Cross-Coupling Reactions |Hot Paper|



Source of Selectivity in Oxidative Cross-Coupling of Aryls by Solvent Effect of 1,1,1,3,3,3-Hexafluoropropan-2-ol

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Abstract: Solvents such as 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) with a high capacity for donating hydrogen bonds generate solvates that enter into selective cross-coupling reactions of aryls upon oxidation. When electric current is employed for oxidation, reagent effects can be excluded and a decoupling of nucleophilicity from oxidation potential can be achieved. The addition of water or methanol to the electrolyte allows a shift of oxidation potentials in a specific

Introduction

The synthesis of non-symmetrical biaryls is a very commonly applied transformation in organic synthesis.^[1] Direct cross-dehydrogenative coupling is of utmost interest because the absence of leaving groups in the substrates avoids by-products and thus contributes to "greener" chemistry.^[2] The latest methods developed by Kita et al. exploit hypervalent iodine oxidants, allowing direct synthesis with a wide range of substituted biaryls.^[3] O₂ also showed good results when used as an oxidant in transition-metal catalyzed cross-coupling reactions.^[4] However, a drawback of these new methodologies is the use of expensive catalysts or reagents, sometimes applied in overstoichiometric amounts.^[5] Employing electric current as oxidant is an alternative and has turned out to be a particularly powerful method for synthesizing biaryls.^[6] The use of 1,1,1,3,3,3hexafluoropropan-2-ol (HFIP) and boron-doped diamond (BDD) as anode material has given promising results for cross-coupling of phenols and aryls.^[7] Because of the unique ability of the fluorinated solvent to stabilize radical intermediates,^[8] HFIP

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range, creating suitable systems for selective anodic crosscoupling reactions. The shift in the redox potentials depends on the substitution pattern of the substrate employed. The concept has been expanded from arene–phenol to phenol– phenol as well as phenol–aniline cross-coupling. This driving force for selectivity in oxidative coupling might also explain previous findings using HFIP and hypervalent iodine reagents.

is frequently found in reactions using hypervalent iodine oxidants. $^{\rm [3a,b,9]}$

When directly electrolyzing two aromatic components **a** and **b** (Scheme 1) the major products are expected to be the homo-coupling products **aa** or **bb** because the electron densities (and therefore the nucleophilicities) of the individual substrates used determine the outcome of the reaction. Intuitively, the compound with a higher electron density has a lower oxidation potential and therefore, will be preferentially oxidized at the anode. Since electron density and nucleophilicity are directly linked, the same compound will enter the reaction sequence for a subsequent nucleophilic attack. With this sequence only homo-coupling products are expected. The formation of homo-coupling products is well-known and has to be suppressed. Yoshida et al. circumvent this preferential formation pool method.^[10a]

Generation of the desired mixed biaryl **ab** by this strategy is rather difficult. It is statistically underrepresented because the electrochemical potential is a strong driving force for selectivity. Yoshida et al. circumvent formation of the undesired symmetrical biphenyls in an extraordinarily effective way by electrolyzing only one component at low temperature, the second substrate being added subsequently to this cation-pool;^[10] when combined efficiently with flow techniques, this ensures



Scheme 1. The products anticipated for direct anodic cross-coupling of arenes.

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control of selectivity.^[10b,11] In direct electrolysis, mixtures of HFIP and other protic additives like water or methanol significantly and positively influence the yield and selectivity of anodic phenol–arene cross-coupling reactions (see Scheme 2).^[7]

Despite these promising results and the ensuing quick access to biaryls, a rationale could not be provided for the outstandingly high selectivity. Here, we describe the effect of, and correlation between, HFIP/MeOH mixtures; adjustment of selectivity; and a means of predicting the electrochemical crosscoupling reaction.

Results and Discussions

During investigation of the reaction to **1 ab** in HFIP/MeOH mixtures (Scheme 2), it was surprisingly found that no homo-coupling of **1a** occurred. Optimization of the electrolysis parameters by adding MeOH resulted in varying quantities of the undesired symmetrical biaryl **1bb** (shown in the lower part of Figure 1). Hence, a decoupling of the oxidation potential of phenol **1a** and its nucleophilicity is most likely. It is noteworthy that if no **1b** is present, a non-symmetrical biphenol is obtained.^[6h]

Because the anodic cross-coupling reaction is strongly electrolyte dependent, cyclic voltammetry experiments can also be performed with a glassy carbon electrode tip. Cyclic voltamme-



Scheme 2. Example of phenol-arene cross-coupling investigation to illustrate the strong influence of protic additives on product distribution.



