

Notes

Critical Role of the Coordination Environment of Palladium Dichloride on the Course of Its Reaction with Secondary Benzylic Alcohols: Selective Oxidation or Etherification Catalysts

Sandrine Bouquillon, Françoise Hénin, and Jacques Muzart*

Unité Mixte de Recherche "Réactions Sélectives et Applications", CNRS–Université de Reims Champagne-Ardenne, B.P. 1039, 51687 Reims Cédex 2, France

Received December 6, 1999

Summary: In refluxing 1,2-dichloroethane under an argon atmosphere, 1-indanol led to a high yield of 1-indanone in the presence of sodium carbonate and catalytic amounts of $(R_4N)_2PdCl_4$, while the use of $PdCl_2-(RCN)_2$ as catalyst afforded di(1-indanyl) oxide quantitatively. These distinct reactive pathways would be due to the different electronic properties of the catalysts. The etherification reaction is limited to primary and secondary benzylic alcohols.

Previously, we have described the oxidation of saturated, allylic and benzylic alcohols using sodium carbonate and catalytic amounts of both palladium chloride (**1**) and Adogen 464¹ in refluxing 1,2-dichloroethane (DCE) under an air atmosphere.^{2,3} The catalytic cycle we have proposed for the regeneration of the active Pd-species involves the insertion of a reduced Pd-species into a C–Cl bond of DCE followed by a β -elimination reaction which leads to ethylene and Pd(II).^{2a} In using 1-indanol (**2**) as substrate, we have disclosed that its conversion to 1-indanone (**3**) was strongly decreased when Adogen 464 was omitted from the reaction mixture.^{2a} Subsequently, we have observed that quaternary ammonium salts, R_4NCl , react with palladium chloride to yield characterizable salts, $(R_4N)_2PdCl_4$, which are as effective as " $PdCl_2 + 2 R_4NCl$ " for the catalytic oxidation of 1-indanol.⁴ In contrast to **1**, these ammonium–palladium salts are readily soluble in DCE. Thus, we postulated that the differences between the efficiencies of $PdCl_2$ and $(R_4N)_2PdCl_4$ were relative to their different solubilities.⁵ This prompted us to test other soluble Pd^{II} chloride catalysts (eq 1). The surprising results we have obtained are presented herein.

To eliminate any role of oxygen on the course of the reactions and to obtain more accurate and reliable results, (i) all new experiments reported here (Table 1) were carried out under an argon atmosphere,^{6,7} and (ii)

Table 1. Reaction of 1-Indanol at 80 °C for 6 h in the Presence of Pd-Catalyst (0.1 equiv) and Na_2CO_3 (2 equiv) under an Argon Atmosphere

run	catalyst	solvent	recovered compds, % yield ^a		
			2	3	8
1	$PdCl_2 + 2$ Adogen 464	DCE	14	81	0
2	$(n-Bu_4N)_2PdCl_4$, 0.5 H ₂ O	DCE	6	92	0
3	$PdCl_2(MeCN)_2$	DCE	0	0	98
4	$PdCl_2(PhCN)_2$	DCE	0	0	99
5	$PdCl_2(t-BuCN)_2$	DCE	0	0	97
6	$PdCl_2(PPh_3)_2$	DCE	93	5	0
7	Na_2PdCl_4	DCE	79	11	4
8	$PdCl_2$	DCE	81	0	19
9 ^b	$PdCl_2(MeCN)_2$	DCE	0	0	99
10	5a + 2 Adogen 464	DCE	0	98	0
11	no catalyst	DCE	99	0	0
12 ^b	$PdCl_2(MeCN)_2$	MeCN	34	0	62
13 ^b	$PdCl_2(MeCN)_2$	BTF	0	0	97

^a Determined by HPLC. ^b Reaction carried out in the absence of Na_2CO_3 .

