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# Dehydrative Coupling of Benzylic Alcohols Catalyzed by Brønsted Acid/Lewis Base

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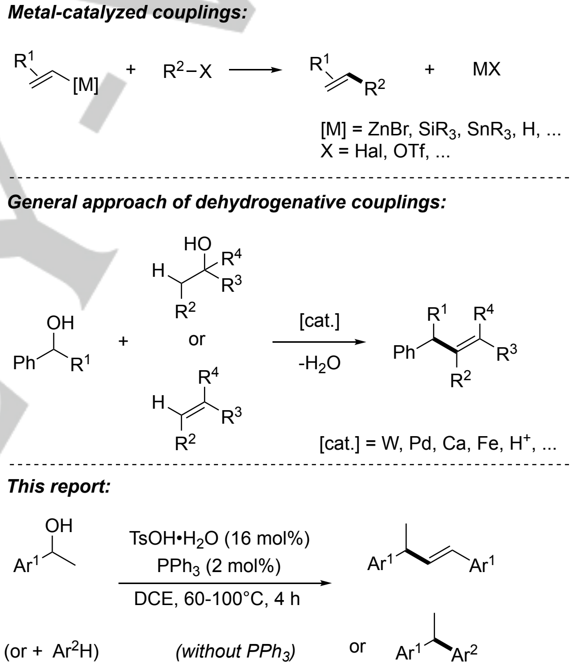
**Abstract:** Traditional cross-coupling reactions show some disadvantages like the use of organohalides or the production of stoichiometric amounts of waste. The dehydrative homo- or heterocoupling of alcohols therefore arises as interesting approach for a highly atom-economical formation of carbon-carbon bonds, since water is produced as only byproduct. We herein report a simple and direct, metal-free protocol for the synthesis of olefins by applying catalytic amounts of a sulfonic acid and triphenylphosphine under air. A variety of olefins could be synthesized from benzylic alcohols under relatively mild conditions. Additionally, dehydrative hydroarylation of benzylic alcohols with electronrich arenes was possible by using only Brønsted acid under otherwise same reaction conditions. We could show that phosphine additives are essential to overcome oligomerization as main side reaction by occupancy of the reactive carbocation intermediate.

## Introduction

One of the most fundamental subjects in organic chemistry is the efficient and selective formation of carbon-carbon bonds. Especially transition-metal catalyzed cross-coupling reactions emerged as important tool for the construction of $sp^3$-$sp^2$ C-C bonds and have been widely investigated and developed.[1] Nevertheless, most of these protocols show disadvantages in respect to the aspects of green chemistry.[2] Often, additional preparative steps are necessary, as well as the application of hazardous reagents and nobel metal catalysts. Also the production of stoichiometric amounts of waste is unattractive. In recent years, the direct dehydrative homocoupling of simple alcohols and heterocoupling of alcohols and alkenes or arenes to substituted olefins arose as interesting alternatives due to the advantage of producing water as only byproduct (Scheme 1).[3]

However, since hydroxy groups in alcohols are intrinsically poor leaving groups, an activation by transformation in a better one has to occur.[4] This dehydroxylation can be conducted indirectly by conversion into tosylates,[5] triflates,[6], mesylates,[7} acetates[8] and halides.[9] Direct substitution of the hydroxy group is more attractive and can be achieved in $S_N2$ reactions by using stoichiometric reagents via oxyphosphonium intermediates, as in the Mitsunobu[10} or Appel reaction.[11] Besides, also catalytic alcohol activation has been reported in recent years.[12] Additionally, it was reported that strong Brønsted acids are able to catalyze dehydrative substitutions, mainly by an $S_N1$ mechanism.[13]

When looking on the history of direct dehydrative coupling of benzylic alcohols, metal catalysts are mainly represented as activation agents in earlier reports. In 2006, Muzart and co-workers reported the application of the Wells-Dawson tungsten heteropolyacid $H_2P_2W_{18}O_{62}$ as catalyst for the homocoupling of 1-indanol and of 1-phenylethanol in 1,2-dichloroethane.[14] The reaction, however, suffered from low yields. Yamamoto *et al.* disclosed a Pd(II)-catalyzed heterocoupling of benzylic alcohols with styrenes shortly afterwards.[15] The desired substituted olefins were obtained in moderate yields by applying 3 equivalents of $(CF_3CO)_2O$ as additive and $PPh_3$ as ligand. In addition, catalysts based on Cu,[16] Fe,[17] Ru[18] and Ca[19] were employed in similar transformations.