Figure 1. Yield and selectivity of 1 ab formed as a function of the amount of methanol in HFIP. [a] Selectivity determined by GC.

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Figure 2. Shift of oxidation potentials with increasing mole fraction of MeOH in HFIP. Blue diamonds: **1 a**, green squares: **1 b**. WE: glassy carbon electrode tip, 2 mm diameter; AE: glassy carbon rod; RE: Ag/AgCl in saturated LiCl/ EtOH. Solvent: HFIP + 0-25 %v/v MeOH. Criteria for oxidation: $j=0.1 \text{ mA cm}^{-2}$; $v=50 \text{ mV s}^{-1}$; $T=20 \degree$ C. Stirring conditions during measurement. c(substrate) = 151 mM, supporting electrolyte: 0.09 M Bu₃NMe O₃SOMe.

try investigations of substrates **1a** and **1b** (Figure 2) indicate a clear shift of oxidation potentials in HFIP when MeOH is added to the electrolyte. In neat HFIP, the predominant formation of **1bb** is consistent with the preparative electrolysis: due to the lower oxidation potential, **1b** is preferentially oxidized and subsequently reacts with a second molecule of **1b**. In contrast, when using 18%v/v MeOH the oxidation potential of **1a** is decreased by almost 100 mV and the oxidation potential of **1b** shifted in the opposite direction, leading to a reversal of the oxidation potentials. However, no homo-coupling to biphenols is detected, clearly indicating that the solvent system used must also influence the nucleophilicity of the substrates employed.

After selective generation of phenoxyl radicals (step I) by shifting the oxidation potentials, the solvent system prevents nucleophilic attack of **1a** in step II, inhibiting formation of the corresponding phenol homo-coupling product (Scheme 3). Instead, **1b** enters the reaction sequence to form the intermediate accomplishing the desired cross-coupling product **1ab** after a second oxidation step (step III) and aromatization. However, the selectivity in step II has not so far been explained and must be attributed to some kind of solvent effect.

Several studies have shown a broad variety of solvent structures in HFIP/H₂O mixtures, ranging from micelle-like clusters to helical chains comparable to those in solid HFIP.^[12] Furthermore, changes in the nucleophilicity of the solvent with increasing amounts of H₂O have been shown to be relevant in solvolytic studies^[13] for S_N1 and S_N2 reactions.^[14] This led us to conclude that, on the one hand, differences in solvation around the coupling partners **1a** and **1b** determine nucleophilicity and, on the other, methanol additives act as weak bases affecting oxidation potentials (Scheme 4).

DOSY experiments on **1a** and **1b** were performed to detect any irregular changes in the solvation shells of these two substrates upon addition of MeOH to HFIP (see Supporting Information). The near-linear behavior of the system provides no supportive argument, since the viscosity is strongly altered upon MeOH addition. However, the specific interaction of HFIP with phenols and anilines was treated in detail by calculations and kinetic studies.^[15]

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Scheme 3. Proposed mechanism for anodic phenol–arene cross-coupling with 18 %v/v MeOH in HFIP.



Scheme 4. Decoupling of oxidation potential and nucleophilicity by HFIP clusters/solvates. The color indicates the density of the solvation sphere.

In polar solvents, solvates of phenols are more pronounced than those of arenes, due to the ability of phenols to participate in hydrogen bonding. In the present case, 4-methylguaiacol (**1a**) is strongly shielded in pure HFIP (**A**), which prevents nucleophilic attack on the generated radical cations of 1,2,4-trimethoxybenzene. The more electron-rich substrate **1b** is therefore selectively oxidized and undergoes homo-coupling. Methanol additives act like bases when added to a solution of **1a** in HFIP. Implemented MeOH weakens the solvate with phenol but also facilitates deprotonation of **1a** by interacting via hydrogen bonding. This shifting of oxidation potential by MeOH does not occur when less electron-rich arenes are cross-coupled with 4-methylguaiacol. A selection of simple coupling partners, along with the corresponding oxidation potentials depending on the amount of MeOH, is shown in Figure 3. In neat HFIP, the E_{Ox} of every substrate is suitable for cross-coupling with **1a**. Addition of methanol results in a too large difference in the E_{Ox} (= ΔE_{Ox}) of the respective coupling partners. When ΔE_{Ox} is too large for a substrate combination, alternative reaction pathways might be opened up.