Table 2. Reaction of Benzylic Alcohols at 80 °C for 6 h in DCE in the Presence of $PdCl_2(MeCN)_2$ (0.1 equiv) under an Argon Atmosphere

run	RR'CHOH	conversion, % ^a	(RR'CH) ₂ O, % yield ^a
14	PhMeCHOH	71	61
15	9-fluorenone	82	78
16	1-tetralol	85	81
17	PhCH ₂ OH	29	6 ^b
18	1-naphthylCH ₂ OH	29	18
19	2-naphthylCH ₂ OH	35	23

^a Conversions and yields are here determined from isolated compounds. ^b Benzaldehyde (12%) was also isolated.

the contents of the reaction mixture were analyzed by HPLC on the crude reaction mixture. Consequently, the oxidation of **2** using either "**1** + 2 Adogen 464" or the soluble ammonium–palladium salt **4** as catalyst was

* Corresponding author. Fax: 03 26 91 31 66. E-mail: jacques.muzart@univ-reims.fr.

(1) Adogen 464 is a registered trademark of Ashland Chemical Co. for methyltrialkyl(C_8-C_{10})ammonium chloride.

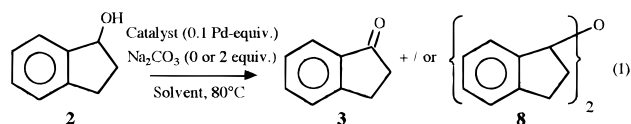
(2) (a) Ait-Mohand, S.; Hénin, F.; Muzart, J. *Tetrahedron Lett.* **1995**, 36, 2473. (b) Ait-Mohand, S.; Muzart, J. *J. Mol. Catal.* **1998**, 129, 135.

(c) Ait-Mohand, S. Ph.D. Thesis, University of Reims Champagne-Ardenne, 1997.

(3) The oxidation was somewhat less effective under an argon atmosphere.^{2a,c}

(4) Bouquillon, S.; du Moulinet d'Hardemare, A.; Averbuch-Pouchot, M.-Th.; Hénin, F.; Muzart, J. *Polyhedron* **1999**, 18, 3511.

(5) The commercial samples of $PdCl_2$ exhibit an oligomeric structure: (a) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vol. 1, p 43. (b) Hartley, F. R. *The Chemistry of Platinum and Palladium*; J. Wiley: New York, 1973; p 470.



Catalyst: PdCl_2 (**1**), $(n\text{-Bu}_4\text{N})_2\text{PdCl}_4$, 0.5 H_2O (**4**), $\text{PdCl}_2(\text{MeCN})_2$ (**5a**), $\text{PdCl}_2(\text{PhCN})_2$ (**5b**), $\text{PdCl}_2(t\text{-BuCN})_2$ (**5c**), $\text{PdCl}_2(\text{PPh}_3)_2$ (**6**), Na_2PdCl_4 (**7**).

analyzed again under these conditions to have basic standard results (runs 1 and 2). In agreement with previous results,^{2a,4} **3** was efficiently obtained. Surprisingly, $\text{PdCl}_2(\text{MeCN})_2$ (**5a**), which also has good solubility in DCE, induced a completely different reaction, which proceeded to completion and afforded di(1-indanyl) oxide (**8**) quantitatively (run 3). Switching from acetonitrile as the palladium ligand to benzonitrile (**5b**) or pivalonitrile (**5c**) did not apparently modify the reactivity of **2** since the same ether was obtained with similar high efficiency (runs 4 and 5). In contrast, triphenylphosphine as ligand (i.e., **6** as catalyst) strongly inhibited the conversion of **2** and moreover led to **3** (run 6). Sodium tetrachloropalladate (**7**) is poorly soluble in DCE and its use as catalyst provided only low conversion, yielding a mixture of **3** and **8** (run 7). The conversion of **2** was similar when **7** was replaced by the very slightly soluble palladium chloride (**1**), but the use of this latter catalyst resulted in the exclusive production of **8** (run 8).

The formation of **8** remains very effective when **5a** was used in the absence of base (run 9), while using the same palladium complex in the presence of sodium carbonate, the addition of Adogen 464 shifted the reaction pathway toward the exclusive production of **3** (run 10). As suspected, **2** failed to undergo reaction when no Pd-catalyst was added to the reaction mixture (run 11).

