Transition-Metal-Catalyzed Rearrangement of 1,1-(Oligomethylene)-4-aryl-2-butene-1,4-diols: Ring Expansion vs. Aryl Group Migration

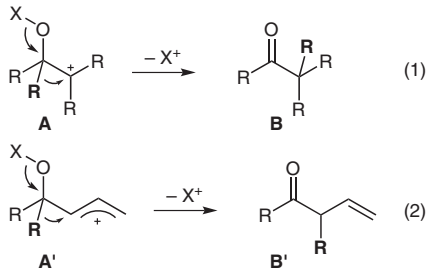
Alex Lange, Wolfgang Heydenreuter, Helge Menz, Stefan F. Kirsch*

Department Chemie and Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85747 Garching, Germany
Fax +49(89)13115; E-mail: stefan.kirsch@ch.tum.de

Received 13 July 2009

Abstract: The transition-metal-catalyzed rearrangement of 1,1-(oligomethylene)-4-aryl-2-butene-1,4-diols was investigated. In the presence of $PdCl_2(MeCN)_2$ and $Cu(OTf)_2$, a rapidly equilibrating 1,3-isomerization is followed by 1,2-migration to produce cyclopentanones or cyclohexanones through expansion of four- or five-membered ring systems. When employing larger ring systems or acyclic cores, aryl migration provides 2-aryl aldehydes.

Key words: rearrangements, alkenes, diols, transition metals, catalysis



Scheme 1 Pinacol-type rearrangements of carbocations

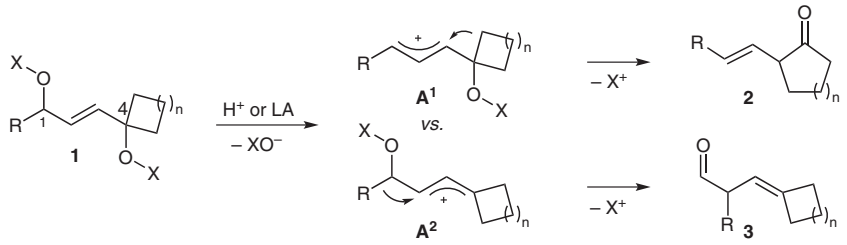
The scope and synthetic value of pinacol-type rearrangements have expanded greatly since the initial discovery of the pinacol–pinacolone rearrangement[1,2] about 150 years ago. While the classical rearrangement is the acid-catalyzed rearrangement of vicinal diols to aldehydes or ketones,[3] one might generally term all such 1,2-migrations that proceed through a carbocationic species with an adjacent hydroxyl group pinacol-type rearrangements (**A** → **B**; Scheme 1). Their utility has been demonstrated for a wide variety of synthetic applications,[4] in particular for the termination of cationic cyclization reactions.[5–8] Furthermore, the generation of carbocations **A** through direct alkene activation of vinyl carbinols also has been developed extensively,[9] and shown to be effective at ring expansion of cyclopropane and cyclobutane derivatives.

Although extensive studies have been conducted on the utility of pinacol-type rearrangements (through **A**), the related 'vinylogous' rearrangement of allylic cations of type **A′** has received much less attention (Scheme 1, eq. 2). In part, this neglect is due to the fact that the release of ring strain plays an important role to achieve clean rearrangement of allylic cation **A′** produced from a 2-butene-1,4-diol unit. Thus, this strategy was used almost exclusively for the pinacol-type ring expansion of vinylcyclopropanols.[10,11] Few protocols allow the pinacol-type rearrangement of other 2-butene-1,4-diol-containing substrates, all of which requiring strong protic acids and elevated temperatures.[12] For example, the *trans*-vinylog of benzpinacol was shown to undergo 1,2-phenyl group migration to give the β,γ-unsaturated ketone in boiling acetic acid.[12a] To our surprise, the general capability of substrates with 2-butene-1,4-diol units to trigger a pinacol-type rearrangement under formation of β,γ-unsaturated ketones and/or aldehydes was not evaluated.

As part of our program to explore pinacol-terminated cascade reactions,[8] we became interested in the synthetic potential of rearrangements resulting from putative cations of type **A′**. We felt that 2-butene-1,4-diol moieties may possess a greater value than shown before, and are prone to undergo 1,2-shifts in the presence of fairly mild protic acid and/or transition-metal catalysts. As will be demonstrated subsequently, pinacol-type rearrangements that yield carbonyl compounds can indeed be performed with aryl-substituted 2-butene-1,4-diols. Our studies also clarify the role of several reaction intermediates that occur in the course of the conversion.

