$(EtO)_3SiH$-Promoted Palladium-Catalyzed Isomerization of Olefins: Convenient Synthesis of Internal Alkenes from Terminal Alkenes

Xing-Feng Bai,[a,b] Tao Song,[a] Wen-Hui Deng,[a] Yun-Long Wei,[a] Li Li,*[a] Chun-Gu Xia,[b] Li-Wen Xu*[a,b]

[a] Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310012, P. R. of China
Fax +(86)57128868918; E-mail: liwenxu@hznu.edu.cn; E-mail: licpxulw@yahoo.com

[b] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics and University of Chinese Academy of Sciences, Chinese Academy of Sciences, Lanzhou 730000, P. R. of China

Received: 16.09.2013; Accepted after revision: 17.10.2013

Abstract: The catalytic activity of an in situ forming palladium catalyst system generated from $PdCl_2(PPh_3)_2$ and hydrosilane [$(EtO)_3SiH$] was revealed in the one-carbon migration and isomerization of 4,4-biaryl-substituted 1-butenes, in which the $(EtO)_3SiH$ plays a key role in the palladium-catalyzed one-carbon migration and subsequent isomerization of terminal alkenes. This catalytic protocol is applied in the synthesis of a key building block of cassumunin C in high yield and promising selectivity.

Key words: olefin, palladium, isomerization, cassumunin, organosilicon

Olefins represent key and basic structural features in numerous organic compounds and occupy an important position in organic synthesis, since it can readily be transformed into a wide variety of functional molecules.[1] At present, there are various synthetic methods for the construction of carbon–carbon double bonds, including the Wittig reaction,[2] Peterson olefination,[3] or Takai reaction.[4] In addition, the isomerization of olefins shares the importance of olefination and is a generally essential route in the clean synthesis of *E*-alkenes.[5] The catalytic isomerization of alkenes to form a single isomer of alkenes is both a 100% atom efficient reaction and an extremely useful process, either for the preparation of starting materials in the flavor and fragrance industry, or for stereocontrolled rearrangement of functionality along the carbon chain.[6] Nowadays, transition-metal catalysis exhibited excellent properties in olefin isomerization, in which diverse processes with various transition metals (e.g., Pd, Rh, Pt, Ir, or Ni) for olefin isomerization are known.[7] Despite the popularity of ruthenium-based systems,[8] which are known to be effective catalysts in the isomerization of terminal alkenes, the use of palladium catalysts presents an attractive alternative. In this regard, Skrydstrup and Lindhardt have reported recently that the application of an in situ generated bulky palladium hydride catalyst obtained from $Pd(dba)_2$, $P(t\text{-}Bu)_3$, and *i*-PrCOCl provided an efficient protocol for the *cis–trans* isomerization and migration of allylic or terminal alkenes.[9] Very recently, Bercaw's[10] and Trapp's[11] research groups also demonstrated the catalytic activity of novel palladium catalyst systems for the isomerization of terminal alkenes independently. Notably, Wang and coworkers[12] reported an *ortho*-phenol hydroxyl group mediated isomerization of alkenes in the presence of a palladium and iron-based bimetallic catalyst system, in which the catalytic isomerization of various 2-(but-3-enyl)phenol substrates resulted in the formation of conjugated arylalkenes in good yields.

We have recently reported a highly efficient catalytic protocol for the isomerization of substituted amide-derived olefins, which was presented successfully using a palladium hydride catalyst system generated from $PdCl_2(PPh_3)_2$ and $(EtO)_3SiH$.[13] The *Z*-to-*E* isomerization was carried out smoothly and resulted in geometrically pure substituted olefins. This process is simply and can be operated easily. Although the isomerization mechanism via a palladium(dihydrido)olefin complex in the isomerization of substituted amide-derived olefins required some direct evidence, we suggested that the in situ generated palladium hydride complex from $PdCl_2(PPh_3)_2$ and $(EtO)_3SiH$ was the key catalyst in this reaction.[13] Herein, we wish to contribute to this important field of research by application of this catalyst system to the controllable one-carbon migration of terminal alkenes to 2-alkenes. We chose 4,4-biaryl-substituted but-1-enes as benchmark substrates since they are high-value molecules. More interestingly, the hydrosilane play a key role in the isomerization but not in the reduction of terminal olefins. In addition, this catalytic protocol could produce a convenient route to the key building block of cassumunin C.