The formation of **3** and **8** can be rationalized through two competitive pathways as illustrated in Scheme 1, paths *a* and *b*. From PdCl_2L_2 ($\text{L} = \text{Cl}^-$, RCN, PPh_3), the first reaction step would be ligand exchange to give the intermediate complex **A**.

For path *a*, the evolution of **A** involves the insertion of Pd^{II} into the O–H bond, which leads to hydrogen chloride and to the alkoxy palladium intermediate **B**. Then, β -elimination of HPdClL_n gives **3**. The active catalyst is regenerated through a reaction with DCE.^{2a} The two molecules of hydrogen chloride formed in the course of the process are neutralized by sodium carbonate. In addition, the base could interfere in the oxidation mixture at other stages.⁸ In particular, the base could enhance the nucleophilicity of the alcohol; this would promote the formation of **B**. Possibly, the base gives the

corresponding sodium alkoxide as assumed for some metal-catalyzed oxidations;⁹ if $\text{L} = \text{Cl}^-$, this alkoxide would react with the catalyst through a $\text{S}_{\text{N}}2$ pathway which displaces a chloride ligand and affords **B** directly without the formation of the intermediate **A**. The base could also mediate the termination of the catalytic cycle in abstracting the hydrogen geminal to the palladium alkoxy group of **B**¹⁰ or in taking part in the reductive elimination of HCl from HPdClL_n .¹¹

The formation of ethers from alcohols in the presence of catalytic amounts of transition metals has already been reported;^{12,13} this reaction exploits the Lewis acid properties of the transition metal.¹³ Thus, an electrophilic palladium complex could induce the heterolytic cleavage of the C–O bond of **A** to give **C** (Scheme 1, path *b*). The reaction of this ionic species with **2** will deliver **8**, water, and L_nPdCl_2 . No acid is formed in the course of such a catalytic cycle; this is in agreement with the results of run 9, where **8** was quantitatively obtained in the absence of base. Since the Pd(II) oxidation state is preserved along the different steps of path *b*, we can expect that the etherification could also proceed in solvents other than DCE; indeed, DCE was originally used to regenerate Pd(II) from Pd(0).^{2a} Consequently, we examined the $\text{PdCl}_2(\text{MeCN})_2$ -catalyzed reaction of **2** in acetonitrile and benzonitrile (BTF)¹⁴ in the absence of base (runs 12 and 13). Consistent with our assumption, **8** was readily obtained, in particular when BTF was the solvent.

As documented in Table 1, the nature of the Pd-catalyst has a dramatic effect on the selectivity toward **3** or **8**. We ascribe this to different electrophilicities of the catalysts we have used in the present study.¹⁵

The neutral complexes, PdCl_2 and $\text{PdCl}_2(\text{RCN})_2$, are electrophilic;^{16–18} this allows the reactive pathways described in Scheme 1, path *b*, to proceed (runs 3–5 and

(9) (a) Tamaru, Y.; Yamada, Y.; Inoue, K.; Yamamoto, Y.; Yoshida, Z. *J. Org. Chem.* **1983**, *48*, 1286. (b) Almeida, M. L. S.; Beller, M.; Wang, G.-Z.; Bäckvall, J.-E. *Chem. Eur. J.* **1996**, *48*, 1533.

(10) (a) Trost, B. M.; Masuyama, Y. *Tetrahedron Lett.* **1984**, *25*, 173. See also: (b) Schwarz, I.; Braun, M. *Chem. Eur. J.* **1999**, *5*, 2300.

(11) Zhao, F.; Bhanage, B. M.; Shirai, M.; Arai, M. *J. Mol. Catal. A: Chem.* **1999**, *142*, 383.

(12) Ait-Mohand, S.; Lunak, S.; Muzart, J. *Chem. Ber./Recl.* **1997**, *130*, 1655.

(13) Salehi, P.; Iranpoor, N.; Behbahani, F. K. *Tetrahedron* **1998**, *54*, 943.

