JOC*Note*

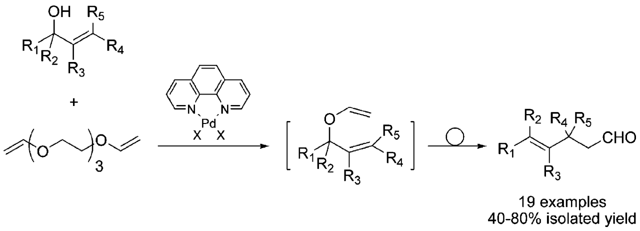
Tandem Pd(II)-Catalyzed Vinyl Ether Exchange−Claisen Rearrangement as a Facile Approach to γ,δ-Unsaturated Aldehydes

Xudong Wei,* Jon C. Lorenz, Suresh Kapadia, Anjan Saha,
Nizar Haddad, Carl A. Busacca, and Chris H. Senanayake

Department of Chemical Development, Boehringer Ingelheim
Pharmaceuticals, Inc., 900 Ridgebury Road,
Ridgefield, Connecticut 06877

xwei@rdg.boehringer-ingelheim.com

Received December 12, 2006



A sequential allyl vinyl ether formation−Claisen rearrangement process catalyzed by a palladium(II)−phenanthroline complex is reported. The effects of allylic alcohol structure, type of vinylating agent, and palladium catalysts are discussed. This method provides a convenient approach to γ,δ-unsaturated aldehydes under mild conditions that avoid the use of toxic Hg(II) catalysts. The new methodology has been successfully demonstrated on the kilogram scale.

Recently in our research work we needed a series of low molecular weight γ,δ-unsaturated aldehydes as building blocks for SAR studies. Although many of these compounds are known, surprisingly few practical laboratory methods suitable for their preparation in the gram to kilogram scale are available. Synthesis of the requisite γ,δ-unsaturated ester or ketone from an allylic alcohol and an ortho ester or enol ether catalyzed by protic acid (the Johnson−Claisen ortho ester Claisen rearrangement)[1,2] is a well-established reaction, and the corresponding aldehydes are often prepared from the esters by further reduction/reoxidation steps.[1b,3] Drawbacks associated with this three-step sequence are not only the use of moisture-sensitive reductants and oxidants, which is undesirable in large-scale synthesis, but also the lengthy and sometimes problematic workup operations. The difficulty behind a direct Claisen approach to aldehydes is,[4] in many cases, the formation of allyl vinyl ethers from acetal elimination, presumably due to the lack of additional oxygen stabilization of the carbocation intermediate. A Lewis acid-catalyzed vinyl ether exchange process has been proven to be mild and specific, but so far only toxic Hg(II) has been successfully applied in such a tandem vinyl ether exchange−Claisen rearrangement process.[5] Alternative approaches to allyl vinyl ethers include the reaction of allyl esters with Tebbe's reagent,[6] preparation from silyl enol ethers,[7] and aldol condensation of unsaturated esters.[8] Several elegant vinyl ether formation−Claisen rearrangement sequences leading to γ,δ-unsaturated aldehydes are known, including the β-haloethyl allyl ammonium salt approach developed by Laird,[9] the β-halo ethyl ether elimination approach developed by Dulcère,[10] the allyl oxide addition to (*E*)-carboxyvinyltrimethylamonium betaine Claisen rearrangement−decarboxylation method developed by Büchi,[11] the Rh(II)-catalyzed Bamford−Stevens/Claisen rearrangement sequence developed by Stoltz,[12] a copper-catalyzed C−O coupling−Claisen rearrangement process developed by Buchwald,[13] and the diallyl ether isomerization method developed by Nelson.[14] While often useful, some of these methods require harsh conditions, are limited to certain types of substitution patterns, or need high loadings of catalysts and reagents.