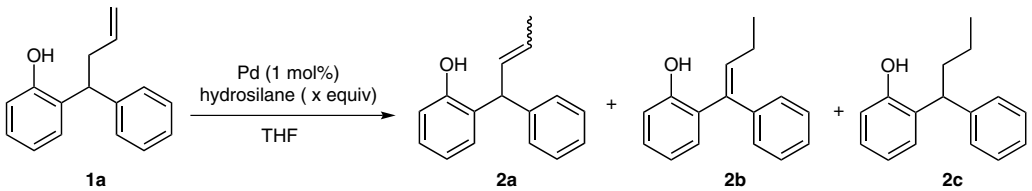
Initially, to extend the utility of the $PdCl_2(PPh_3)_2/(EtO)_3SiH$ catalyst system and with the aim of establishing a more easily accessible and active system for the migration–isomerization reaction of terminal alkenes than those previously reported, we proceeded to evaluate its activity in a model isomerization–migration reaction of 2-(1-phenylbut-3-enyl)phenol (**1a**). As shown in Table 1, the catalytic transformation of olefin **1** could lead to three different products **2a**–**c** because of reduction, one-carbon migration, and two-carbon migration of the carbon–carbon double bond as well as isomerization. Under the reaction conditions reported previously[13] [$PdCl_2(PPh_3)_2$ (1 mol%), $(EtO)_3SiH$ (1 equiv), THF] the

SYNLETT 2014, 25, 0417–0422
Advanced online publication: 04.12.2013
DOI: 10.1055/s-0033-1340290; Art ID: ST-20136-W0884-L

conversion of compound **1a** was almost completed. Product **2a** resulting from the one-carbon migration of the carbon–carbon double bond and the reduced compound **2c** were obtained in a ratio of 79:21 (Table 1, entry 1). Although the reaction result is not good enough in selectivity, this preliminary result revealed that the $PdCl_2(PPh_3)_2/(EtO)_3SiH$ catalyst system could promote the migration and isomerization of a terminal alkene to an internal alkene. As expected, **1a** almost cannot be isomerized to the corresponding compound **2a**, **2b**, or **2c**. Only **2a** was detected in poor conversion (15%, Table 1, entry 2), which further supported the crucial role of hydrosilane in this isomerization reaction. Interestingly, the use of commercial available palladium salts [$PdCl_2$ and $Pd(OAc)_2$] instead of $PdCl_2(PPh_3)_2$ resulted in complicated products, and compound **2c** obtained from reduction was the major product (Table 1, entries 3 and 5). Comparably, $PdCl_2$ was an effective catalyst in this isomerization reaction in the absence of $(EtO)_3SiH$. However, the chemoselectivity of the present reaction was not good (Table 1, entry 4).

For further optimization of reaction conditions, we investigated the effect of the amount of $(EtO)_3SiH$ on the $PdCl_2(PPh_3)_2$-catalyzed isomerization–migration reaction of 2-(1-phenylbut-3-enyl)phenol (**1a**). Fortunately, when the amount of $(EtO)_3SiH$ was reduced to 20 mol%, both the conversion and chemoselectivity were excellent, and **2a** was obtained as sole product in excellent yield (93% isolated yield) from the one-carbon migration of the carbon–carbon double bond (Table 1, entry 7). However, a lower amount of $(EtO)_3SiH$ resulted in decreased yield (Table 1, entry 8). Different solvents were also screened, such as 1,2-dichloroethane and ethanol. 1,2-Dichloroethane also provided a good result in terms of conversion and chemoselectivity, but 1,2-dichloroethane and ethanol exhibited inferior compared to THF (Table 1, entries 9 and 10 for DCE and THF, respectively). Encouraged by these results, we continued to investigate the activity of the palladium catalyst in the presence of other hydrosilanes, such as Et_3SiH and poly(methylhydrosiloxane) (PMHS).[14] Unlike $(EtO)_3SiH$, trace of product **2a** was observed in the presence of Et_3SiH (Table 1, entry 11). The PMHS-promoted palladium-catalyzed one-carbon migration–isomerization reaction of **1a** undergoes in promising conversion (69%, Table 1, entry 12), unfortunately, the chemoselectivity was not good due to the low ratio of **2a**/**2c** (ca. 2:1). In summary, the expected internal alkene **2a** was formed in an *E*/*Z* ratio of 80:20 under the optimized reac-

Table 1 Optimization of the Palladium-Catalyzed Isomerization–Migration Reaction of 2-(1-Phenylbut-3-enyl)phenol (**1a**)[a]



