CB-808700). S.M. is a Qiu Shi Adjunct Professor at Zhejiang University. We thank Mr. Jiajia Chen in this group for reproducing the results presented in entries 4 and 11 in Table 2 and eq 6 in Scheme 4.

Supporting Information Available. General procedure and spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(18) Bestmann, H.-J.; Hartung, H. *Chem. Ber.* **1966**, *99*, 1198.
(19) Romo, J.; Rosenkranz, G.; Sondheimer, F. *J. Am. Chem. Soc.* **1954**, *79*, 5034.

(20) Ma, S.; Gu, Z.; Deng, Y. *Chem. Commun.* **2006**, 94.