It has long been known that Pd(II) salts such as Pd(OAc)$_2$ or **I** are also effective Lewis acid catalysts for the vinyl ether exchange reaction.[15] McKeon and Fitton reported that Pd(OAc)$_2$ can be stabilized by *cis*-bidentate ligands such as phenanthroline or 2,2′-bipyridyl while still maintaining its activity.[16] These catalysts have been employed for the synthesis of vinyl ethers of steroids, glycidol, and sugars.[17] Recently, Schlaf and Bosch optimized the vinyl ether exchange reaction by using a more soluble and Lewis acidic complex of palladium trifluoroacetate and 4,7-diphenyl-1,10-phenanthroline (**IVb**) as catalyst.[18] In addition, an elegant Ir-catalyzed vinyl ether synthesis with vinyl acetate/Na_2CO_3 has been developed by Ishii et al.[19] However, a *tandem* Pd(II)-catalyzed allyl vinyl ether formation−Claisen rearrangement process has not yet been reported.

---

[1] For Ireland−Claisen and the Johnson ortho ester Claisen rearrangements: (a) Ireland, R. E.; Mueller, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 5897. (b) Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.-T.; Faulkner, D. J.; Petersen, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741.

[2] For a most recent review of Claisen rearrangement: Castro, A. M. M. *Chem. Rev.* **2004**, *104* (6), 2939 -3002.

[3] For example: Valentine, J. C.; McDonald, F. E.; Neiwert, W. A.; Hardcastle, K. I. *J. Am. Chem. Soc.*; **2005**, *127*, 4586−4587. Baldwin, I. R.; Whitby, R. J. *Chem. Commun.* **2003**, 2786−2787.

[4] H^+ catalyzed: Thomas, A. F. *J. Am. Chem. Soc.* **1969**, *91*, 3281. Dauben, W. G.; Dietsche, T. J. *J. Org. Chem.* **1972**, *37*, 1212.

[5] Hg^{2+} catalyzed: (a) Watanabe, W. H.; Conlon, L. E. *J. Am. Chem. Soc.* **1957**, *79*, 2828. Church, R. F.; Ireland, R. E.; Marshall, J. A. *J. Org. Chem.* **1966**, *31*, 2526. (b) Saucy, G.; Marbet, R. *Helv. Chim. Acta* **1967**, *50*, 2091.

[6] Kinney, W. A.; Coghlan, M. J.; Paquette, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 7352−7360.

[7] Maeda, K.; Shinokubo, H.; Oshima, K.; Utimoto, K. *J. Org. Chem.* **1996**, *61*, 2262−2263.

[8] Hiersemann, M. *Synthesis* **2000**, 1279−1290.

[9] Laird, T.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1477−1486.

[10] Dulcère, J.-P.; Rodriguez, J. *Synthesis* **1993**, 399.

[11] Büchi, G.; Vogel, D. E. *J. Org. Chem.* **1983**, *48*, 5406−5408.

[12] May, J. A.; Stoltz, B. M. *J. Am. Chem. Soc.* **2002**, *124*, 12426.

[13] Nordmann, G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 4978−4979.

[14] Nelson, S. G.; Wang, K. *J. Am. Chem. Soc.*, **2006**, *128*, 4232−4233 and references cited therein.

[15] McKeon, J. E.; Fitton, P.; Griswold, A. A. *Tetrahedron* **1972**, *28*, 227−232.

[16] McKeon, J. E.; Fitton, P. *Tetrahedron* **1972**, *28*, 233−238.

[17] (a) Weintraub, P. M.; King, C.-H. *J. Org. Chem.* **1997**, *62*, 1560−1562. (b) Tachibana, T.; Aihara, T. CAN: 112:138900; JP 01272577; Seimi Chemical Co., Ltd. Japan, 1989. (c) Handerson, S.; Schlaf, M. *Org. Lett.* **2002**, *4*, 407−409.

[18] Bosch, M.; Schlaf, M. *J. Org. Chem.* **2003**, *68*, 5225−5227.

[19] Okimoto, Y.; Sakaguchi, S.; Ishii, Y. *J. Am. Chem. Soc.* **2002**, *124*, 1590.