1a **2a** **2b** **2c**

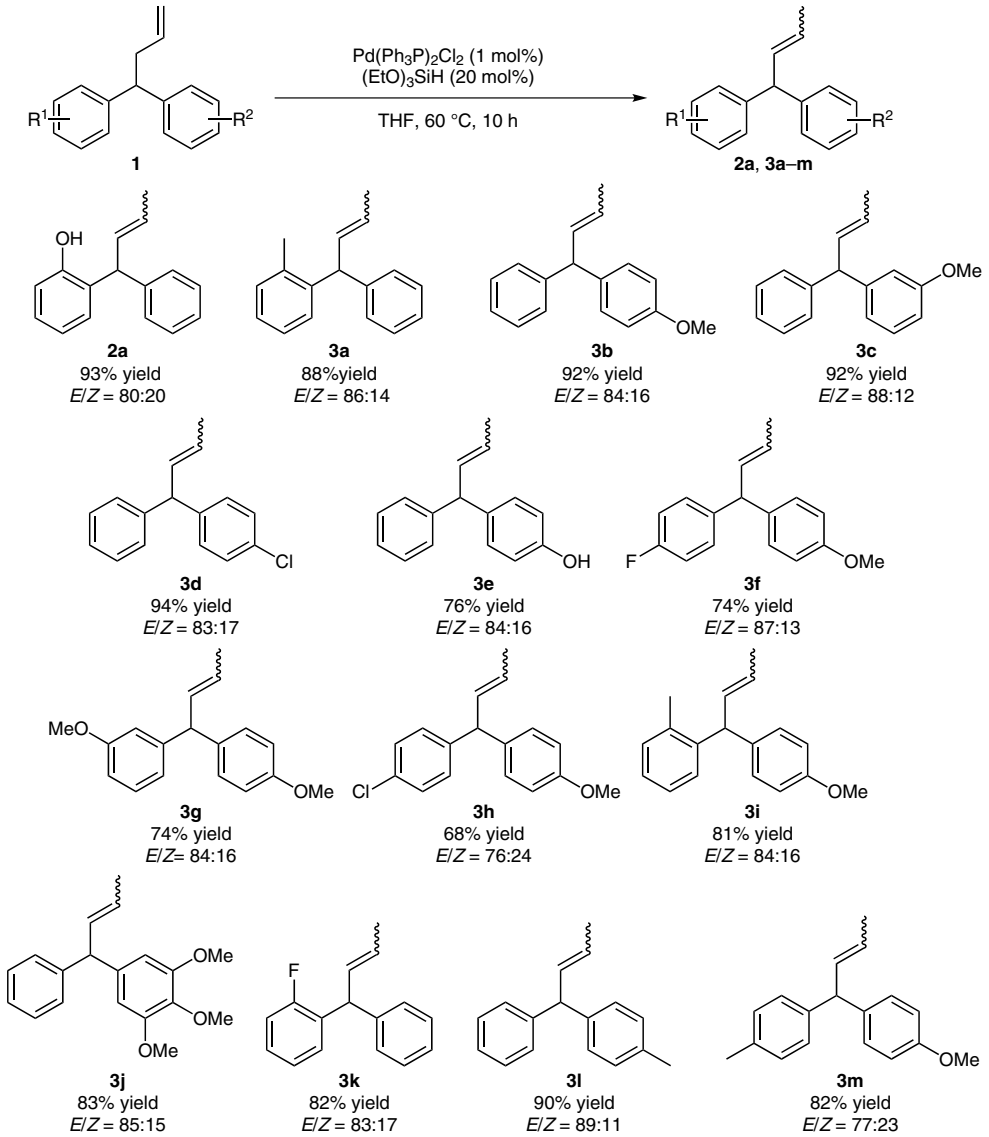
Entry	Pd catalyst	Silane	x	Conversion (%)	**2a**/**2b**/**2c** (%)[b]
1	$PdCl_2(Ph_3P)_2$	$(EtO)_3SiH$	1.0	>99	79:0:21
2	$PdCl_2(Ph_3P)_2$	–[d]	0	15	15:0:0
3	$PdCl_2$	$(EtO)_3SiH$	1.0	–[c]	**2c** >50
4	$PdCl_2$	–[d]	0	>99	56:44:0
5	$Pd(OAc)_2$	$(EtO)_3SiH$	1.0	–[c]	**2c** >80
6	$PdCl_2(Ph_3P)_2$	$(EtO)_3SiH$	0.5	81	59:0:22
7	$PdCl_2(Ph_3P)_2$	$(EtO)_3SiH$	0.2	>99	>99:0:0
8	$PdCl_2(Ph_3P)_2$	$(EtO)_3SiH$	0.1	70	>99:0:0
9	$PdCl_2(Ph_3P)_2$	$(EtO)_3SiH$	0.2	>99	94:6:0[e]
10	$PdCl_2(Ph_3P)_2$	$(EtO)_3SiH$	0.2	59	59:0:0[f]
11	$PdCl_2(Ph_3P)_2$	Et_3SiH	0.2	trace	3:0:0
12	$PdCl_2(Ph_3P)_2$	PMHS	0.2	69	48:0:21

[a] Reaction conditions: terminal olefin **1** (0.5 mmol), Pd catalyst (1 mol%), hydrosilane (x equiv), solvent (e.g., THF, 1 mL), 60 °C, 10 h.
[b] The selectivities were determined by GC and ^1H NMR analysis.
[c] The conversion is not determined because unidentified byproducts were formed and the selectivity could not be detected by GC–MS and NMR analysis under these reaction conditions.
[d] No use of hydrosilanes and any additives.
[e] Solvent: DCE.
[f] Solvent: EtOH.

tion conditions [$PdCl_2(PPh_3)_2$ (1 mol%), $(EtO)_3SiH$ (20 mol%), 60 °C, THF].