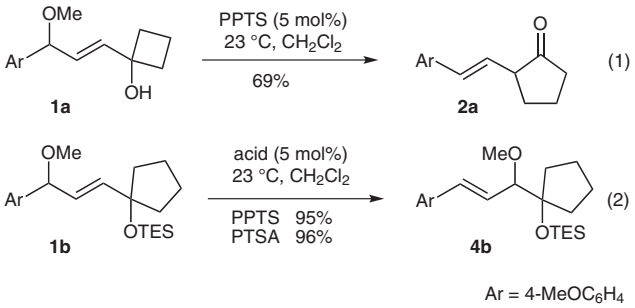
As illustrated in Scheme 2, treatment of 2-butene-1,4-diols of type **1** with protic acids or Lewis acids was expected to give allylic cations ($\mathbf{A^1}$ or $\mathbf{A^2}$) and subsequent 1,2-migration. At the outset of our studies, the focus was clearly on the ring expansion of cyclic systems other than cyclopropanols to produce cyclic ketones **2**. The first strategy identified for obtaining rearranged products involved substrates that would form an extended conjugated system upon cation formation in the presence of protic acids. We proposed that the rearrangement of 1-aryl-2-alkenol substrates would result in the direct formation of the ring-expansion product **2** due to the greater thermodynamic stability of cationic intermediate $\mathbf{A^1}$ when R = 4-$MeOC_6H_4$. Indeed, rearrangement of the four-membered ring system **1a** to afford cyclopentanone **2a** occurred readily at 23 °C in CH_2Cl_2 in the presence of catalytic amounts of various Brønsted acids. For example, pyridinium 4-toluenesulfonate (PPTS) was employed as a mild acid to provide **2a** in 69% yield after 12 hours (Scheme 3, eq. 1). Side products were not identified under the reaction conditions. To our surprise, the corresponding five-membered ring system **1b** did not undergo ring expansion

SYNLETT 2009, No. 18, pp 2987–2991
Advanced online publication: 09.10.2009
DOI: 10.1055/s-0029-1218274; Art ID: G23209ST



Scheme 2 Possible pathways

on treatment with a number of protic acids (Scheme 3, eq. 2). Experiments performed with **1b** at 23 °C in CH_2Cl_2 showed rapid consumption of the starting material. In all cases, conjugated system **4b** was formed in good yields upon isomerization. The use of other solvents led to no improvement with regard to the desired pinacol shift. Increasing the reaction temperature to 50 °C in $CDCl_3$ resulted in complete decomposition.[13]

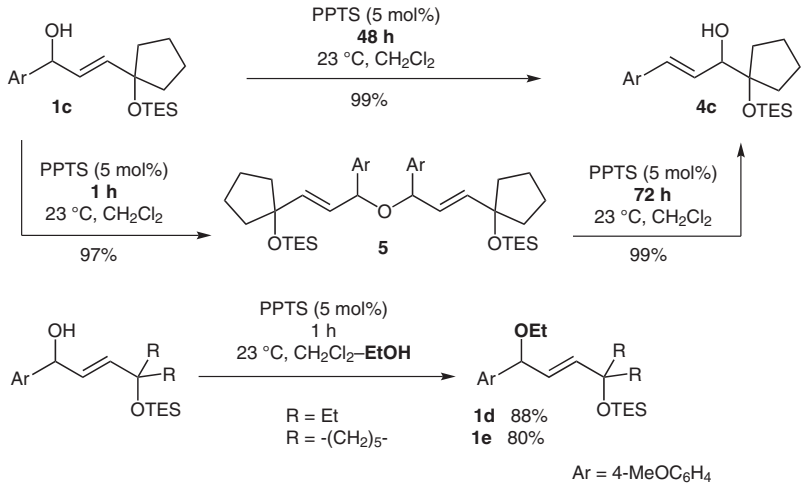


Scheme 3 H^+-catalyzed rearrangements of allylic ethers

It merits note that the ease with which methyl ether **1b** converts into isomer **4b** is somewhat uncommon although proton catalysis and transition-metal catalysis were reported to be highly effective for promoting the direct isomerization of arylpropenyl carbinols.[14,15] Accordingly, allylic alcohol **1c** also underwent clean 1,3-isomerization in the presence of PPTS under open-flask conditions (Scheme 4). This rearrangement proceeds through the rapid formation of diallylic ether intermediate **5**.[16] The regioselective substitution might be useful to construct various ethers as exemplified for the smooth formation of **1d** and **1e**.

