



Palladium-catalyzed asymmetric arylation of 2,3-dihydrofuran with aryl triflates in water in the presence of surfactants

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Abstract

Palladium-catalyzed asymmetric arylation of 2,3-dihydrofuran with aryl triflates occurred in water in the presence of surfactants under very mild conditions. In the presence of $C_{16}H_{33}N^+Me_2(CH_2)_3SO_3^-$ (HDAPS) as the surfactant and Binap as the chiral ligand, enantiomeric excess up to 67% with a conversion of 73% after 2 h were obtained.

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1. Introduction

Organometallic homogeneous catalysis is now a widely-used methodology in organic chemistry [1,2]. This is mainly due to the high activity and selectivity of such systems, and also the good reproducibility under generally very mild conditions. Most chemical transformations of organic substrates are performed in organic solvents, in the laboratory as well as in the industry. Recently, the development of organic reactions in alternative media such as water [3–6], ionic liquids [7,8], supercritical fluids [9], or fluorosolvents [10], is becoming an important chemical research topic. Some advantages of these non-usual media could be higher activity and selectivity, easy product separation, and eventually catalyst recycling. The substitution of organic solvents by water in both academic and industrial research seems advantageous for environmental and economic reasons; indeed, water is safe, benign, non-toxic, environmentally friendly, and cheap compared to organic solvents. However, most organic products as well as organometallic catalysts are insoluble in water.

One way to circumvent this problem is the use of water-soluble organometallic catalysts [3–6], obtained by incorporation into the complex of strongly hydrophilic lig-

ands; in this case there is generally the need to use a biphasic aqueous/organic system when the organic substrates are not water-soluble. The main drawback of this approach is the phase-transfer limitation of the reactants leading very often to lower reaction rates; sometimes the reaction rate could be reduced to such an extent that it becomes unacceptable, for example in the high olefin hydroformylation.

The second approach in order to improve the solubility of organic substrates is the use of surfactants that can form micelles. Such a system could improve the rate by bringing both the substrate(s) and the organometallic catalyst in close proximity in the hydrophobic part of the micelle. This approach has been successfully applied in hydrogenation [11–23], hydroformylation [24,25], alkylation reaction [26–32], Suzuki coupling [33,34], Heck reaction [35], carbonylation [36], and aldol reaction [37]. More recently it was shown that asymmetric hydrogenation [11–23] and allylic alkylation [29–32] occurred readily using such a system. In hydrogenation, higher enantioselectivities were obtained in the rhodium-catalyzed reduction of α -amino acid precursors in water in the presence of surfactants than in usual organic solvents. Palladium-catalyzed asymmetric allylic alkylation was also performed using an immobilized complex of a chiral ligand on an amphiphilic resin [27,28] or chiral diphosphines in the presence of a surfactant [29–31], enantioselectivities of up to 95% being obtained.

The palladium-catalyzed arylation of olefins (Heck reaction) has been widely applied in organic synthesis for many

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years [38–40]. Both intramolecular and intermolecular asymmetric versions have been reported. In the intermolecular version, Pd(OAc)₂/Binap catalyst system was firstly used by Ozawa et al. [41–44] and Koga et al. [45]; more recently Pfaltz et al. [46–47] and Helmchen [48] reported that diphenylphosphinoxazoline was also an efficient chiral ligand in the same type of asymmetric intermolecular Heck reaction, enantioselectivities as high as 95% being attained. It was shown that palladium-catalyzed arylation of methyl acrylate in the presence of an alkali metal carbonate can be performed in water alone upon addition of a tetraalkylammonium salt [49,50]; however the salt used was generally a tetrabutylammonium salt, which is not a surfactant. Following our continuing interest in the asymmetric catalyzed carbon–carbon bond formation in water [29–31], we reported in this paper the use of palladium complexes in an asymmetric Heck reaction in water in the presence of surfactants.

2. Experimental

2.1. General

All reactions were conducted in Schlenk tubes under nitrogen. NMR spectra were recorded on a Bruker 300 MHz instrument and referenced to Me₄Si as internal standard. Conversion was determined by GC using a Quadrex OV1 column (30 m × 0.25 mm), enantiomeric excess was determined by GC using a Cydex β column (25 m × 0.25 mm) for **3a–c** and HPLC with Chiralpak^{AD} column (25 cm × 4.6 mm) using *n*-hexane/isopropanol (93:7) as the eluent, the flow rate being 0.5 ml/min, for **3d**.

