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formed without an organic solvent, an important ecological advantage. In this case the functionalization of the silica with the correct balance of polyethers is critical (Figure 3). Use of hydrophilic PEO yielded only low rates and conversions. Non-



Figure 3. Oxidation of cyclooctene with 30% H_2O_2 catalyzed by supported $Q_3PO_4[W(O)(O_2)]_4$. Reaction conditions: cyclooctene (1 mmol), 30% H_2O_2 (2 mmol), $Q_3PO_4[W(O)(O_2)]_4/20\%$ PEO/PPO-SiO₂ (100 mg) containing 0.005 mmol of the POM at 23 °C. Cyclooctene oxide was the sole product. C = conversion.

supported $Q_3PO_4[W(O)(O_2)]_4$, that is, solid POM that is slightly dissolved in cyclooctene, was also inactive. On the other hand, a mixture of 10% PEO and 10% PPO-SiO₂ gave the optimal catalyst particle. The hydrophilic-hydrophobic balance of the catalyst particle must be adjusted to optimize the solubility of both cyclooctene and hydrogen peroxide in the polyetherbound phase. The catalyst 20% PPO-SiO₂ was almost as effective, but further increases in PPO content reduced the activity. The catalyst particle was recycled five times without loss of catalytic activity. Use of a reaction filtrate showed no catalytic species and no catalytic activity.

The new concept of solvent-anchored supported liquid phase catalysis has been introduced and demonstrated for oxidation reactions catalyzed by polyoxometalates. These new catalytic systems are more active and selective than analogous nonsupported systems, and catalytic activity is retained after recycling. Use of this technique will be expanded to other reactions and catalysts.

Experimental Section

Monomers 1 were prepared by allowing (CH₃O)₃SiPhCH₂Cl (25 mmol) to react with $CH_3(OCH_2CH_2)OH$ (MW = 350; 25 mmol) or $CH_3(OCH(CH_3)CH_2)OH$ (MW = 200; 25 mmol) in acetone (100 mL) in the presence of solid K₂CO₃ (125 mmol) at reflux for 18h. The solid salts were removed by centrifugation, and the solvent removed under vacuum. No further purification was carried out at this point. The functionalized xerogels were prepared by dissolving appropriate amounts of 1 and Si(OEt)₄ (in total 5 mmol) in acetone (20 mL). Water (10 equiv) and dibutyltin dilaurate (0.01 equiv) were added to initiate polymerization. The reaction mixture was held at 60 °C for three hours and left to concentrate by evaporation of solvent for two days at room temperature. The functionalized silica particles were carefully washed twice with water and ethanol and dried under vacuum. Final catalytic assembles were prepared by impregnating the polyoxometalates onto the silicates as follows: For the reaction in Equation (a) H₅PV₂Mo₁₀-O40 x H2O (440 mg, 0.2 mmol) was dissolved in acetone (10 mL) and added to 20% PEO-SiO₂ (1.5 g), and the solvent removed. The silicate was then dried overnight under vacuum at room temperature. The procedure was identical for the reaction in Equation (b) except that $H_5PV_2Mo_{10}O_{40} \cdot xH_2O$ (165 mg, 0.075 mmol) was used. For the reaction in Equation (c) $[(C_6H_{13})_4N]_3PO_4[W(O)(O_2)]_4$ (1.04 g, 0.5 mmol) was dissolved in CHCl₃ (20 mL) and added to 20% PEO/PPO-SiO₂. The mixture was then treated as above.

Typical oxidations were carried out in S-mL, magnetically stirred vials. Material quantities and reaction conditions are given in the text. The reaction mixtures were analyzed by GLC (HP 5890) with a RTX-1 column (30 m, 0.32 mm ID, 0.25 μ m methylsilicone coating). The catalyst was recovered by filtration followed by washing to remove reaction remnants and drying.