10.1021/jo062548f CCC: $37.00

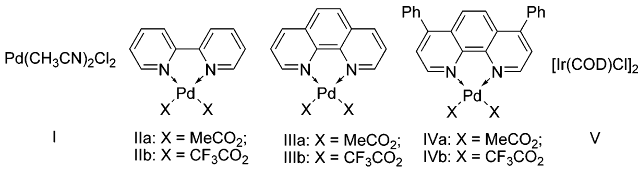


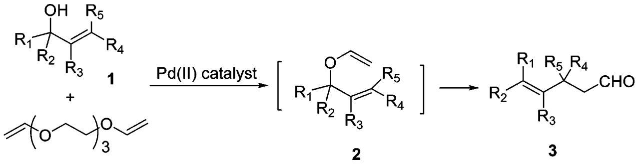
FIGURE 1. Pd(II) and Ir(I) catalysts.

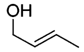
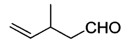
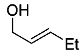
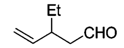
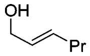
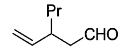
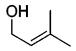
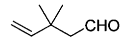
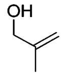
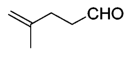
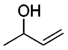
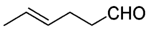
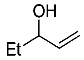
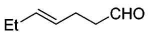
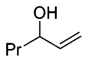
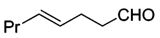
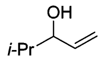
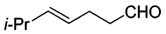
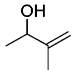
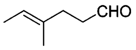
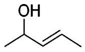
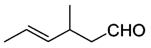
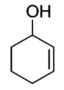
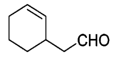
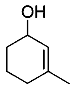
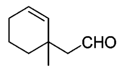
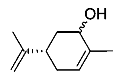
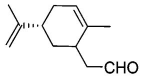
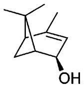
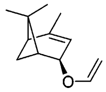
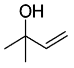
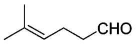
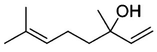
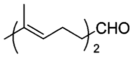
In view of the low cost of many vinylating reagents, fair catalytic turnover numbers, and mild reaction conditions, we explored the possibility of devising a tandem Pd(II)-catalyzed vinylation−Claisen rearrangement process for the preparation of the desired γ,δ-unsaturated aldehydes.[20] Herein we report our results.

Results and Discussion. Several incorporated design features should be noted here. (1) As many Claisen rearrangements require a high temperature to proceed, a vinylating agent with a high boiling point is desired. The large difference between the boiling points of vinylating agent and product should also facilitate distillative isolation. (2) The equilibrium nature of the vinylation reaction requires an excess of vinylating agent. To achieve atom and volume efficiency, a vinyl ether with low molecular weight is therefore preferred. (3) A more polar reaction medium would be expected to increase the reaction rate. (4) Both the vinylating reagent and the catalyst have to be commercially available and inexpensive. Commercial triethyleneglycol divinyl ether (TGDV) fulfills all of the above requirements. It possesses a high boiling point (>120 °C/18 mmHg), relatively low molecular weight (as two vinyl ether units are available in one molecule), increased polarity, and a modest price of ca. $90/kg.

Using 1.5 equiv of TGDV as starting material and solvent, we were delighted to find that a series of primary allylic alcohols underwent the vinyl ether exchange reaction efficiently at 70−75 °C when the complex of Pd(OAc)$_2$ and 1,10-phenanthroline was used as catalyst (Table 1, entries a to e). The superior ligand 4,7-diphenyl-1,10-phenanthroline, used in ref 18 for better solubility, is not necessary here, because TGDV dissolves the less soluble 1,10-phenanthroline complex catalyst without any difficulties. Claisen rearrangement, however, proceeded very slowly under these conditions, and only trace amounts of aldehyde could be observed even after prolonged reaction time. Reactions at higher temperature were also tried but failed, most likely due to significant decomposition of Pd(II) catalyst at temperatures above ~90 °C giving palladium black. The Pd(OAc)$_2$ complex (**IIIa** or **IVa)** is usually active enough, very likely benefiting from the high polarity of TGDV. For example, reaction of 3-methylbutenol reached its theoretical equilibrium ratio of ca. 75−80% readily within 6 h at 70 °C with Pd(OAc)$_2$ complex **IIIa** or **IVa** in TGDV (Table 1 entry d), but the same vinylation reaction with **IVa** failed when 20 equiv of butyl vinyl ether was used as vinylating agent (Table 1, entry 18 in ref 18). The reaction was normally faster when the Pd(tfa)$_2$ complex (**IIIb**) was employed, but 10−20 mol % of Hünig's base