C₁₆H₃₃NMe₃HSO₄ (CTHSO₄ or cetyltrimethylammonium hydrogen sulfate), C₁₆H₃₃NMe₃Br (CTHB or cetyltrimethylammonium bromide), C₁₂H₂₅OSO₃Na (SDS or sodium dodecyl sulfate), C₁₂H₂₅SO₃Na (sodium dodecyl sulfonate), Brij 35 (polyoxyethylene [23] lauryl ether), Tween-40 (polyoxyethylene sorbitan monopalmitate), C₁₀H₂₁N⁺Me₂(CH₂)₃SO₃[−] (DeDAPS or *N*-decyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate), C₁₂H₂₅N⁺Me₂(CH₂)₃SO₃[−] (DDAPS or *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate), C₁₆H₃₃N⁺Me₂(CH₂)₃SO₃[−] (HDAPS or *N*-hexadecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate), were purchased from Aldrich, (*R*)-Binap, (*R*)-TolBinap, and Pd(OAc)₂ from Strem. (*R*)-MeOBiphep was a gift from Hoffmann la Roche Ltd.

Phenyltriflate **2a** [51], 4-chlorophenyltriflate **2b** [51], 4-methoxyphenyltriflate **2c** [52], and 1-naphthyltriflate **2d** [52] were prepared from the corresponding phenols in accordance with the literature.

2.2. Standard Heck reaction

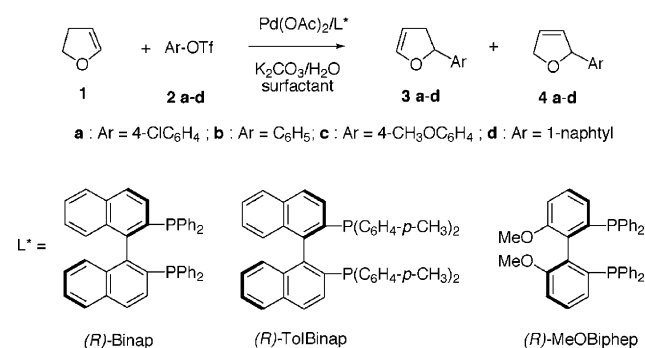
Pd(OAc)₂ (6 mg, 0.026 mmol), Binap (32 mg, 0.052 mmol), and HDAPS (50.8 mg, 0.07 mmol) were placed in a Schlenk

tube under argon and dissolved in H₂O (4 ml). After being stirred for 15 min, this solution was transferred to a Schlenk tube containing the triflate (0.9 mmol) and diphenyloxide (153 mg, 0.9 mmol). After being stirred at room temperature for 5 min, the Schlenk tube was warmed at 45 °C for 5 min. Then dihydrofuran (350 μl, 4.5 mmol) was added to this solution, followed by a solution of K₂CO₃ (373 mg, 2.7 mmol) and HDAPS (50.8 mg, 0.07 mmol) in H₂O (4 ml). After being stirred for 2 h at 45 °C, the solution was cooled, and the aqueous phase was extracted with CH₂Cl₂ (3 × 20 ml). The organic phase was evaporated under reduced pressure. The conversion in **3** and **4** and the enantioselectivity of **3** were determined by GC or HPLC. The structures of compounds **3** and **4** were determined by ¹H NMR and comparison with authentic samples, after purification by column chromatography, and their absolute configuration by correlation with their specific rotations [42].

3. Results and discussion

The reaction that was chosen for the study in water in the presence of surfactants was the Heck reaction between 2,3-dihydrofuran (**1**) and 4-chlorophenyl triflate (**2a**). Binap was also selected as the chiral ligand according to the results obtained previously with this ligand in homogeneous conditions [42–45] as well as in the asymmetric palladium-catalyzed alkylation in aqueous micelles [29–31]. After the survey of several reaction conditions using **1** (5 equiv) and 4-chlorophenyl triflate (1 equiv), the use of 3 mol% Pd(OAc)₂, 6 mol% Binap, K₂CO₃ (3 equiv) at 45 °C were found to be the best, the reaction being quenched after 2 h (Scheme 1).

Under these optimized conditions, we first investigated the influence of the surfactant on the condensation (Table 1). It is to be noticed that reaction occurred in water only, without surfactant; 33% conversion in compound **3a** was observed after 2 h, the enantioselectivity being 60% (*S*) in product **3a** (Table 1, entry 1). Surprisingly, only 5% conversion was obtained in the presence of the cationic surfactant cetyltrimethylammonium hydrogen sulfate (Table 1, entry 2), when the highest activities and enantioselectivities



Scheme 1.