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Palladium-Catalyzed Regioselective Mono- and Diarylation Reactions of 2-Phenylphenols and Naphthols with Aryl Halides**

Tetsuya Satoh, Yuichiro Kawamura, Masahiro Miura,* and Masakatsu Nomura

The palladium-catalyzed substitution reactions of aryl halides and their synthetic equivalents such as aryl triflates are highly useful for the preparation of substituted aromatic compounds. In these reactions arylpalladium(II) complexes occur as common intermediates which react with various reagents including alkenes, alkynes, and a number of organometallic species to give the corresponding products.^[1] While aryl halides may also react

^[*] Prof. Dr. M. Miura, T. Satoh, Y. Kawamura, Prof. Dr. M. Nomura Department of Applied Chemistry, Faculty of Engineering Osaka University, Suita, Osaka 565 (Japan) Fax: Int. code + (6)879-7362 e-mail: miura@ap.chem.eng.osaka-u.ac.jp

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with aromatic compounds accompanied by cleavage of an aromatic C-H bond to give biaryls, only intramolecular cases are known to be generally effective.^[2] Meanwhile, in the course of our study of palladium-catalyzed reactions with phenolic substrates,^[3] we observed that the intermolecular cross-coupling of 2-hydroxybenzaldehydes with aryl iodides proceeded smoothly when the catalyst system PdCl₂/LiCl was used in the presence of sodium carbonate as base. Since the products are 2-aroylphenols, the reaction appears to involve activation of the aldehyde C-H bond.^[3a] The phenolic function seems to act as a good anchor for this reaction, which suggests that arylation of other phenolic substrates should also be possible. Indeed, phenylation of 2-phenylphenol with iodobenzene was found to proceed to some extent, giving a terphenyl derivative; however, the reaction was very sluggish. [3a] We now report our new findings that when an appropriate base is employed, not only monoarylation, but also diarylation of 2-phenylphenols can take place effectively and regioselectively to afford sterically crowded 1,2,3-triarylbenzene derivatives;^[4] and 1- and 2-naphthols can also be arylated.

When iodobenzene (1a; 1.2 mmol) was treated with 2phenylphenol (2; 1.0 mmol) in the presence of $Pd(OAc)_2$ (0.05 mmol) with Cs_2CO_3 as base, a phenyl group was selectively introduced onto the 2'-position of 2 to produce 1,1':2',1''-terphenyl-2-ol (6a) in 76% yield (Scheme 1, Table 1). Other alkaline bases such as K_2CO_3 and Na_2CO_3 were much less effective than Cs_2CO_3 (25 and 13% yield, respectively, under the same conditions). When $PdCl_2$ was used in place of $Pd(OAc)_2$ the yield of 6a was 66%. Increasing the amount of both 1a and the base to 4 mmol led to further arylation to afford the correspond-



Scheme 1. Cross-coupling of 1a, b with 2-5 (see also Table 1).

Table 1. Mono- and diarylation reactions of 2-phenylphenols with aryl iodides **1a,b.** Reaction conditions: A) **1** (1.2 mmol), ArOH (1 mmol), $Pd(OAc)_2$ (0.05 mmol), Cs_2CO_3 (1.2 mmol), molecular sieves 4 Å (200 mg), DMF (5 mL), 100 °C; B) **1** (4 mmol), ArOH (1 mmol), $PdCl_2$ (0.05 mmol), Cs_2CO_3 (4 mmol), DMF (5 mL), 100 C.

Entry	Starting materials					Condi-	Time	Product,
	х	Y	Z	1	ArOH	tions	[h]	yield [%] [a]
1	Н	н	н	la	2	А	22	6a , 76 (63)
2	н	Н	Н	1 a	2	В	44	10a, 62 (56)
3	Н	Me	Н	1a	3	Α	22	7a, 76 (60)
4	н	Me	Н	1 a	3	В	22	11a, (63)
5	н	н	OMe	1 a	4	A[b]	7	8a, 88 (73)
6	н	н	NO ₂	1 a	5	A[b]	44	9a, 87 (72)
7	OMe	н	н	1 b	2	A	22	6b , (70)
8	OMe	Н	Н	1 b	2	В	44	10b, (57)

[a] Determined by gas chromatography based on ArOH used. Value in parentheses indicates yield after isolation. [b] Iodobenzene (1a; 2 mmol) and Cs_2CO_3 (2 mmol) were used.

ing diarylated product 10a in 62% yield along with a minor amount of 6a (25%). The results for the reactions of 4-iodoanisole (1b) with 2 and of 1a with 2-(4-methylphenyl)phenol (3) demonstrate the generality of the present diarylation as well as monoarylation. In the reactions of 3'-substituted 2-phenylphenols 4 and 5 with 1a, however, only the monoarylated products 8a and 9a, respectively, were formed even when an excess of 1a was employed.