Table 1 displays the results of electrolysis of **1a** with arenes of higher oxidation potential in pure HFIP. Exclusive selectivity is obtained in all cases, with individual yields of up to 74% (entry 3). Using MeOH as additive leads to a dramatic decrease in yields in these cases, so that only traces of the desired cross-coupling products are formed. These results show a strong correlation with the CV data and provide a consistent picture.

This concept can also be applied to and further elaborated in a recently reported anodic phenol cross-coupling reaction.^[16]



Figure 3. Shift in oxidation potentials of various arenes. ◆: 1 a, ▲: 3,4-dimethylanisole 2 b, ×: 2,5-dimethylanisole 3 b, ■: 4-isopropyl-3-methylanisole 4 b, ●: 2-isopropyl-5-methylanisole 5 b. CV criteria: see Figure 2.



[a] Electrolysis conditions: solvent: HFIP, I = 50 °C, constant current ($j = 2.8 \text{ mA cm}^{-2}$), BDD anode, nickel-net cathode, undivided cell, Q = 2 F-n (phenol **1 a**); supporting electrolyte: 0.09 M Et₃NMe O₃SOMe. [b] Yields of isolated products. [c] Ratio of cross-coupling product **ab** to homo-coupling product **bb** (bb was not detected by GC).

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For example, when coupling **1a** with *meta*-substituted phenol derivatives (Figure 4), in general high selectivity and good yields are obtained for the desired non-symmetrical biphenols. Here, solvates of phenols with different electronic properties differ in their densities: the more electron-rich the phenol, the more dense the sphere of surrounding solvent should be and therefore, the less nucleophilic the substrate.

In most cases we were able to determine the ideal conditions for cross-coupling reactions of four different classes of phenols with **1a** (see Table 2). By comparing the different substitution patterns of the substrates employed, their individual $E_{\rm Ox}$ values, and the results of the reactions studied, ideal ranges of $\Delta E_{\rm Ox}$ could be very clearly defined (e.g., entry 2, $\Delta E_{\rm Ox} \approx 200$ mV, HFIP + 18%(v/v) MeOH; see also Supporting Information). This estimation of the ideal $\Delta E_{\rm Ox}$ markedly increases the probability of finding possible coupling partners. 4-Methyl-guaiacol shows better results with higher $\Delta E_{\rm Ox}$ when coupled with *meta*-substituted phenols (entry 1), whereas low values of $\Delta E_{\rm Ox}$ are preferred when **1a** is coupled with 2,4-disubstituted



Figure 4. Differences of oxidation potentials of *meta*-substituted phenols relative to 1 a for cross-coupling with 1 a. CV criteria: see Figure 2.

Entry	Substitution pattern	Lowest ΔE_{Ox}	Highest ΔE_{Ox}
1 ^[a]	R ОН	285 mV	409 mV
2 ^[b]	КОН	192 mV	196 mV
3 ^[b]	R'OH R	25 mV	133 mV
4 ^[c]	R'OH	187 mV	326 mV
[a] Optimized reaction conditions in neat HFIP. [b] Optimized reaction			

Table 2. Suitable ranges of ΔE_{Ox} for cross-coupling of **1 a** with phenols of various substitution patterns.

[a] Optimized reaction conditions in neat HFIP. [b] Optimized reaction conditions in HFIP+18%(v/v) MeOH. [c] HFIP+18%(v/v) MeOH showed the best results, except for R=Me, R'=iPr. For CV criteria see Figure 2. R, R'=alkyl, alkoxy, halogen. For exact specification of used substrates see the Supporting Information.

phenols (entry 3). In general, CV helps to indicate the correct stoichiometry for an electrochemical cross-coupling reaction: although, counterintuitively, 2,4-dimethylphenol exhibits a lower E_{Ox} than **1a** in pure HFIP. However, since the substitution pattern will strongly influence the solvate structure and hydrogen bonding, a high level of dependence is understandable. Substituents *ortho* to the phenolic moiety allow only a small potential shift (entry 3).