TABLE 1. Pd(II)-Catalyzed Vinylation−Claisen Rearrangement



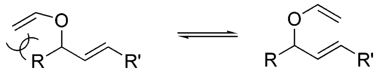
Entry	Alcohol (**1**)	Catalyst[a]/ Condition[b]	Product **3**	Yield (%)[c]
a		IIIa / A IIIb / A		60 (75) 60 (78)
b		IIIa / A IIIb / A		60 (78) 60 (78)
c		IIIa / A		54 (75)
d		IIIa / A IVa / A IIIb / A		60 (75) 60 (75) 60 (75)
e		IIIa / A IIIb / A		52 (70)[e] 60 (80)[e]
f		IIIa / B IIIb / B		68 (85) 60 (90)
g		IIIa / B IIIb / B		72 (92) 72 (91)
h		IIIa / B IIIb / B		72 (90) 71 (88)
i		IIIb / B		73 (92)
j		IIIb / B	 *E*:Z = 8:1	70 (85)
k		IIIa / B IIIb / B		75 (95) 72 (85)
l		IIIa / A		40[d] (75)[e]
m		IIIa / A		55 (76)
n		IIIa / A		70 (75)
o	 verbenol	IIIa / A	 **2o**	75 (83)
p		IIIa / B IIIb / B		68 (90)
q	 linalool	IIIa / B IIIb / B	 *E*:Z = 1.5:1	- (15) 80 (95)

[a] When **IIIb** was used as catalyst, Hünig's base (i-Pr$_2$NEt) was added as counter base to inhibit acetal formation. [b] Condition A: 50 mmol of allylic alcohol, 75 mmol of TGDV, and 0.5 mol % catalyst was stirred at 70 °C for 5−15 h, then 120−150 °C for 5−9 h. Condition B: 50 mmol of allylic alcohol, 75 mmol of TGDV. and 0.5 mol % catalyst was stirred at 85 °C for 24−48 h, then 120 °C for 0.5 h. [c] Isolated yield. Numbers in parentheses are yields based on ^{1}H NMR before isolation. [d] Rearrangement was conducted at 190 °C. [e] About 5−10% impurities remained in the product even after two distillations.

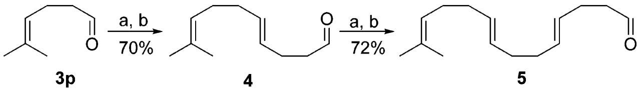
---

(20) Our initial experiments of 3-methyl-2-buten-1-ol and vinyl acetate catalyzed by 1% [Ir(COD)Cl]$_2$ (**V**) at 100 °C in toluene following the method of Ishii (ref 19) gave 3,3-pentenal in ca. 35% yield (NMR) with some difficulties in isolation of the volatile product from the toluene reaction mixture. No reaction was observed with the secondary alcohol 1-penten-3-ol. During the preparation of this paper, Ishii's group published their Ir-catalyzed vinylation−Claisen rearrangement method, yet it was limited to primary allylic alcohols. Masao, M.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **2006**, *71*, 6285−6286.

SCHEME 1. Substitution Effect on Claisen Rearrangement



SCHEME 2. Iterative Vinylation−Claisen Rearrangement[a]



[a] Reagents and conditions: (a) $CH_2{=}CHMgBr$, −78 to 0 °C; (b) 1.5 equiv of TGDV, 0.5% $Pd(OAc)_2$-phenanthroline, 75−80 °C, 48 h.

ortriethylamine had to be used to inhibit acetal formation caused by the higher acidity of trifluoroacetic acid, as described in ref 18. When the vinyl ether exchange step reached equilibrium (easily monitored by ^{1}H NMR), the temperature was raised to ca. 120−150 °C and the Claisen rearrangement initiated immediately, again easily tracked by ^{1}H NMR. When the rearrangement reaction was complete, the product was readily isolated by flash distillation under vacuum (ca. 100 mmHg). The product thus obtained normally contained small amounts of remaining allylic alcohol or other impurities. A second distillation produced highly pure aldehyde suitable for our synthetic purposes.