(14) For metal-catalyzed reactions carried out in BTF, see: (a) Curran, D. P.; Hadida, S. *J. Am. Chem. Soc.* **1996**, *118*, 2531. (b) Curran, D. P.; Hoshim, M. *J. Org. Chem.* **1996**, *61*, 6480. (c) Ryu, I.; Niguma, T.; Minakata, S.; Komatsu, M.; Hadida, S.; Curran, D. P. *Tetrahedron Lett.* **1997**, *38*, 7883. (d) Hoshino, M.; Degenkolb, P.; Curran, D. P. *J. Org. Chem.* **1997**, *62*, 8341. (e) Nishikido, J.; Nakajima, H.; Saeki, T.; Ishii, A.; Mikami, K. *Synlett* **1998**, 1347. (f) Ravikumar, K. S.; Bégue, J. P.; Bonnet-Delpont, D. *Tetrahedron Lett.* **1998**, *39*, 3141. (g) Hanyu, A.; Takezawa, E.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.* **1998**, *39*, 5557. (h) Ravikumar, K. S.; Barbier, F.; Bégue, J.-P.; Bonnet-Delpont, D. *Tetrahedron* **1998**, *54*, 7457. (i) Olofsson, K.; Kim, S.-Y.; Larhed, M.; Curran, D. P.; Hallberg, A. *J. Org. Chem.* **1999**, *64*, 4539. (j) De Campo, F.; Lastécouères, D.; Vincent, J.-M.; Verlhac, J.-B. *J. Org. Chem.* **1999**, *64*, 4969. (k) Delaval, N.; Bouquillon, S.; Hénin, F.; Muzart, J. *J. Chem. Res., Synop.* **1999**, 286. (l) Takezawa, E.; Sakaguchi, S.; Ishii, Y. *Org. Lett.* **1999**, *1*, 713.

(15) Such an explanation has been prompted through the reading of reports from Sen and Lai regarding Pd-catalyzed oligomerizations of alkenes.¹⁶

(16) (a) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627. (b) Sen, A.; Lai, T.-W. *Organometallics* **1983**, *2*, 1059.

(17) (a) Lipshutz, B. H.; Pollart, D.; Monforte, J.; Kotsuki, H. *Tetrahedron Lett.* **1985**, *26*, 705. (b) Tenaglia, A.; Kammerer, F. *Synlett* **1996**, 576.

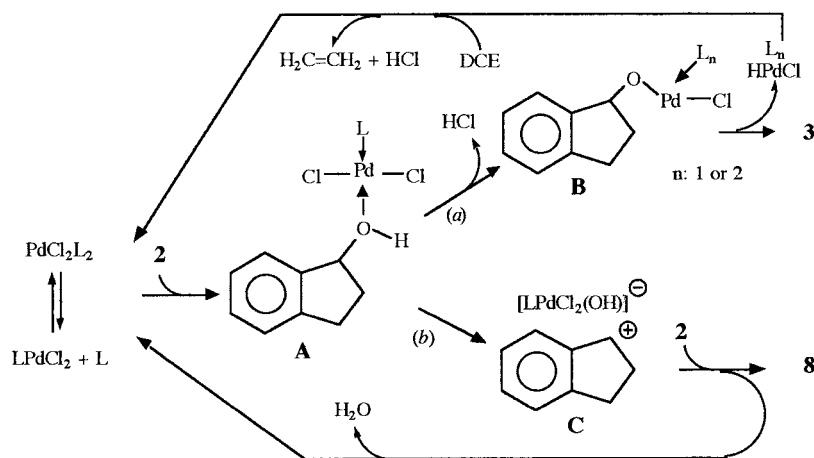
(18) A referee has proposed that $\text{PdCl}_2(\text{RCN})_2$ exists rather in the dimeric form, $\text{Pd}_2\text{Cl}_4(\text{RCN})_2$, in low dielectric solvents. Note that **4** could also give a bimetallic palladium complex.⁴