Table 1
Asymmetric Heck reaction of 2,3-dihydrofuran (**1**) with 4-chlorophenyl triflate (**2a**) catalyzed by Pd(OAc)₂-(*R*)-Binap^a

Entry	Surfactant	Conversion in 3a (%) ^b	ee (%) of 3a (<i>R</i>) ^c
1	No	33	60
2	<i>n</i> -C ₁₆ H ₃₃ N ⁺ Me ₃ HSO ₄ ⁻	5	–
3	<i>n</i> -C ₁₆ H ₃₃ N ⁺ Me ₃ Br ⁻	1	–
4	<i>n</i> -C ₁₂ H ₂₅ OSO ₃ Na	32	41
5	<i>n</i> -C ₁₂ H ₂₅ SO ₃ Na	28	59
6	Brij 35	40	44
7	Tween-40	5	–
8	<i>n</i> -C ₁₀ H ₂₁ N ⁺ Me ₂ (CH ₂) ₃ SO ₃ ⁻	58	58
9	<i>n</i> -C ₁₂ H ₂₅ N ⁺ Me ₂ (CH ₂) ₃ SO ₃ ⁻	18	73
10	<i>n</i> -C ₁₆ H ₃₃ N ⁺ Me ₂ (CH ₂) ₃ SO ₃ ⁻	73	67

^a [1]:[2a]:[Pd(OAc)₂]:[Binap]:[K₂CO₃]:[surfactant] = 175:35:1:2:105:5.5; 45 °C; 2 h; 8 ml H₂O; PhOPh was used as an internal standard.

^b Determined by GC.

^c Determined by HPLC.

were observed in the palladium-catalyzed alkylation in water; cetyltrimethylammonium bromide gave 1% conversion (Table 1, entry 3). It is to be noted that the tetrabutylammonium hydrogen sulfate or bromide gave a quantitative conversion in the arylation of methyl acrylate in neat water [49,50]. The anionic surfactants sodium dodecylsulfonate and sodium dodecylsulfate gave low conversion in **3a** (32 and 28%, respectively) with moderate enantioselectivity (41 and 59% ee) (Table 1, entries 4 and 5). Among the two neutral surfactants studied, Brij 35 gave moderate conversion and enantioselectivity (40% conversion and 44% ee), when only 5% conversion was observed using Tween-40 (Table 1, entries 6 and 7). The zwitterionic surfactants *N*-decyl-, *N*-dodecyl-, and *N*-hexadecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate gave enantioselectivities of up to 58, 73, and 67% ee, respectively (Table 1, entries 8–10). However the conversion in **3a** depends strongly on the chain length of the surfactant: the highest conversion was obtained using HDAPS (73%), the lowest using DDAPS (18%), DeDAPS giving 58% conversion. It is to be noted that the unique regioisomer **3a** was formed, that is the thermodynamic product, whatever the surfactant used, in quite contrast with the formation of the two regioisomers **3a** and **4a** generally observed using Pd(OAc)₂/Binap as the catalyst in benzene. This different behavior is probably due to the very low dissociation rate of the palladium complex from the kinetic 2-aryl-2,5-dihydrofuran **4a** formed, allowing the reinsertion reaction, and so the preferential formation of the thermodynamic product 2-aryl-2,3-dihydrofuran **3a**; both the substrate and the organometallic catalyst are maintained in close proximity in the hydrophobic part of the micelle. The observed enantioselectivity using HDAPS as the surfactant is lower than that reported using diisopropylethylamine as the base in benzene [41], but quite similar to the value obtained in the presence of a mineral base such as Na₂CO₃ [43]. It is to be noted that under these conditions,

Table 2
Influence of the concentration of HDAPS on the coupling of **1** and **2a**^a

Entry	[HDAPS] (mmol l ⁻¹)	Conversion in 3a (%) ^b	ee (%) of 3a (<i>R</i>) ^c
1	0	33	60
2	1	33	81
3	7.5	36	98
4	10	30	73
5	20	73	67
6	40	36	27

^a [1]:[2a]:[Pd(OAc)₂]:[Binap]:[K₂CO₃] = 175:35:1:2:105; 45 °C; 2 h; 8 ml H₂O; PhOPh was used as an internal standard.

^b Determined by GC.

^c Determined by HPLC.

no coupling was observed when diisopropylethylamine or triethylamine was used as the base.

We then examined the effect of the concentration of the surfactant HDAPS on both the activity and the enantioselectivity in the Heck reaction between 2,3-dihydrofuran (**1**) and 4-chlorophenyl triflate (**2a**), Pd(OAc)₂/Binap being used as the catalyst. The results summarized in Table 2 indicated that the highest conversion in **3a** was observed when the concentration of the surfactant was 20 mmol l⁻¹, far from the CMC value of this surfactant (0.15 mmol l⁻¹). However the enantioselectivity of the coupling reaction increased drastically above the CMC: 81 and 98% ee were obtained when the concentration of the surfactant was 1 and 7.5 mmol l⁻¹, respectively; however the conversion after 2 h was only 33 and 36%, respectively (Table 2, entries 2 and 3). This ee value decreased to 73 and 67%, when the conversion was 30 and 73%, at [HDAPS] = 10 and 20 mmol l⁻¹, respectively. When the concentration of HDAPS attained 40 mmol l⁻¹ or more (Table 2, entry 6), both the activity and the enantioselectivity of the catalyst decreased, due probably to the stickiness of the medium.