The monoarylation of 2 serves as an example in a possible mechanism illustrated in Scheme 2 (neutral ligands are omit-



Scheme 2. Possible reaction mechanism for the cross-coupling of aryl iodides with 2-phenylphenol (2) to afford the corresponding monoarylation product.

ted). Oxidative addition of aryl iodide to a palladium(0) species generated in situ followed by reaction with the phenolate forms aryl(aryloxy)palladium intermediate **A**. Then, **A** may be transformed into diarylpalladium species **B**, and the subsequent reductive elimination occurs to give the monoarylated product.^[5] Coordination of the phenolic oxygen to the palladium center in **A**, similar to that in the coupling of 2-hydroxybenzaldehydes with aryl iodides,^[3a] is thus considered to be the key to the effective, regioselective C–H bond activation. The second arylation may proceed by the same mechanism. The results of the reactions of **1a** with **4** and **5** suggest that a) the existence of a substituent at the 3'-position of **2** prevents the second arylation for steric reasons, and b) the transformation of **A** into **B** is feasible even when the substituent is strongly electron-withdrawing or electron-releasing.^[6]

With the present catalytic system 1-naphthol (12) was monophenylated to give 8-phenylnaphthol (13) selectively (Scheme 3). The use of Cs_2CO_3 was also essential for the catalytic reaction to take place smoothly. It was also of considerable interest that when 2-naphthol (14) was treated with two equivalents of bromobenzene (1c) and Pd(OAc)₂/PPh₃, formally diphenylated compound 15 was obtained as the predominant



Scheme 3. Cross-coupling of 1a with 12: DMF, N₂, 110 °C, 10 h.

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Table 2. Selected physical and spectroscopic data [a] for compounds 6b, 7a-9a, 10a, 10b, 11a, and 15.

6b: M.p. 88 °C, ¹H NMR: δ = 3.76 (s, 3H, OMe), 4.77 (s, 1H, OH), 6.75 (dt, J = 8.8, 2.0 Hz, 2H, H-3"), 6.80 (dd, J = 1.0, 7.8 Hz, 1H, H-3), 6.87 (dt, J = 1.0, 7.3 Hz, 1H, H-5), 7.07 (dd, J = 1.5, 7.3 Hz, 1H, H-6), 7.09 (dt, J = 8.8, 2.0 Hz, 2H, H-2"), 7.17 (dt, J = 1.5, 7.8 Hz, 1H, H-4), 7.37–7.49 (m, 4H)

7a: M.p. 64 °C, ¹H NMR: δ = 2.45 (s, 3 H), 4.81 (s, 1 H), 6.78 (dd, J = 1.0, 8.3 Hz, 1 H), 6.81 (dt, J = 1.0, 7.3 Hz, 1 H), 7.01 (dd, J = 1.9, 7.3 Hz, 1 H), 7.11–7.22 (m, 6H), 7.25–7.33 (m, 3 H)

8a: M.p. 136–137 °C, ¹H NMR: δ = 3.84 (s, 3 H), 4.87 (s, 1 H), 6.78 (dd, J = 1.0, 8.3 Hz, 1 H), 6.84 (dt, J = 1.0, 7.3 Hz, 1 H), 6.93 (d, J = 2.4 Hz, 1 H), 7.03 (dd, J = 2.4, 8.3 Hz, 1 H), 7.06 (dd, J = 1.5, 7.3 Hz, 1 H), 7.10–7.21 (m, 6 H), 7.43 (d, J = 8.3 Hz, 1 H)

9a: M.p. 144–145 °C, ¹H NMR: δ = 4.65 (s, 1 H), 6.75 (dd, J = 1.0, 8.3 Hz, 1 H), 6.90 (dt, J = 1.0, 7.3 Hz, 1 H), 7.07 (dd, J = 1.5, 7.3 Hz, 1 H), 7.17–7.28 (m, 6 H), 7.64 (dd, J = 1.5, 8.8 Hz, 1 H), 8.30 (dd, J = 2.4, 8.8 Hz, 1 H), 8.31 (s, 1 H)