**Scheme 1.** Coupling methods for $sp^3$-$sp^2$ C-C bond formation.

Among the metal-free protocols, Sanz *et al.* briefly described dehydrative $sp^3$-$sp^2$ C-C bond formation of benzylic alcohols with trifluoromethanesulfonic acid as catalyst in context of the Brønsted acid catalyzed benzylation of 1,3-dicarbonyl compounds.[20] Nevertheless, only a limited substrate scope and moderate yields could be obtained. The first metal-free route to substituted olefins through the direct heterocoupling of benzylic alcohols with alkenes was reported in 2011 by Yue and co-workers.[21] Formation of the $sp^3$-$sp^2$ C-C bond could be realized by application of trifluoromethanesulfonic acid in catalytic amounts. This report was followed 2014 by a comprehensive publication on metal-free dehydrative homocoupling of benzylic alcohols from Xia *et al.* by applying previously prepared sulfonic

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acid-functionalized ionic liquids.[13c] The substrate scope was mainly based on benzhydrols and benzylic alcohols substituted with halides. Nama and co-workers additionally showed the application of heterogeneous catalysis on dehydrative coupling reactions of benzylic alcohols by using zeolithes.[22] In many reports, the limitations and possible side reaction were not discussed.

We developed a simple, direct metal-free dehydrative coupling starting from widely available and tractable alcohols by using easy-to-handle and commercially available catalysts under mild conditions. The protocol was envisioned to overcome previous issues like the use of transition metals, additional preparative steps, stoichiometric amounts of acid or additives. The reactions are performed with weaker sulfonic acid and triphenylphosphine as a Lewis base co-catalyst, which was not reported before. We focused on the investigation of the homocoupling of benzylic alcohols and the role of the catalyst components in this reaction.

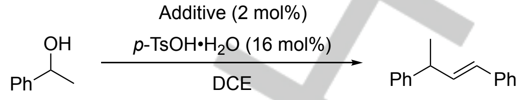
## Results and Discussion

In an initial experiment, toluenesulfonic acid and 1-phenylethanol (**1a**) dissolved in 1,2-dichloroethane (DCE) and heated to 60 °C within 18 h under air, which afforded the respective dimer **2a** in 26% yield (Table 1, entry 1). Application of 2 mol% of triphenylphosphine ($PPh_3$) as additive showed the formation of **2a** in 73% yield (entry 2). This was surprising, since in previous reports, the application of triphenylposphine as additive in substitutions of alcohols was mainly shown in Mitsunobu or Appel-type reactions in stoichiometric amounts.[12e, 23]

Subsequent investigations on amounts, concentration, solvent, acid and temperature were conducted (*see supporting information for further details*). A lower reaction temperature of 40 °C diminished the yield to 16% (Table 1, entry 3) whereas a higher reaction temperature of 100 °C (entry 4) led to the formation of **2a** in 80% yield. Additionally, it was shown that the reaction is already completed after 4 hours (entry 5). Quantitative conversion and observation of styrene (**3**) as intermediate, indicated *in situ* dehydration of **1a**. The formed styrene can undergo oligomerization as main side reaction. Addition of 4-*tert*-butylcatechol as inhibitor could not prevent the oligomerization nor the homocoupling, which excludes the possibility of a radical reaction pathway.

However, the application of a phosphine conversely appears to be a necessity for avoiding oligomerization reactions. Hence, with the optimized reaction conditions in hand, other phosphine additives were tested (entries 6-10). It could be shown, that an electron-donating substituent on the phenylring of triphenylphosphine decreased the yield from 80% to 70% (entry 6). Beside phenyl substituted mono-phosphines, also alkane-substituted phosphines gave **2a** in good yields (74%, entry 7) and heterocyclic tri(2-furyl)phosphine (TFP) showed similar results (75%, entry 8). Bidentate phosphines like BINAP were as well applicable to this kind of reaction providing good yields (70%, entry 9). Interestingly, also triphenylphosphine oxide worked as suitable additive, however, the yield dropped from 80% to 63% (entry 10). Nevertheless, $PPh_3$ was chosen as additive for subsequent reactions, due to its low cost and high stability.