With the optimized reaction conditions in hand, the scope of the regioselective $(EtO)_3SiH$-mediated $PdCl_2(Ph_3P)_2$-catalyzed one-carbon migration–isomerization of the carbon–carbon double bond of various 4,4-diarylbut-1-enes was evaluated. As shown in Scheme 1, all of the substituted 4,4-diarylbut-1-enes tested in this work afforded the desired products **3** though one-carbon migration of the carbon–carbon double bond and further isomerization in good to excellent yields (up to 94% isolated yield). Interestingly, various substituted alkenes with a methyl group or a fluorine atom at the *ortho* position of the aryl rings, instead of a hydroxyl group, also gave the desired products in good isolated yields (81–88%) with a high *E*/*Z* ratio (e.g., 86:14 for **3a** and 83:17 for **3k**). When 4-(1-phenylbut-3-enyl)phenol containing a phenol group at the *para* position was used as substrate in this reaction, the yield of the desired product **3e** was slightly lower than that of 2-(1-phenylbut-3-enyl)phenol (**1a**). It was also shown that the position of the substituted phenol group has slight influence on the *Z*/*E* selectivity of the isomerization reaction but the *ortho*-phenol hydroxyl group was beneficial to the one-carbon migration of the carbon–carbon double bond. Interestingly, the further two-carbon migration of the carbon–carbon double bond did not occur during the isomerization of 4,4-diarylbut-1-enes, in which it is different from that of palladium-iron-catalyzed isomerization of terminal alkenes.[12]

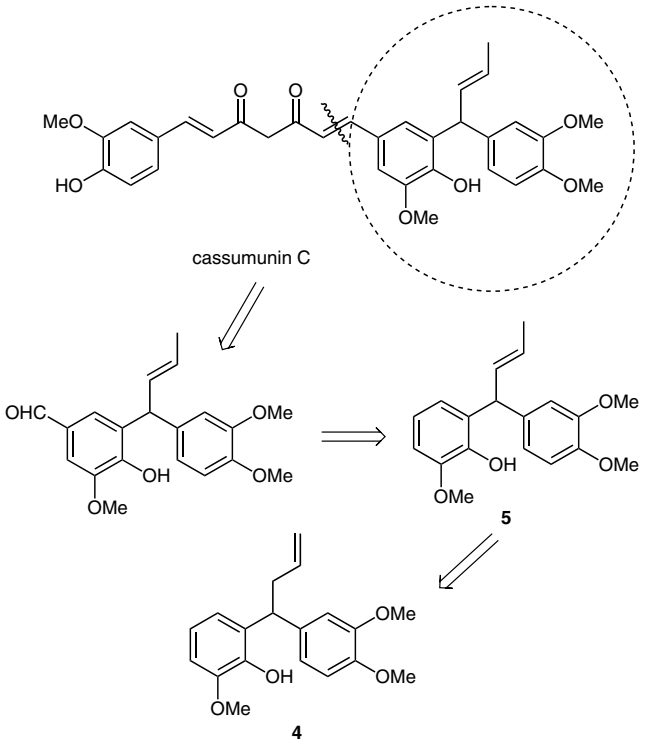
In view of internal olefin as a salient structural feature in many bioactive natural products, we next turned our attention to the construction of such backbone. For example, cassumunins that contain internal olefin backbones are a family of curcuminoids, and their activity was shown to be stronger than curcumin.[15] In the past years, total syntheses of cassumunin A and cassumunin B have been achieved by Masuda et. al.[16] However, the synthesis of



Scheme 1 Regioselective $(EtO)_3SiH$-mediated $PdCl_2(Ph_3P)_2$-catalyzed isomerization–migration reaction of various substituted 4,4-diarylbut-1-enes

cassumunin C that has both antioxidant and anti-inflammatory activities has not been reported up now.