The reaction of acyclic secondary allylic alcohols (Table 1, entries f to k) showed interesting differences from those of primary alcohols. Vinyl ether exchange can also be catalyzed by either **IIIa** or **IIIb** efficiently, usually requiring less than 24 h to finish. However, the Claisen rearrangement step itself seems to proceed at a faster rate, as rearranged product can be observed even at a temperature as low as 80 °C, within the same temperature range for the vinyl ether exchange step. This facilitates the overall reaction significantly, as the irreversible Claisen rearrangement consumes the allyl vinyl ether, therefore driving the equilibrium further to the right-hand side, so a higher conversion may be achieved with the same or even lower amount (such as 1 equiv) of TGDV (Table 1, entries f−k). Reactions of secondary allylic alcohols all proceeded smoothly at 85 °C, with the formation of allyl vinyl ether intermediates followed by in situ Claisen rearrangement, giving >90% conversion (NMR) and usually over 70% yield after isolation.

The faster Claisen rearrangement observed here is in agreement with results reported in literature that radical stabilizing substituents at C-4 can accelerate reaction rates significantly.[21] In addition, the α-alkyl group may also help the allyl vinyl ether to reach the concerted chairlike transition state for rearrangement by a steric effect (Scheme 1). Along this line, reaction of two tertiary allylic alcohols 2-methyl-3-buten-2-ol and linalool were examined (Table 1, entries p and q). Under the same conditions, we found both of these reactions proceeded smoothly with catalyst **IIIb**, generating the corresponding aldehyde directly and cleanly in ~90% yields (^{1}H NMR). None of the allyl vinyl ether intermediate was observed, suggesting a much faster Claisen rearrangement is occurring at this temperature, in agreement with the trend observed above. Due to its nonvolatile nature, the rearranged product from linalool was isolated easily in 80% yield by flash column chromatography. It should also be noted that vinylation of the sterically demanding tertiary allylic alcohol linalool failed in the literature with **IVb** as catalyst and butyl vinyl ether as vinylating agent.[18]

Finally, cyclohexenols (Table 1, entries l to o) can be vinylated readily as well in ca. 5 h, but the rate of the rearrangement was found to be strongly dependent on the structure. Vinyl cyclohexenyl ether (entry l) rearranges only at 190 °C. The sterically more hindered 3-methylcyclohexenol (entry m) and carveol (entry n) can actually rearrange at slightly lower temperature (150 °C), although the rationale for this is unclear. In the case of verbenol (entry o), no rearrangement was observed. The reaction of cyclic allylic alcohols is well-known to be problematic since adoption of the chairlike transition state suffers from *syn*-pentane interactions and the boat transition state is inherently higher in energy.[22]

The potential of this methodology to access more complicated compounds has been explored as shown in Scheme 2. Starting from a rearranged product 3-methyl-4-hexenal (**3p** of Table 1, entry p), a diene aldehyde **4** was easily obtained in 70% overall yield by a standard vinyl magnesium bromide addition followed by a tandem vinyl ether exchange−Claisen rearrangement of the resulting allylic alcohol. Aldehyde **4** was again subjected to the same iterative reaction sequence and, to our delight, the above result was almost exactly reproducible, generating the desired triene aldehyde **5** in ~50% overall yield in just 4 steps from 3-methyl-4-hexenal (**3p**). Polyene aldehydes are useful building blocks, e.g., in the synthesis of polyene type natural products[1b] and brevetoxin-type polycyclic ethers.[3] By directly generating the aldehyde functionality instead of the esters, this method avoids the reduction−oxidation steps, and is therefore superior in terms of simplicity and convenience, particularly when several skipped alkene units need to be constructed in a linear sequence. The mild reaction conditions should also tolerate more functional groups in complex molecules sensitive to acid or severe oxidation/reduction conditions.