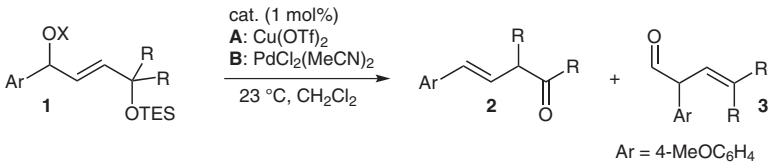
Next, we examined the use of transition-metal catalysts to trigger a pinacol-type rearrangement with substrates other than **1a** as this four-membered ring system is prone to ring expansion. Initial survey experiments showed that the rearrangement of five-membered ring systems **1b** to the corresponding cyclohexanone **2b** was promoted in $CDCl_3$ at 23 °C by addition of 1 mol% of various Lewis acids: $Zn(OTf)_2$ (13%, 12 h), $KAuCl_4$ (92%, 1 h), $Yb(OTf)_3$ (16%, 12 h), $PtCl_2$ (96%, 12 h), $AgSbF_6$ (98%, 10 min), $PdCl_2(MeCN)_2$ (84%, 12 h), $Cu(OTf)_2$ (94%, 30 min), $Bi(OTf)_3$ (79%, 12 h).[17] In particular with $PdCl_2(MeCN)_2$ and $Cu(OTf)_2$ (Table 1, entries 2 and 3), the reaction was remarkably free of competing side reactions proceeding more rapidly with the latter catalyst.[18] Analogous substrates such as allylic alcohol **1c** and silyl ether **1f** also undergo the rearrangement indicating that the exact type of leaving group (XO^-) at C1 has only a minor influence on the reaction outcome (Table 1).

As shown in Table 1, substrates containing a six-membered and a seven-membered ring system **1g–i** do not undergo ring expansion under the reaction conditions.[19] Instead, exclusive aryl-group migration takes place to yield cleanly aldehydes **3a** and **3b**.[20] In the presence of $Cu(OTf)_2$, these reactions were considerably slower than the corresponding reactions with smaller ring systems that gave carbonyls of type **2**. In the case of acyclic substrate **1j** with R = Et, a mixture of aldehyde **3c** (63% formed by



Scheme 4 H^+-catalyzed rearrangements of allylic alcohols

Table 1 Transition-Metal-Catalyzed Rearrangements[a]

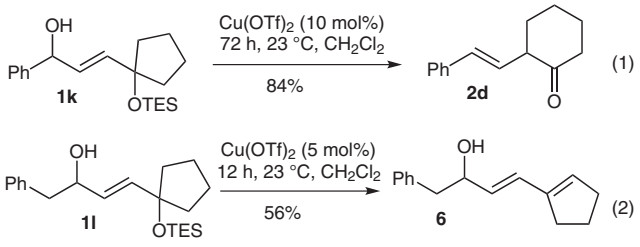


Entry	R	X	1	Cat.	Time (h)	Yield of **2** (%)[b]	Yield of **3** (%)[b]
1[d,f]	-$(CH_2)_3$-	Me	**1a**	**A**	0.5	72 (**2a**)	0
2[d]	-$(CH_2)_4$-	Me	**1b**	**A**	0.5	94 (**2b**)	0
3[d]	-$(CH_2)_4$-	Me	**1b**	**B**	12	84 (**2b**)	0
4[d]	-$(CH_2)_4$-	H	**1c**	**A**	0.5	96 (**2b**)	0
5	-$(CH_2)_4$-	TES	**1f**	**B**	12	78[c] (**2b**)	0
6	-$(CH_2)_5$-	H	**1g**	**A**	0.5	0	9[c] (**3a**)
7[e]	-$(CH_2)_5$-	H	**1g**	**A**	12	0	79 (**3a**)
8[e]	-$(CH_2)_5$-	H	**1g**	**B**	12	0	81 (**3a**)
9[e]	-$(CH_2)_6$-	H	**1h**	**B**	12	0	80 (**3b**)
10[e]	-$(CH_2)_6$-	Me	**1i**	**A**	12	0	82 (**3b**)
11	Et	H	**1j**	**A**	12	12 (**2c**)	63 (**3c**)