(6) The more or less effective palladium-catalyzed oxidation of alcohols with oxygen as terminal oxidant has been reported: (a) Lloyd, W. G. *J. Org. Chem.* **1967**, *32*, 2816. (b) Blackburn, T. F.; Schwartz, J. S. *Chem. Commun.* **1977**, 157. (c) Gomez-Bengoa, E.; Noheda, P.; Echavaren, A. E. *Tetrahedron Lett.* **1994**, *35*, 7097. (d) Kaneda, K.; Fujii, M.; Morioka, K. *J. Org. Chem.* **1996**, *61*, 4502. (e) Kaneda, K.; Fujie, Y.; Ebitani, K. *Tetrahedron Lett.* **1997**, *38*, 9023. (f) Nishimura, T.; Onoue, T.; Ohe, K.; Uemura, S. *Tetrahedron Lett.* **1998**, *39*, 6011. (g) Peterson, K. P.; Larock, R. C. *J. Org. Chem.* **1998**, *63*, 3185. (h) Nagata, H.; Ogasawa, K. *Tetrahedron Lett.* **1999**, *40*, 6617. (i) Nishimura, T.; Onoue, T.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1999**, *64*, 6750.

(7) Indeed, we have observed that some experiments reported in the present paper were very air sensitive.

(8) Bouquillon, S.; Ait-Mohand, S.; Muzart, J. *Eur. J. Org. Chem.* **1998**, 2599.

Scheme 1



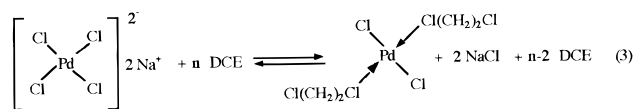
8). The low catalytic activity of **1** is certainly due to its very low solubility in DCE. We suspect that some dissolution of the oligomeric palladium chloride⁵ is obtained owing to coordination of the solvent, leading to the formation of $\text{PdCl}_2(\text{DCE})_2$ (eq 2).¹⁹



The exchange of the two RCN ligands of **5** by the more electron-donating PPh_3 decreases strongly the electrophilicity of the resulting complex, i.e., **6**.^{16a} This lowered electrophilicity of palladium is preserved in corresponding **A**, where L is PPh_3 ; that gives rise to the formation of **B** rather than of **C** and then to **3** instead of **8** (run 6). The poor catalytic activity of $\text{PdCl}_2(\text{PPh}_3)_2$ compared with $\text{PdCl}_2(\text{RCN})_2$ was a priori unexpected since all these catalysts are readily soluble in DCE.²⁰ In fact, this is due to the different properties of the ancillary ligands; PPh_3 is bulkier and more strongly bound to the palladium atom than MeCN. Thus **6** lacks an easily available coordination site on the metal. Consequently, the ligand exchange that is required to afford the initial intermediate **A** is attained more easily using **5** than **6**.

The soluble anionic complexes, $[\text{PdCl}_4]^{2-}[(\text{R}_4\text{N})_2]^{2+}$, have no electrophilic properties;²¹ thus **3** was exclusively obtained with these complexes (runs 1²² and 2). The similar result obtained when 2 equiv of Adogen 464 was added to $\text{PdCl}_2(\text{MeCN})_2$ (run 10) indicates a MeCN/Cl^- exchange of the ancillary ligands.²³ Sodium tetrachloropalladate (**7**) differs from $(\text{R}_4\text{N})_2\text{PdCl}_4$ by the nature

of the associated cations, which leads to strong differences in solubility between these two salts. As pointed out above, **7** and **1** are barely soluble in DCE. Therefore, it is not surprising that **7** led to a low conversion (run 7) as for **1** (run 8). However and contrary to $(\text{R}_4\text{N})_2\text{PdCl}_4$ and PdCl_2 , which induced selective reactions leading to **3** (runs 1 and 2) and **8** (run 8) respectively, **7** affords a mixture of **3** and **8**. The most likely explanation for this is to consider a partial dissociation of **7** in DCE as shown in eq 3;²⁴ this would be facilitated by the large amount of DCE relative to that of NaCl. Such equilibria with palladium salts have already been reported in other solvents.²⁵ If we consider the presence of these two Pd-species in the reaction medium, the formation of both **3** and **8** is thus easily rationalized: the anionic species, Na_2PdCl_4 , leads to **3**, as for $(\text{R}_4\text{N})_2\text{PdCl}_4$, while the electrophilic neutral species, $\text{PdCl}_2(\text{DCE})_2$, provides **8**, as for PdCl_2 and $\text{PdCl}_2(\text{RCN})_2$.