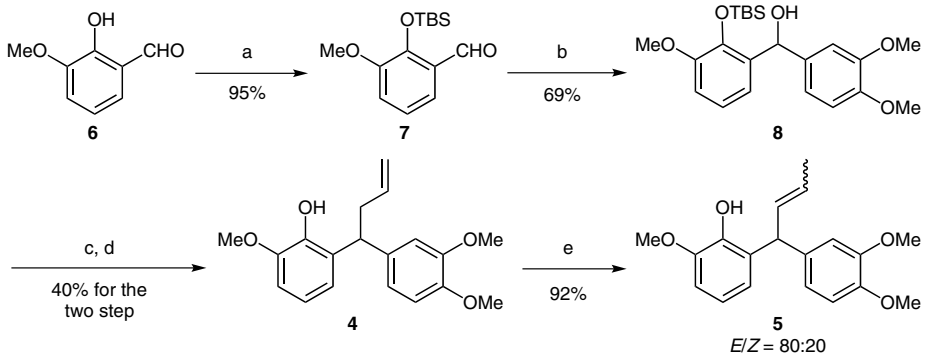
In this work, we tried to apply the palladium-catalyzed isomerization reaction to the construction of the key intermediate of cassumunin C. The natural product cassumunin C is equipped with a 4,4-diarylbut-2-ene, therefore, the molecule (*E*)-2-[1-(3,4-dimethoxyphenyl)but-2-enyl]-6-methoxyphenol (**5**) could be a key intermediate framework of cassumunin C (Scheme 2). In this synthetic scenario, we hypothesized that the catalyst system of $PdCl_2(Ph_3P)_2$ and $(EtO)_3SiH$ could promote the isomerization of 2-[1-(3,4-dimethoxyphenyl)but-3-enyl]-6-methoxyphenol (**4**) to the synthesis of compound **5** through one-carbon migration and isomerization of the carbon–carbon double bond.



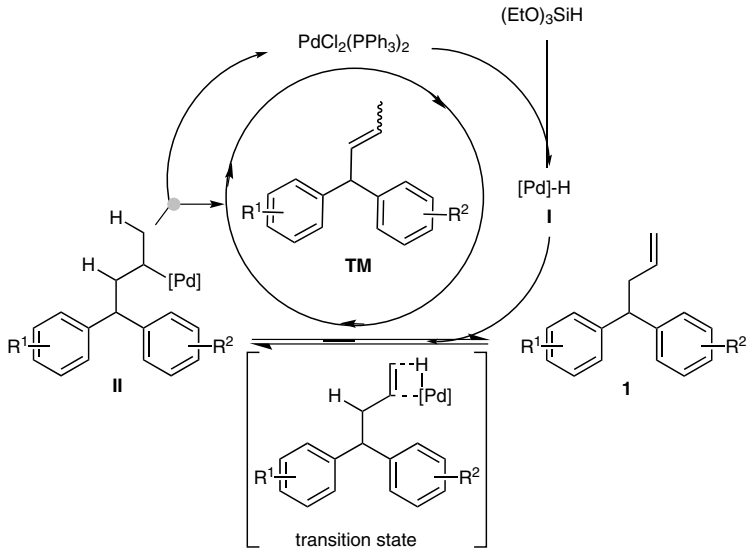
Scheme 2 The possible synthetic strategy for cassumunin C through catalytic isomerization of allylic intermediate **4**

Initially, the commercially available *o*-vanillin (**6**) was used as the starting material in the protection of **6** with TBSCl in DCE, in which the desired product **7** was obtained in high yield (95%). Then 1,2-nucleophilic addition of (3,4-dimethoxyphenyl)lithium to **7** proceeded smoothly at –78 °C in THF. Deprotection of **8** by TBAF (1.0 equiv) for 0.5 hours led to the formation of 2-[(3,4-dimethoxyphenyl)(hydroxy)methyl]-6-methoxyphenol. And then, the introduction of an allylic group to this molecule was carried out through a $FeCl_3$-catalyzed allylation with allyltrimethylsilane,[17] in which the important intermediate **4** was obtained in promising yield. The next task was the conversion of compound **4** into the desired product **5**. The optimized conditions for isomerization of compound **4** were $PdCl_2(PPh_3)_2$ (1 mol%) and $(EtO)_3SiH$ (20 mol%) in THF (Scheme 3, step e), which afforded the desired product successfully in 92% yield. Although the pure *E* isomer of **5** has not been obtained through this procedure (92% isolated yield with an *E*/*Z* ratio up to 81:19), the application of this hydrosilane-mediated palladium-catalyzed migration–isomerization protocol provide a simple and efficient strategy for the synthesis of an internal alkene from a terminal alkene (Scheme 3).