To extend the applicability of this study to cross-coupling reactions with new substitution patterns, we created a database with a large number of E_{Ox} values for different components including phenols, arenes, anilines, and acetamides (see Supporting Information). In general, oxidative treatment of aniline derivatives promotes their polymerization.^[17] Consequently, overoxidation is a serious problem in anodic cross-coupling, and organocatalytic reactions currently use N-protection to prevent formation of undesired by-products.^[3a] When using hypervalent iodine mediated coupling, N-mesyl protected anilines give good yields but require a waste- and time-intensive deprotection sequence to obtain non-symmetrical aminobiphenyls.^[3a] With our method, we are able to cross-couple unprotected and N-acetyl protected anilines with phenols in acceptable yields (for a direct conversion), and often with exclusive selectivity (Table 3, entries 2 and 3). We thus offer a method for straightforward synthesis of highly substituted unsymmetrical biphenyls. Even bromo and chloro substituents are tolerated by electrolysis in HFIP (entries 1 and 2).



[a] For electrolysis conditions see Table 1. Q=2 F·*n* (component **a**). [b] Yields of isolated products. [c] Ratio of cross-coupling product **ab** to homo-coupling product **bb** (determined by GC). [d] **bb** was not detected. Side products consist of oligomeric species, which were not further characterized.

Conclusion

Direct anodic cross-coupling of phenols with arenes or other phenols in HFIP can be efficiently influenced by water or methanol as additive. This solvent effect shifts the oxidation potentials of the individual substrates and creates matching pairs for cross-coupling reactions. The formation and influence of these

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solvates is highly dependent on the substitution pattern of the individual substrate. On the basis of this knowledge we were able to screen for successful cross-coupling reactions significantly more efficiently. Since nucleophilicity can to a certain extent be decoupled from oxidation potential, very good selectivity for the cross-coupling was obtained. This concept was extended to the cross-coupling of phenols with anilines and aniline derivatives. The identified source of selectivity might also be a key factor in other oxidative coupling reactions where stoichiometric reagents are used.

Experimental Section

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Electrochemical cross-coupling reaction

An experimental setup is shown in Figure S1 and S2 in the Supporting Information. A solution of phenol component (0.005 mol), arene component (0.015 mol), and *N*-methyl-*N*,*N*,*N*-triethylammonium methylsulfate (Et₃NMe O₃SOMe, 0.68 g, 0.003 mol) in 1,1,1,3,3,3 hexafluoropropan-2-ol/methanol (33 mL; 0–18% v/v) was transferred into an undivided electrolysis cell equipped with a BDD anode. At 50 °C, a constant current electrolysis with a current density of 2.8 mAcm⁻² was performed. After 965 C (2 F per mol phenol) the electrolysis was stopped and the solvent mixture was recovered in vacuo (50 °C, 150 mbar). Non-converted starting materials were recovered by short-path distillation (120–145 °C, 10^{-3} mbar), and purification of the crude products by column chromatography (SiO₂, ethyl acetate/cyclohexane) afforded the coupling products. If necessary, products were recrystallized by dissolving in dichloromethane and solvent diffusion of cyclohexane.

Cyclic voltammetry

Voltammetric studies were performed with a Metrohm 663 VA Stand equipped with a µAutolab type III potentiostat (Metrohm AG, Herisau, Switzerland). WE: glassy carbon electrode tip, 2 mm diameter; AE: glassy carbon rod; RE: Ag/AgCl in saturated LiCl/ EtOH. Solvent: HFIP + 0-25 %v/v MeOH. Criteria for oxidation: $j = 0.1 \text{ mA cm}^{-2}$; $v = 50 \text{ mV s}^{-1}$; $T = 20 \degree$ C. Stirring conditions during measurement. c(substrate) = 151 mM, supporting electrolyte: Et₃NMe O₃SOMe (MTES), c(MTES) = 0.09 M.

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Keywords: biaryls · cross-coupling · electrolysis · hydrogen bonds · solvent effects

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