The influence of the nature of the solvent on the efficiency of the **5a**-catalyzed transformation of **2** to **8** is established by the results of runs 9, 12, and 13: the reaction is more sluggish in MeCN than in DCE or BTF. As proposed above, the formation of **8** involves intermediate **A**; this requires the displacement of an acetonitrile ligand of **5a** by **2** (Scheme 1). When acetonitrile is used as solvent, the high MeCN/**2** ratio retards such an exchange.

Unlike the oxidation reaction that we have previously reported,^{2a} the scope of the present Pd-catalyzed etherification has to be investigated; this has been examined under conditions of run 9. No evolution of the substrate was observed when saturated (2-butanol), allylic (geraniol), or tertiary (*tert*-butyl alcohol, triphenylmethanol, cumyl alcohol) alcohols were used. In contrast, secondary benzylic alcohols led to the corresponding

(19) This implies that in Scheme 1 $\text{L} = \text{DCE}$ when PdCl_2 was used as catalyst.

(20) The poor activity of $\text{PdCl}_2(\text{PPh}_3)_2$ as catalyst for the oxidation of alcohols under phase transfer conditions has been reported: Choudary, B. M.; Reddy, N. P.; Kantam, M. L.; Jamil, Z. *Tetrahedron Lett.* **1985**, 26, 6257.

(21) Even with $\text{Pd}(0)$, it has been argued that the coordination of chloride ions to palladium makes it more nucleophilic: Larock, R. C. *J. Organomet. Chem.* **1999**, 576, 111.

(22) The addition of 2 equiv of Adogen 464 to PdCl_2 leads to $[\text{Me}(\text{H}_{17-21}\text{C}_{8-10})_3\text{N}]_2\text{PdCl}_4 \cdot \text{H}_2\text{O}$.⁴ Thus, we consider that in run 1 this latter salt is the active catalyst.

(23) The PPh_3/Cl^- exchange from **6** in the presence of an excess of *n*-Bu₄NCl has been demonstrated: Amatore, C.; Jutand, A.; Mottier, L. *Eur. J. Inorg. Chem.* **1999**, 1081. The MeCN/Cl^- exchange is undoubtedly easier from **5a** since MeCN has a lower coordinating ability than PPh_3 .

(24) The mixture could also contain some $\text{NaPdCl}_3(\text{DCE})$.²⁵ As remarked by a referee, eq 3 is almost certainly an oversimplification.

(25) (a) Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; D. Reidel: Dordrecht, 1979; pp 11–16. (b) Sarhan, J. K. K.; Foong Murray, S.-W.; Asfour, H. M.; Green, M.; Wing, R. M.; Parra-Haake, M. *Inorg. Chem.* **1986**, 25, 243.

symmetrical ethers with high selectivities (Table 2, runs 14–16). Primary alcohols were more reluctant to react (runs 17–19). Furthermore, while naphthyl methanols led selectively to the corresponding ethers, benzyl alcohol, in disagreement with the above results, led to a mixture of benzaldehyde and ether (run 17). We have already observed the particular reactivity of benzyl alcohol under metal catalysis.^{2c}

Thus, it appears that the efficiency of the reaction depends highly on the heterolytic dissociation energy of the C–OH bond and possibly on the stability and steric hindrance of the resulting carbocation. Nevertheless, this catalytic procedure, which operates under almost neutral conditions and without producing any inorganic waste, is a new environmentally benign method for the synthesis of symmetrical benzyl ethers from primary and especially secondary benzyl alcohols.²⁶

In conclusion, we have shown that the nature of the ancillary ligands attached to palladium dichloride has a dramatic effect upon the reactivity of the Pd(II) compounds toward benzylic alcohols. In using proper ligands and experimental conditions, we have been able to obtain selectively either ketones^{2a} or symmetrical ethers.