Although the primary aim of this work is to disclose this new methodology for the migration–isomerization of terminal alkenes and the true mechanism was not clear at present, the possible mechanism is shown in Scheme 4 on the basis of experimental results. This mechanism involves the formation of palladium hydride complexes via a repeated olefin addition and a β-hydride elimination.[13,18] In our proposed mechanism of the palladium-catalyzed one-carbon migration–isomerization of olefins **1**, an equilibrium between intermediate **II** and palladium catalyst (palladium hydride or palladium dihydride complex **I**), possibly generated in situ from $PdCl_2(Ph_3P)_2$ and $(EtO)_3SiH$, in which the hydride addition of the palladium hydride complex **I** to terminal alkenes through a four-membered transition state led to the formation intermediate **II**. Then β-hydride elimination occurred to complete the one-carbon migration and further *cis*-*trans* isomerization of the carbon–carbon double bond (Scheme 4). Notably, the conversion of 2-alkenes into 3-alkenes did not occur under the reaction conditions, possibly owing to the



Scheme 3 Synthesis of the key building block of cassumunin C. *Reagents and conditions*: (a) TBSCl (1.5 equiv), Et_3N (2.0 equiv), DMAP (5 mol%); (b) THF, (3,4-dimethoxyphenyl)lithium (1.2 equiv), –78 °C to r.t.; (c) TBAF, r.t.; (d) $FeCl_3$ (5 mol%), allyltrimethylsilane (1.5 equiv), DCE, 50 °C; (e) $PdCl_2(Ph_3P)_2$ (1 mol%), $(EtO)_3SiH$ (20 mol%), THF, 60 °C, 12 h.



Scheme 4 Plausible reaction mechanism

weak activity of palladium hydride complex **I** in the hydride addition with 2-alkenes. It is also a further indication for this mechanism involving a hydride addition–elimination procedure instead of a π-allylic pathway.[19]

In summary, we have shown that the in situ formed palladium catalyst system, generated from $PdCl_2(PPh_3)_2$ and $(EtO)_3SiH$, is a very useful catalyst for the one-carbon migration and subsequent isomerization of 4,4-biaryl-substituted 1-butenes, in which the hydrosilane [$(EtO)_3SiH$] plays a key role in the palladium-catalyzed isomerization of terminal alkenes. Various terminal alkenes tested in this work afforded the desired products though one-carbon migration of the carbon–carbon double bond and subsequent isomerization in good to excellent yields (up to 94% isolated yield) and good diastereoselectivity (*E*/*Z* ratio is up to 89:11).[20] Furthermore, this method provides a convenient access to the key building block of natural product cassumunin C in high yield and good diastereoselectivity (*E*/*Z* ratio = 4:1). Further studies on expanding the substrate scope with higher diastereoselectivity and exploring their applications in the synthesis of high value molecules are ongoing.

Acknowledgment

Financial support by the National Natural Science Foundation of China (NSFC Grant No. 21173064), Zhejiang Provincial Natural Science Foundation of China (ZPNSFC, Q12B020037), and Program for Excellent Young Teachers in Hangzhou Normal University (HNUEYT, JTAS 2011-01-014) is appreciated. XLW thank Dr. W.F. Chen of Hangzhou Normal University for helpful discussions.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

References and Notes

(1) Selected reviews: (a) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863. Selected examples: (b) Takahashi, A.; Kirio, Y.; Sodeoka, M.; Sasai, H.; Shibasaki, M. *J. Am. Chem. Soc.* **1989**, *111*, 643. (c) Williams, R. B.; Norris, A.; Slebodnick, C.; Merola, J.; Miller, J. S.; Andriantsiferana, R.; Rasamison, V. E.; Kingston, D. G. I. *J. Nat. Prod.* **2005**, *68*, 1371. (d) Jager, W. F.; de Jong, J.; de Lange, B.; Huck, N. P. M.; Meetsma, A.; Feringa, B. L. *Angew. Chem. Int. Ed.* **1995**, *34*, 348. (e) Vicario, J.; Walko, M.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2005**, *128*, 5127. (f) Lin, T. C.; Zheng, Q.; Chen, C. Y.; He, G. S.; Huang, W. J.; Ryasnyanskiy, A. I.; Prasad, P. N. *Chem. Commun.* **2008**, 389. (g) Lin, T. C.; Chen, Y. F.; Hu, C. L.; Hsu, C. S. *J. Mater. Chem.* **2009**, *19*, 7075. (h) Wakabayashi, R.; Ikeda, T.; Kubo, Y. Z.; Shinkai, S.; Takechi, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 6667. (i) Würthner, F.; Kaiser, T. E.; Saha-Möller, C. R. *Angew. Chem. Int. Ed.* **2011**, *50*, 3376. (j) Xu, L. W.; Chen, X. H.; Shen, H.; Deng, Y.; Jiang, J. X.; Jiang, K.; Lai, G. Q.; Sheng, C. Q. *Eur. J. Org. Chem.* **2012**, 290; and references cited therein.