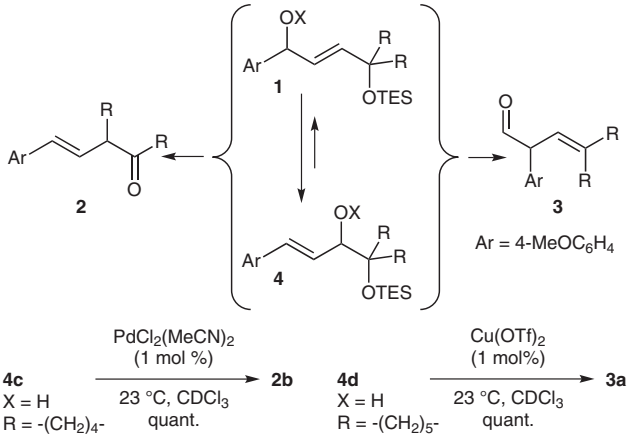
[a] Conditions: 1 mol% catalyst [**A**: $Cu(OTf)_2$; **B**: $PdCl_2(CH_3CN)_2$], [substrate] = 0.1 M, 23 °C, CH_2Cl_2.
[b] Yield after column chromatography unless otherwise indicated.
[c] Determined by ^1H NMR.
[d] Formation of **3** was not observed in the ^1H NMR of the crude reaction mixture.
[e] Formation of **2** was not observed in the ^1H NMR of the crude reaction mixture.
[f] Compound **1a** contains a free hydroxy instead of triethylsilyloxy.

aryl-group migration) and ketone **2c** (12% formed by ethyl-group migration) was obtained. The use of other solvents and other transition-metal catalysts led to little alteration in the product distribution.

To confirm that the substituent R at C1 plays a significant role in the catalyzed rearrangements reported here, substrates with R ≠ 4-$MeOC_6H_4$ were examined under similar conditions. When **1k** (R = Ph) was treated with 10 mol% of $Cu(OTf)_2$, the reaction required 72 hours to obtain full conversion, thus indicating a significant rate contribution through the methoxy substituent at the *para* position of the phenyl (Scheme 5, eq. 1). As exemplified for the reaction of **1l** (R = Bn), if substrates with substituents other than aryl are employed, no rearrangement occurs leading instead to elimination products.[21]



Scheme 5 Influence of substituents at C1 on the reaction outcome



Scheme 6 Evidence for rapid equilibrium of **1** and **4** in the presence of Lewis acids

Although we feel a detailed discussion of the mechanism of the transition-metal-catalyzed rearrangement is premature at this point, ^1H NMR monitoring of the reaction of **1c** in the presence of $PdCl_2(MeCN)_2$ shows the expected 1,3-isomerization into intermediate **4c** (via **5**), which subsequently undergoes ring expansion to **2b**. When monitoring the conversion of **1g** in the presence of $Cu(OTf)_2$, we observed that 1,3-isomerization providing **4d** occurs more rapidly than transformation into aldehyde **3a**. Since both

isolated **4c** and isolated **4d** undergo quantitative 1,2-migration to the corresponding rearrangement products (**2b** and **3a**) when transition-metal catalysts are present (Scheme 6), these observations are most consistent with the rapid equilibrium of **1** and **4**.[22] Nevertheless, that **1** and **4** are equilibrated more rapidly than they undergo a pinacol-type shift does not explain why the selectivity (formation of **2** vs. **3**) is completely reversed when going from the five-membered to the six-membered ring system.

In conclusion, we have described the first studies on transition-metal-catalyzed rearrangements of aryl-substituted 2-butene-1,4-diol units. While cyclobutane **1a** and cyclopentanes **1b–f** and **1k** were shown to undergo clean ring expansion to 2-styryl-substituted cyclopentanones and cyclohexanones of type **2**, aryl-group migration yielding 2-aryl aldehydes **3** was found to be the preferred pathway when employing substrates that possess either other ring sizes or an acyclic core.[23] The reaction outcome is predictable, and the 1,2-migration follows a rapidly equilibrating 1,3-isomerization.