Experimental Part

All reactions were carried out under a rigorous argon atmosphere and with deoxygenated solvents. ¹H and ¹³C NMR spectra were recorded on a AC 250 Bruker in CDCl₃. IR spectra were recorded with Spectrafile IR Plus M.I.D.A.C. as KBr pellets. The physical properties of the isolated ethers, except those of di(1-tetralyl) oxide, have already been reported.^{12,27}

Procedure Used for Experiments of Table 1. Anhydrous

(26) For recent work on catalytic symmetrical etherifications, see: Bagnell, L.; Cablewski, T.; Strauss, C. R. *Chem. Commun.* **1999**, 283.

solvent (10 mL) containing the catalyst was stirred and degassed by bubbling argon during 15 min. Next, Na₂CO₃ (2 mmol) and alcohol (1 mmol) were added, and the mixture was heated at 80 °C for 6 h. After cooling to room temperature, the resulting mixture was filtered on a short pad of silica gel eluting with CH₂Cl₂/MeOH (4:1). After evaporation of the solvents under reduced pressure, the crude residue was analyzed by HPLC (column, Licrosphere Si 60, 5 μm; eluant, hexane/*i*-PrOH, 97:3) using acetophenone as internal standard.

Etherification Procedure (Table 2). A deoxygenated solution of PdCl₂(MeCN)₂ (0.1 mmol) and alcohol (1 mmol) in 1,2-dichloroethane (10 mL) was heated at 80 °C for 6 h. After elimination of the catalyst by filtration on a short pad of silica gel and evaporation of the solvents, the products were isolated by flash chromatography eluting with EtOAc/petroleum ether (1:9).

Di(1-tetralyl) Oxide.²⁸ A 1:1 mixture of diastereoisomers was recrystallized in EtOH/acetone, producing white crystals, mp 43–47 °C. IR (KBr): 3042, 2938, 2853, 1487, 1454, 1069, 775, 734 cm⁻¹. ¹H NMR (CDCl₃, 250 MHz): δ 7.10–7.90 (8H, Ar), 4.70 (t, 1H, ³J = 6.8 Hz, OCH), 4.45 (t, 1H, ³J = 6.8 Hz, OCH), 2.98 (m, 2H, ArCH₂), 2.65 (m, 2H, ArCH₂), 1.70–2.30 (8H, ArCH₂CH₂CH₂). ¹³C NMR (CDCl₃, 63 MHz): δ 137.5, 129.6, 129.0, 128.8, 127.3, 127.2, 125.8 and 125.6 (aromatic C), 73.8 and 72.7 (OCH), 29.7 and 29.3 (ArCH₂), 29.0 and 28.4 (ArCHCH₂), 19.0 and 18.9 (ArCH₂CH₂).

Acknowledgment. We are grateful to Engelhard Company and to Rhône-Poulenc Industrialisation for generous gifts of palladium and benzotrifluoride, respectively. We thank Dr. S. Aït-Mohand for preliminary studies and Dr. G. Bird (AstraZeneca, Reims) for help with the text of the manuscript.

OM990961Q

(27) (a) Balsells, R. A.; Frasca, A. R. *Tetrahedron* **1982**, 38, 2525. (b) Johnson, A. L. *J. Org. Chem.* **1982**, 47, 5220. (c) Liotta, L.; Gamen, B. *Tetrahedron Lett.* **1989**, 30, 4759. (d) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1996**, 61, 324. (e) Malkar, N. B.; Kumar, V. G. *Synth. Commun.* **1998**, 28, 971.

(28) Bellesia, F.; Ghelfi, F.; Pagoni, U. M.; Pinetti, A. *Gazz. Chim. Ital.* **1992**, 122, 437.