(2) (a) Boutagy, J.; Thomas, R. *Chem. Rev.* **1974**, *74*, 87. (b) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863. (c) Phillips, D. J.; Pillinger, K. S.; Li, W.; Taylor, A. E.; Graham, A. E. *Chem. Commun.* **2006**, 2280. (d) Molander, G. A.; Figueroa, R. *J. Org. Chem.* **2006**, *71*, 6135. (e) Alonso, F.; Riente, P.; Yus, M. *Eur. J. Org. Chem.* **2009**, 6034. (f) Ramirez, E.; Sanchez, M.; Meza-Leon, R. L.; Quintero, L.; Sartillo-Piscil, F. *Tetrahedron Lett.* **2010**, *51*, 2178. (g) Dong, D. J.; Li, H. H.; Tian, S. K. *J. Am. Chem. Soc.* **2010**, *132*, 5018. (h) Zhou, R.; Wang, C. Z.; Song, H. B.; He, J. *Org. Lett.* **2010**, *12*, 976.

(3) (a) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780. (b) Ager, D. J. *Org. React.* **1990**, *38*, 1. (c) Assadi, N.; Pogodin, S.; Agranat, I. *Eur. J. Org. Chem.* **2011**, 6773. (d) Wei, G. Q.; Cohen, T. *Synlett* **2011**, 2697. (e) McNulty, J.; Das, P.; Gosciniak, D. *Tetrahedron Lett.* **2008**, *49*, 281. (f) Fernndez, M. C.; Diaz, A.; Guillin, J. J.; Blanco, O.; Ruiz, M.; Ojea, V. *J. Org. Chem.* **2006**, *71*, 6958. (g) Pulido, F. J.; Barberdo, A. *Nat. Protoc.* **2006**, *1*, 2068.

(4) Takai, K.; Nitta, K.; Utimoto, K. *J. Am. Chem. Soc.* **1986**, *108*, 7408.

(5) (a) Larock, R. C. *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*; Wiley-VCH: New York, **1999**, 2nd ed.. (b) Mackenzie, K. *The Chemistry of Alkenes*; Patai, S., Ed.; Wiley: New York, **1964**, 338–413.
(6) (a) Canovese, L.; Santo, C.; Visentin, F. *Organometallics* **2008**, *27*, 3577. (b) Kim, I. S.; Dong, G. R.; Jung, Y. H. *J. Org. Chem.* **2007**, *72*, 5424. (c) Yu, J.; Gaunt, M. J.; Spencer, J. B. *J. Org. Chem.* **2002**, *67*, 4627.
(7) For recent examples, see: (a) Manini, S.; Nelson, D. J.; Nolan, S. P. *ChemCatChem* **2013**, *5*, 2848. (b) Okamoto, R.; Tanaka, K. *Org. Lett.* **2013**, *15*, 2112. (c) Chianese, A. R.; Shaner, S. E.; Tendler, J. A.; Pudalov, D. M.; Shopov, D. Y.; Kim, D.; Rogers, S. L.; Mo, A. *Organometallics* **2012**, *31*, 7359. (d) Quintard, A.; Alexakis, A.; Mazet, C. *Angew. Chem. Int. Ed.* **2011**, *50*, 2354. (e) Lastra-Barreira, B.; Francos, J.; Crochet, P.; Cadierno, V. *Green Chem.* **2011**, *13*, 307. (f) Mantilli, L.; Gérard, D.; Toeche, S.; Besnard, C.; Mazet, C. *Chem. Eur. J.* **2010**, *16*, 12736. (g) Scarso, A.; Colladon, M.; Sgarbossa, P.; Santo, C.; Michelin, R. A.; Strukul, G. *Organometallics* **2010**, *29*, 1487. (h) Lim, H. J.; Smith, C. R.; RajanBabu, T. V. *J. Org. Chem.* **2009**, *74*, 4565. (i) Jennerjahn, R.; Pair, I.; Jackstell, R.; Franke, R.; Wiese, K. D.; Beller, M. *Chem. Eur. J.* **2009**, *15*, 6383. (j) Mantilli, L.; Gérard, D.; Toeche, S.; Besnard, C.; Mazet, C. *Angew. Chem. Int. Ed.* **2009**, *48*, 5143.
(8) For a highlight, see: Donohoe, T. J.; O'Riordan, T. J. C.; Rosa, C. P. *Angew. Chem. Int. Ed.* **2009**, *48*, 1014.
(9) Gauthier, D.; Lindhardt, A. T.; Olsen, E. P. K.; Overgaard, J.; Skrydstrup, T. *J. Am. Chem. Soc.* **2010**, *132*, 7998.
(10) Winston, M. S.; Oblad, P. F.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem. Int. Ed.* **2012**, *51*, 9822.
(11) Spallek, M. J.; Stockinger, S.; Goddard, R.; Trapp, O. *Adv. Synth. Catal.* **2012**, *354*, 1466.
(12) Fan, J.; Wan, C.; Wang, Q.; Gao, L.; Zheng, X.; Wang, Z. *Org. Biomol. Chem.* **2009**, *7*, 3168.
(13) Bai, X. F.; Xu, L. W.; Zheng, L. S.; Jiang, J. X.; Lai, G. Q.; Shang, J. Y. *Chem. Eur. J.* **2012**, *18*, 8174.
(14) Bai, X. F.; Ye, F.; Zheng, L. S.; Lai, G. Q.; Xia, C. G.; Xu, L. W. *Chem. Commun.* **2012**, *48*, 8592.
(15) (a) Masuda, T.; Jitoe, A.; Kida, A.; Takeda, Y. *Nat. Prod. Lett.* **1997**, *10*, 13. (b) Masuda, T.; Matsumura, H.; Oyama, Y.; Takeda, Y.; Jitoe, A.; Kida, A.; Hidaka, K. *J. Nat. Prod.* **1998**, *61*, 609. (c) Masuda, T.; Jitoe, A.; Nakatani, N. *Chem. Lett.* **1993**, 189. (d) Jitoe, A.; Masuda, T.; Mabry, T. J. *Tetrahedron Lett.* **1994**, *35*, 981.
(16) Masuda, T.; Jitoe, A. *J. Agric. Food Chem.* **1994**, *42*, 1850.
(17) (a) Han, J.; Cui, Z.; Wang, J.; Liu, Z. *Synth. Commun.* **2010**, *40*, 2042. (b) Jiang, Z. Y.; Zhang, C. H.; Gu, F. L.; Yang, K. F.; Lai, G. Q.; Xu, L. W. *Synlett* **2010**, 1251.
(18) Metal hydrides generated using hydrosilanes have been reported previously, for selected examples see: (a) Tanase, T.; Ohizumi, T.; Kobayashi, K.; Yamamoto, Y. *Organometallics* **1996**, *15*, 3404. (b) Schmidt, B. *J. Org. Chem.* **2004**, *69*, 7672. (c) Rahaim, R. J.; Maleczka, R. E. *Org. Lett.* **2005**, *7*, 5087.
(19) (a) Hosokawa, T.; Yamanaka, T.; Itotani, M.; Murahashi, S.-I. *J. Org. Chem.* **1995**, *60*, 6141. (b) Negishi, E.-i. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Vol. 2; John Wiley and Sons: New York, **2002**, 3424.
(20) **Typical Procedure for the Palladium-Catalyzed Isomerization**