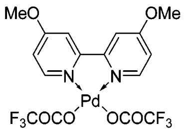
One of the future directions to optimize this method would be to design more stable catalysts that tolerate higher temperatures so that the Claisen rearrangement can proceed at a faster rate. As a result, the equilibrium may be driven to the right side even more efficiently, improving yield, particularly for the reactions of primary alcohols. The catalysts used in Table 1 are stable only up to ca. 90 °C. 2,2-Dipyridyl has been proposed to be an effective ligand for this transformation as well,[15,17] but reaction conditions and results are not available. For comparison purposes, reactions with complex **IIb** and its methoxy-substituted version **VI** were examined (Table 2). However, none of them was found to be superior in terms of stability and activity. For the reaction of a primary alcohol (Table 2, entry 1), 1.2 mol % of **IIb** or **VI** had to be used to achieve a 60% yield, likely due to decomposition of the catalyst. Vinylation of a secondary alcohol (1-penten-3-ol) failed completely (entry 2). Instead, 3-pentanone was identified by ^{1}H NMR, suggesting an isomerization reaction of 3-pentenol predominated. Interestingly, the enolization seemed to be sensitive to an increased steric hindrance on the double bond such as that imposed by an additional methyl group (entry 3). In this case, slow vinyl ether exchange was observed and the aldehyde was obtained in ca. 40% yield after 48 h. These results suggest that dipyridyls are an inferior ligand class when compared to the phenanthrolines, and further efforts at optimizing the ligand must continue in the future.

---

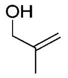
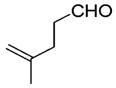
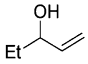
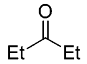
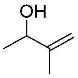
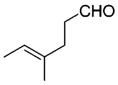
(21) For discussion of substituent effects in the Claisen rearrangement, see: Burrows, C. J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 6983−6984. Gajewski, J. J.; Gee, K. R.; Jurayj, J. *J. Org. Chem.* **1990**, *55*, 1813−1822.

(22) Bartlett, P. A.; Pizzo, C. F. *J. Org. Chem.* **1981**, *46*, 3896−3900.

TABLE 2. Reaction Catalyzed by Dipyridinyl Type Complexes[a]



VI

Entry	alcohol	Cat.	Condition	Product, yield[b]
1		1.2% IIb 1.2% VI	72 °C, 36 h then 120 °C, 2 h	 60 % 57 %
2		0.5% IIb 0.5% VI	80 °C, 4 h	 22 % 80 %
3		0.5% VI	85 °C, 48 h	 40 %

[a] A mixture of 25 mmol of alcohol and 75 mmol of vinylating agent TGDV was stirred with 0.5 mol % catalyst and 5 mol % Hünig base (i-Pr$_2$NEt) at 75−85 °C. [b] NMR yield reported.

In summary, we describe the first tandem Pd(II)-catalyzed vinyl ether formation−Claisen rearrangement process using the readily available palladium acetate−phenanthroline catalyst in combination with TGDV as the vinyl ether starting material. This provides a convenient approach to a series of γ,δ-unsaturated aldehydes under mild conditions that avoids the use of toxic Hg(II). This method is very practical and volume efficient, and we have prepared some volatile aldehydes on >20 kg scale successfully using this methodology. In addition, remote alkene units are intact under these conditions, which allows the efficient synthesis of polyene-type compounds. Further optimization of the reaction system by exploring better designed catalyst, as well as its application to more elaborate allylic alcohols, is ongoing in our laboratories. Results will be reported in due course.

Experimental Section

Preparation of Catalysts (II, III, IV, and VI). All catalysts used in this study were prepared in almost quantitative yield by stirring a 1:1 (mol) mixture of palladium salt (Pd(OAc)$_2$ or Pd(tfa)$_2$) and the corresponding organic ligand in DME (~5 mL/mmol of complex). A yellowish solid precipitated out and was isolated by filtration, rinsed with diethyl ether, and dried in an oven at 50 °C under reduced pressure.