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

Acknowledgment

This project was supported by the Deutsche Forschungsgemeinschaft (DFG). We thank Prof. Dr. Th. Bach for fruitful discussions and generous support.

References and Notes

(1) (a) Fittig, R. *Justus Liebigs Ann. Chem.* **1859**, *110*, 23. (b) Butlerov, A. *Justus Liebigs Ann. Chem.* **1874**, *174*, 125. (c) Mundy, B. P.; Otzenberger, R. D. *J. Org. Chem.* **1973**, *38*, 2109.

(2) For an Essay on the discovery, see: Berson, J. A. *Angew. Chem. Int. Ed.* **2002**, *114*, 4849.

(3) Collins, C. J. *Q. Rev. Chem. Soc.* **1960**, *14*, 357.

(4) For recent examples, see inter alia: (a) Suzuki, K.; Takikawa, H.; Hachisu, Y.; Bode, J. W. *Angew. Chem. Int. Ed.* **2007**, *46*, 3252. (b) Reisman, S. E.; Ready, J. M.; Hasuoka, A.; Smith, C. J.; Wood, J. L. *J. Am. Chem. Soc.* **2006**, *128*, 1448. (c) Alvarez-Manzaneda, E.; Chahboun, R.; Barranco, I.; Cabrera, E.; Alvarez, E.; Lara, A.; Alvarez-Manzaneda, R.; Hmamouchi, M.; Es-Samti, H. *Tetrahedron* **2007**, *63*, 11943. (d) Frongia, A.; Girard, C.; Ollivier, J.; Piras, P. P.; Secci, F. *Synlett* **2008**, 2823.

(5) (a) Trost, B. M.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 6556. (b) Trost, B. M.; Brandi, A. *J. Am. Chem. Soc.* **1984**, *106*, 5041. (c) Sworin, M.; Neumann, W. L. *J. Org. Chem.* **1988**, *53*, 4894. (d) Nakamura, T.; Matsui, T.; Tanino, K.; Kuwajima, I. *J. Org. Chem.* **1997**, *62*, 3032. (e) Youn, J.-H.; Lee, J.; Cha, J. K. *Org. Lett.* **2001**, *3*, 2935.

(6) For a review on Prins pinacol cascades, see: (a) Overman, L. E.; Pennington, L. D. *J. Org. Chem.* **2003**, *68*, 7143. For selected examples and synthetic applications, see: (b) Grese, T. A.; Hutchinson, K. D.; Overman, L. E. *J. Org. Chem.* **1993**, *58*, 2468. (c) Hirst, G. C.; Johnson, T. O.; Overman, L. E. *J. Am. Chem. Soc.* **1993**, *115*, 2992. (d) Mulzer, J.; Greifenberg, S.; Buschmann, J.; Luger, P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1173. (e) MacMillan, D. W. C.; Overman, L. E.; Pennington, L. D. *J. Am. Chem. Soc.* **2001**, *123*, 9033.

(7) For a review on the use of carbophilic Lewis acids in combination with pinacol-type rearrangments, see: Crone, B.; Kirsch, S. F. *Chem. Eur. J.* **2008**, *14*, 3514.

(8) For our works in the field, see: (a) Kirsch, S. F.; Binder, J. T.; Crone, B.; Duschek, A.; Haug, T. T.; Liébert, C.; Menz, H. *Angew. Chem. Int. Ed.* **2007**, *46*, 2310. (b) Menz, H.; Binder, J. T.; Crone, B.; Duschek, A.; Haug, T. T.; Kirsch, S. F.; Klahn, P.; Liébert, C. *Tetrahedron* **2009**, *65*, 1880. (c) Kirsch, S. F.; Binder, J. T.; Liébert, C.; Menz, H. *Angew. Chem. Int. Ed.* **2006**, *45*, 5878. (d) Binder, J. T.; Crone, B.; Kirsch, S. F.; Liébert, C.; Menz, H. *Eur. J. Org. Chem.* **2007**, 1636. (e) Crone, B.; Kirsch, S. F. *J. Org. Chem.* **2007**, *72*, 5435. (f) Baskar, B.; Bae, H. J.; An, S. E.; Cheong, J. Y.; Rhee, Y. H.; Duschek, A.; Kirsch, S. F. *Org. Lett.* **2008**, *10*, 2605.