4,4-Diarylbut-1-enes (0.5 mmol), $(EtO)_3SiH$ (0.1 mmol, 18.5 μL, 0.2 equiv) and a catalytic amount of $Pd(Ph_3P)_2Cl_2$ (0.005 mmol, 1 mol%) were added to a dry tube, and then the mixture was solved with dry THF (1 mL). The resulting mixture was stirred at 60 °C for 10 h. The mixture was then cooled to r.t., quenched by the addition of H_2O, and extracted by the addition of CH_2Cl_2. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography to give corresponding 4,4-diarylbut-1-enes. All the products were confirmed by GC–MS, NMR and IR spectrosopy. These data are provided in the Supporting Information.

Analytical Data for 1-Methyl-2-(1-phenylbut-2-enyl)benzene (3a)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (t, *J* = 6.8 Hz, 2 H), 7.23 (*J* = 6.8 Hz, 3 H), 7.14 (d, *J* = 6.8 Hz, 2 H), 6.87 (d, *J* = 6.8 Hz, 2 H), 5.94 (dd, *J* = 13.6, 7.6 Hz, 1 H), 5.74–5.68 (m, 0.14 H), 5.47 (dq, *J* = 14.8, 6.4 Hz, 0.88 H), 5.02 (d, *J* = 9.6 Hz, 0.14 H), 4.66 (d, *J* = 7.2 Hz, 0.86 H), 3.81 (s, 3 H), 1.77 (d, *J* = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 144.6, 136.5, 133.9, 129.5, 128.5, 128.3, 126.7, 126.1, 113.8, 55.3, 53.3, 18.0 ppm. GC–MS: *m/z* calcd for $C_{17}H_{18}$ $[M]^+$: 222.3; found: 222.1. IR (KBr): ν_{max} = 3412, 3059, 3025, 3000, 2957, 2931, 2853, 2835, 1653, 1608, 1510, 1493, 1448, 1302, 1250, 1178, 1150, 1034, 971, 830, 700, 560 cm^{-1}.