Tandem Pd(II)-Catalyzed Vinyl Ether Exchange−Claisen Rearrangement. (A) Typical Procedure for Primary Allylic Alcohols and Cyclic Cyclohexenols: Method A. To a solution of triethyleneglycol divinyl ether (303 g, 1.5 mol) and the corresponding allylic alcohol (1 mol) in a 1 L flask equipped with an efficient condenser was added the catalyst 1,10-phenathroline-Pd(OAc)$_2$ complex (2.0 g, 0.005 mol) or 1,10-phenathroline-Pd(CF$_3$CO$_2$)$_2$ (2.6 g, 0.005 mol). When Pd(CF$_3$CO$_2$)$_2$ complex was used as catalyst, *N*,*N*-diisopropylethylamine (6.4 g, 0.05 mol) was added to inhibit acetal formation as a side reaction. The reaction condenser should be opened to air and NOT inerted by N$_2$ or argon. The mixture was heated gently to 70 °C. (An oil bath or water bath is preferred to a heating mantle for better temperature control. Decomposition of catalyst was often observed due to some "hot spots" when heated by a heating mantle.) The reaction mixture became a clear yellow solution. After the solution was stirred for 5−7 h, NMR showed that the allylic alcohol was converted to its vinyl ether to the extent of 75−80%. The mixture was then heated to ca. 120 °C and reflux started. The temperature was raised gradually to 140−145 °C and stirring was continued at this temperature for 5−10 h until ^{1}H NMR showed the rearrangement was complete. For some reaction of cyclohexenols, the rearrangement was carried out at a higher temperature, up to 190 °C. When the reaction was finished, the reaction mixture was distilled with an oil bath temperature of ca. 110−140 °C and under ca. 300 mmHg pressure to give the crude product that was normally subjected to a second distillation to produce high-purity product. For compounds with a high boiling point (**3*l*−o**,**q**), distillation was not practical, and flash column chromatography on silica gel (hexanes) was used, giving pure product after evaporation of solvent.

(B) Typical Procedure for Secondary and Tertiary Allylic Alcohols: Method B. To a solution of triethyleneglycol divinyl ether (303 g, 1.5 mol) and the corresponding allylic alcohol (1 mol) in a 1 L flask equipped with an efficient condenser was added the catalyst 1,10-phenathroline-Pd(OAc)$_2$ (2.0 g, 0.005 mol) or 1,10-phenathroline-Pd(CF$_3$CO$_2$)$_2$ (2.6 g, 0.005 mol). When Pd(CF$_3$CO$_2$)$_2$ complex was used as catalyst, *N*,*N*-diisopropylethylamine (6.4 g, 0.05 mol) was added to inhibit acetal formation as a side reaction. The condenser should be opened to air and NOT inerted by N$_2$ or argon. The mixture was heated gently to 75−80 °C. (An oil bath or water bath is preferred to a heating mantle for better temperature control. Decomposition of catalyst was often observed due to some "hot spots" when heated by a heating mantle.) The reaction mixture became a clear yellow solution. Reaction was monitored by NMR, and formation of vinyl ether and aldehyde was usually >90% after 24 to 48 h. The mixture was then heated to ca. 100−120 °C and stirred at this temperature until NMR showed all of the remaining vinyl ether had rearranged to aldehyde. When the reaction was finished, the reaction mixture was distilled with an oil bath temperature of ca. 110−140 °C and under ca. 300 mmHg pressure to give the crude product that was normally subjected to a second distillation to produce high-purity product. For compounds with a high boiling point (**3q**, **4**, **5**), distillation was not practical, and flash column chromatography on silica gel (hexanes) was used, giving pure product after evaporation of solvent.

Acknowledgment. The authors thank Prof. Erick M. Carreira at ETH, Prof. Peter Wipf at the University of Pittsburgh, and Prof. Scott Denmark at the University of Illinois, Urbana for helpful discussions. Dr. Vittorio Farina is thanked for constructive discussion in the preparation of the paper.

Supporting Information Available: Characterization of new compounds and copies of NMR spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

JO062548F