(9) (a) Wassermann, H. H.; Cochoy, R. E.; Baird, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 2375. (b) Wassermann, H. H.; Hearn, M. J.; Cochoy, R. *J. Org Chem.* **1980**, *45*, 2874. (c) Wienand, A.; Reissig, H.-U. *Chem. Ber.* **1991**, *124*, 957. (d) Nishimura, T.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **1999**, *121*, 2645. (e) Hegedus, L. S.; Ranslow, P. B. *Synthesis* **2000**, 953. (f) Nishimura, T.; Ohe, K.; Uemura, S. *J. Org. Chem.* **2001**, *66*, 1455. (g) Markham, J. P.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 9708.

(10) For seminal works, see: (a) Ollivier, J.; Legros, J.-Y.; Fiaud, J.-C.; de Meijere, A.; Salaün, J. *Tetrahedron Lett.* **1990**, *31*, 4135. (b) Ollivier, J.; Salaün, J. *Tetrahedron Lett.* **1984**, *25*, 1269. (c) Salaün, J.; Karkour, B. *Tetrahedron Lett.* **1988**, *29*, 1537. (d) Funayama, S.; Eda, S.; Komiyama, K.; Ohmura, S.; Tokunaga, T. *Tetrahedron Lett.* **1989**, *30*, 3151. (e) Salaün, J.; Karkour, B. *Tetrahedron Lett.* **1987**, *28*, 4669.

(11) For an asymmetric Wagner–Meerwein shift related to this pinacol rearrangement, see: Trost, B. M.; Yasukata, T. *J. Am. Chem. Soc.* **2001**, *123*, 7162.

(12) (a) Lutz, R. E.; Bass, R. G.; Boykin, D. W. *J. Org. Chem.* **1964**, *29*, 3660. (b) Saito, K.; Horie, Y.; Mukai, T.; Toda, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3118. (c) Uyehara, T.; Kawai, Y.; Yamada, J.-i.; Kato, T. *Chem Lett.* **1987**, *16*, 137.

(13) Exposure of six-membered ring substrate **1c** to 5 mol% of PPTS at 23 °C in CH_2Cl_2 provided an inseparable mixture of **3c** and **4c** in low yields (e.g., 29% after 14 h).

(14) Protic acid catalysis: (a) Braude, E. A.; Fawcett, J. S.; Newman, D. D. E. *J. Chem. Soc.* **1950**, 793. (b) Braude, E. A.; Jones, E. R. H.; Stern, E. S. *J. Chem. Soc.* **1946**, 396. (c) Braude, E. A.; Jones, E. R. H. *J. Chem. Soc.* **1944**, 436. (d) Braude, E.; Stern, E. *J. Chem. Soc.* **1947**, 1096. (e) Sanz, R.; Martínez, A.; Miguel, D.; Álvarez-Gutiérres, J. M.; Rodríguez, F. *Adv. Synth. Catal.* **2006**, *348*, 1841.

(15) Lewis acid catalysis: (a) Mukhopadhyay, M.; Reddy, M. M.; Maikap, G. C.; Iqbal, J. *J. Org. Chem.* **1995**, *60*, 2670. (b) Li, C.-J.; Wang, D.; Chen, D.-L. *J. Am. Chem. Soc.* **1995**, *117*, 12867. (c) Malkov, A. V.; Baxendale, I.; Mansfield, D. J.; Kocovsky, P. *Tetrahedron Lett.* **1995**, *38*, 6351. (d) Morrill, C.; Beutner, G. L.; Grubbs, R. H. *J. Org. Chem.* **2006**, *71*, 7813. (e) Kitamura, M.; Hayashi, H.; Yano, M.; Tanaka, T.; Maezaki, M. *Heterocycles* **2007**, *71*, 2669.

(16) For a related case, see inter alia: Wang, J.; Huang, W.; Zhang, Z.; Xiang, X.; Liu, R.; Zhou, X. *J. Org. Chem.* **2009**, *74*, 3299.