10a: M.p. 150–151 °C, ¹H NMR: δ = 4.66 (s, 1 H), 6.54 (dd, J = 1.0, 8.3 Hz, 1 H), 6.58 (dt, J = 1.0, 7.3 Hz, 1 H), 6.76 (dd, J = 1.5, 7.3 Hz, 1 H), 6.94 (dt, J = 1.5, 7.3 Hz, 1 H), 7.09–7.18 (m, 10 H), 7.45–7.53 (m, 3 H)

10b: M.p. 153–154 °C, ¹H NMR: δ = 3.74 (s, 6H, OMe), 4.63 (s, 1H, OH), 6.61 (dd, J = 1.0, 8.3 Hz, 1H, H-3), 6.64 (dt, J = 1.0, 7.3 Hz, 1H, H-5), 6.71 (dt, J = 8.8, 2.0 Hz, 4H, H-3"), 6.77 (dd, J = 1.5, 7.3 Hz, 1H, H-6), 6.99 (dt, J = 1.5, 8.3 Hz, 1H, H-4), 7.04 (dt, J = 8.8, 2.0 Hz, 4H, H-2"), 7.42–7.52 (m, 3H)

11a: M.p. 122.5–123.5 °C, ¹H NMR: δ = 2.49 (s, 3 H), 4.63 (s, 1 H), 6.57 (dd, J = 1.0, 7.3 Hz, 1 H), 6.60 (dt, J = 1.0, 7.3 Hz, 1 H), 6.76 (dd, J = 1.5, 7.3 Hz, 1 H), 6.96 (dt, J = 1.5, 7.3 Hz, 1 H), 7.11–7.18 (m, 10 H), 7.31 (s, 2 H)

15: M.p. 117–118 °C, ¹H NMR: δ = 4.93 (s, 1 H, OH), 7.02–7.10 (m, 6H), 7.27 (dt, J = 1.5, 8.1 Hz, 1 H, H-6), 7.31 (dt, J = 1.5, 8.1 Hz, 1 H, H-7), 7.36 (d, J = 8.1 Hz, 1 H, H-8), 7.41 (d, J = 7.3 Hz, 1 H, H-3'), 7.54 (dt, J = 2.2, 7.3 Hz, 1 H, H-4'), 7.59 (dt, J = 1.5, 7.3 Hz, 1 H, H-5'), 7.62 (dd, J = 2.2, 7.3 Hz, 1 H, H-6'), 7.69 (d, J = 8.8 Hz, 1 H, H-4), 7.73 (d, J = 8.1 Hz, 1 H, H-5)

[a] ¹H NMR: 400 MHz, CDCl₃, TMS.

product (Scheme 4). The first step of this reaction, monophenylation at the 1-position of 14, may involve nucleophilic attack of the corresponding naphtholate on a phenylpalladium(II) species generated in situ. Note that while palladium-catalyzed intramolecular coupling of aryl halides with enolates in-



Scheme 4. Cross-coupling of 1c with 14: DMF, N₂, 150 °C, 1.5 h.

cluding phenolates is known,^[7] the corresponding intermolecular version has been limited to only few reactions in which nitriles function as carbon nucleophiles.^[8] Nevertheless, the present procedure was found to bring about the intermolecular cross-coupling of **1a** with 1,3-diphenyl-2-propanone (**16**) to give 1,1,3,3-tetraphenyl-2-propanone (**17**; Scheme 5).



17; 48 %

Scheme 5. Cross-coupling of 1a with 16: DMF, N2, 100 °C, 5 h.

Experimental Section

A mixture of 1 (1.2–4 mmol), ArOH 2–5, 12, or 14 (1 mmol), a palladium catalyst (0.025-0.05 mmol), Cs₂CO₃ (1.2–4 mmol), and DMF (5 mL) was stirred in the presence or absence of molecular sieves 4 Å (200 mg) under nitrogen at 100–150 °C for 1.5–44 h. After cooling, the reaction mixture was poured into dilute hydrochloric acid, extracted with ether, and dried over sodium sulfate. The product was isolated by column chromatography on silica gel using hexane/dichloromethane or hexane/ethyl acetate as eluent.

Selected data for the new products obtained are listed in Table 2. The structures were determined with the aid of ¹H NMR, NOE, COSY, and HOHAHA experiments. Satisfactory combustion analysis data were also obtained. Compounds 6a[9], 13[10], and 17[11] are known.

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