We used other atropisomeric ligands in this coupling reaction under the optimized conditions found for Binap

Table 3
Influence of the ratio ligand/Pd(OAc)₂ and of the nature of the ligand on the coupling reaction of **1** and **2a**^a

Entry	Ligand	Surfactant	[ligand]/[Pd]	Conversion in 3a (%) ^b	ee (%) of 3a (<i>R</i>) ^c
1	(<i>R</i>)-Binap	No	2	33	60
2	(<i>R</i>)-Binap	HDAPS	2	73	67
3	(<i>R</i>)-Binap	No	1	28	54
4	(<i>R</i>)-Binap	HDAPS	1	79	53
5	(<i>R</i>)-TolBinap	HDAPS	2	27	55
6	(<i>R</i>)-MeOBiphep	No	2	13	74
7	(<i>R</i>)-MeOBiphep	HDAPS	2	15	83
8	(<i>R</i>)-MeOBiphep	No	1	32	79
9	(<i>R</i>)-MeOBiphep	HDAPS	1	32	84

^a [1]:[2a]:[Pd(OAc)₂]:[K₂CO₃]:[HDAPS] = 175:35:1:105:5.5; 45 °C; 2 h; 8 ml H₂O; PhOPh was used as an internal standard.

^b Determined by GC.

^c Determined by HPLC.

Table 4
Coupling of **1** with various triflates^a

Entry	Ar	HDAPS	Conversion in 3 + 4 (%) ^b	Ratio 3/4 ^b	ee (%) of 3 (<i>R</i>) ^c
1	4-ClC ₆ H ₄	No	33	100/0	60
2	4-ClC ₆ H ₄	Yes	73	100/0	67
3	C ₆ H ₅	No	18	100/0	58
4	C ₆ H ₅	Yes	86	96/4	50
5	4-MeOC ₆ H ₄	No	7	100/0	–
6	4-MeOC ₆ H ₄	Yes	80	100/0	53
7	1-naphtyl	No	19	91/9	43
8	1-naphtyl	yes	54	71/29	52

^a [1]:[2]:[Pd(OAc)₂]:[Binap]:[K₂CO₃]:[HDAPS] = 175:35:1:2:105:5.5; 45 °C; 2 h; 8 ml H₂O; PhOPh was used as an internal standard.

^b Determined by GC.

^c Determined by HPLC.

(Table 3). Surprisingly (*R*)-TolBinap gave a low conversion (27% after 2 h) with an enantioselectivity quite similar to that obtained with Binap (55% ee) (Table 3, entry 5), when (*R*)-MeOBiphep gave low conversion, but enantioselectivity up to 83% (Table 3, entry 7). It is to be noted that decreasing the ratio Binap/Pd from 2 to 1 gave the same conversion in **3a** (73 versus 79%), but lower enantioselectivity (67 versus 53% ee) (Table 3, entries 2 and 4). For (*R*)-MeOBiphep changing this ratio from 2 to 1 gave higher conversion and the same enantioselectivity, whatever the conditions used (Table 3, entries 7 and 9). These results showed that the size of the complex, and so of the ligand, is very important for obtaining both a high activity and enantioselectivity.

This coupling reaction was extended using other aryl triflates. Phenyl triflate (**2b**) and 4-methoxyphenyl triflate (**2c**) gave the expected products **3b** and **3c** (86 and 80% conversion) with 50 and 53% ee, respectively, in water in the presence of HDAPS (Table 4, entries 4 and 6). It is to be noted that in water without any added surfactant, practically no reaction occurred after 2 h (Table 4, entries 3 and 5). Naphtyl triflate (**2d**), a more hydrophobic substrate, afforded a 91/9 mixture of **3d/4d** in neat water with a low conversion (19%), the ee of **3d** being 43% (Table 4, entry 7). Addition of HDAPS as the surfactant increased the conversion to 54%; however a 71/29 mixture of **3d/4d** was now obtained, the ee of **3d** being 52% (Table 4, entry 8).

4. Conclusion

In conclusion, we have shown that asymmetric intermolecular Heck reaction can be performed in water in the presence of surfactants. The proper choice of the surfactant allows the reaction to occur in a short time under very mild conditions with higher conversion than in neat water; the thermodynamic compound was predominantly obtained, if not only, with ee up to 67% under the optimized conditions. Work is in progress in order to increase the enantioselectiv-

ity of the reaction and to extend this coupling to other chiral ligands such as phosphinooxazoline and to other triflates.

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