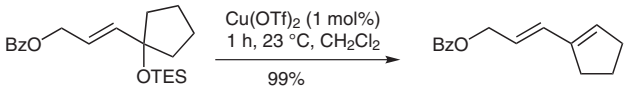
(17) Reaction of **1b** in the presence of $MgBr_2$ (5 mol%) led to clean formation of **4b** without traces of **2b** (or **3b**).

(18) **Synthesis of (*E*)-2-(4-Methoxystyryl)cyclohexanone (2b)**
$Cu(OTf)_2$ (1 mg, 0.003 mmol, 1 mol%) was added to a solution of (*E*)-1-(4-methoxyphenyl)-3-(1-(triethylsilyloxy)cyclopentyl)prop-2-en-1-ol (**1c**, 100 mg, 0.28 mmol) in CH_2Cl_2 (2.8 mL) and stirred at r.t. for 30 min (until TLC analysis indicated complete conversion). The reaction mixture was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica (pentanes–Et_2O = 95:5). Compound **2b** was obtained as a colorless solid in 96% yield (62 mg, 0.27 mmol). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.69–1.83 (m, 3 H), 1.89–1.96 (m, 1 H), 2.01–2.09 (m, 1 H), 2.14–2.20 (m, 1 H), 2.31–2.40 (m, 1 H), 2.45–2.51 (m, 1 H), 3.17 (ddd, *J* = 0.9, 6.4, 11.3 Hz, 1 H), 3.80 (s, 3 H), 6.27 (dd, *J* = 5.9, 16.1 Hz, 1 H), 6.33 (d, *J* = 16.1 Hz, 1 H), 6.77–6.91 (m, 2 H), 7.29–7.33 (m, 2 H). ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 24.4 (t), 27.6 (t), 34.5 (t), 41.7 (t), 54.0 (d), 55.3 (d), 113.9 (d), 125.3 (d), 127.4 (d), 130.0 (s), 130.8 (d), 159.0 (s), 211.3 (s). LRMS (EI): *m/z* = 230 (100)[M^+], 202 (26), 173 (25), 159 (21), 134 (38), 121 (37). HRMS: *m/z* calcd for $C_{15}H_{18}O_2$ [M^+]: 230.1307; found: 230.1307.

(19) For the construction of seven-membered ring systems through pinacol-type ring expansion, see the following review: Kantorowski, E. J.; Kurth, M. J. *Tetrahedron* **2000**, *56*, 4317.

(20) **Synthesis of 3-Cyclohexylidene-2-(4-methoxyphenyl)-propanal (3a)**
Following the procedure to prepare **2b**,[18] allylic alcohol **1g** (100 mg, 0.26 mmol) was converted into the corresponding aldehyde **3a** in the presence of $Cu(OTf)_2$ (1 mg, 1 mol%). The reaction mixture was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica (pentanes–Et_2O = 95:5). Compound **3a** was obtained in 79% yield (50 mg, 0.20 mmol). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.45–1.59 (m, 6 H), 2.12–2.20 (m, 4 H), 3.80 (s, 3 H), 4.41 (dd, *J* = 2.6, 8.8 Hz, 1 H), 5.39–5.46 (m, 1 H), 6.88–6.94 (m, 2 H), 7.13–7.19 (m, 2 H), 9.55 (d, *J* = 2.6 Hz, 1 H). ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 26.6, 27.6, 28.5, 29.6, 37.3, 55.3, 56.3, 114.4, 115.1, 128.9, 129.4, 145.7, 158.8, 198.5. LRMS (EI): *m/z* = 244 (2) [M^+], 215 (100), 147 (23), 121 (25). HRMS: *m/z* calcd for $C_{16}H_{20}O_2$ [M^+]: 244.1463; found: 244.1468.

(21) We also observed a high-yielding elimination when using 2-butene-1,4-diols that possess Bz-protected primary allylic alcohols. According to preliminary studies, this elimination appears to be quite general (Scheme 7).



Scheme 7

(22) In seminal studies on related 1,3-isomerizations of phenylpropenyl carbinols, chirality transfer was reported:

(23) (a) Kenyon, J.; Partridge, S. M.; Phillips, H. *J. Chem. Soc.* **1937**, 207. (b) See also: Vikhe, Y. S.; Hande, S. M.; Kawai, N.; Uenishi, J. *J. Org. Chem.* **2009**, *74*, 5174.

(24) This correlates with the migratory aptitude observed in Wagner–Meerwein shifts.