**Table 1.** Initial screening experiments for the homocoupling of benzylic alcohols.



**1a** **2a**

| Entry | Additive | T [°C] | t [h]] | Yield of **2a** [%][a] |
|---|---|---|---|---|
| 1[b] | – | 60 | 18 | 26 |
| 2[b] | $PPh_3$ | 60 | 18 | 73 |
| 3[b] | $PPh_3$ | 40 | 18 | 16 |
| 4 | $PPh_3$ | 100 | 18 | 80 |
| 5 | $PPh_3$ | 100 | 4 | 80 |
| 6 | $P(4\text{-}OMeC_6H_4)_3$ | 100 | 4 | 70 |
| 7[c] | $PCy_3$ | 100 | 4 | 74 |
| 8 | TFP | 100 | 4 | 75 |
| 9 | BINAP | 100 | 4 | 70 |
| 10 | $O{=}PPh_3$ | 100 | 4 | 64 |

*General reaction conditions*: **1a** (0.5 mmol, 61 µL), *p*-TsOH•$H_2O$ (16 mol%), additive (2 mol%), 1,2-dichloroethane (1.5 mL), under air; [a] Yields were determined *via* quantitative GC-FID; [b] **1a** (1.0 mmol, 121 µL), *p*-TsOH•$H_2O$ (16 mol%), additive (2 mol%), 1,2-dichloroethane (3 mL), under air [c] under inert conditions in degassed 1,2-dichloroethane as solvent.

For further mechanistic insights, the reaction progress under optimized reaction conditions was evaluated (Figure 1). As already observed, styrene (**3**) was formed *in situ* from **1a** and reached a maximum yield of 84% after 20 minutes and was then continuously converted to dimer **2a**. Additionally, an ether formation from **1a** to (oxybis(ethane-1,1-diyl))dibenzene (**4**) took place within the first 15 minutes. Compound **4** however, was consumed quite rapidly within the first 30 minutes. This also explains the sigmoidal curve of the formation of **2a**, which reached a maximum yield of 80% after 4 h. Leftover styrene was further consumed, but it did not enhance the yield of **2a**.

In order to clarify the influence of the additive, several mechanistic investigations were conducted (Scheme 2). Firstly, it was observed, that styrene (**3**) reacts like **1a** smoothly to **2a** under the optimized reaction conditions (Scheme 2A). Without the addition of $PPh_3$, **2a** was only obtained in poor yields (17%), while **3** was fully converted. Hence, in the model reaction of **1a** (Figure 1), the additive must have the most impact on the transformation of **3** to **2a**. Full conversion in both reactions provides another hint for the role of $PPh_3$ as inhibitor for the oligomerization.

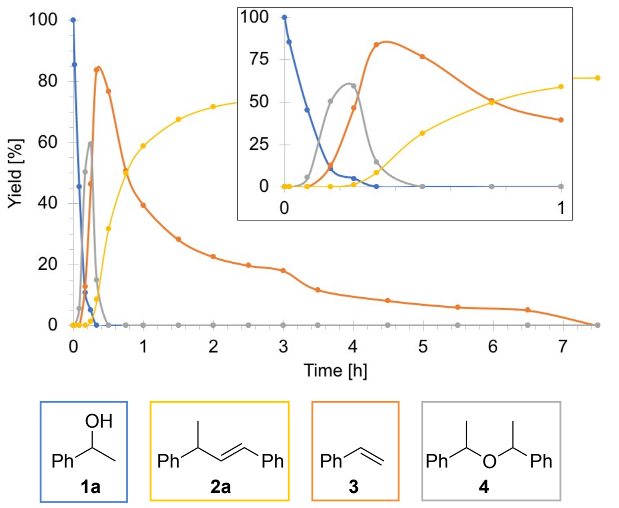
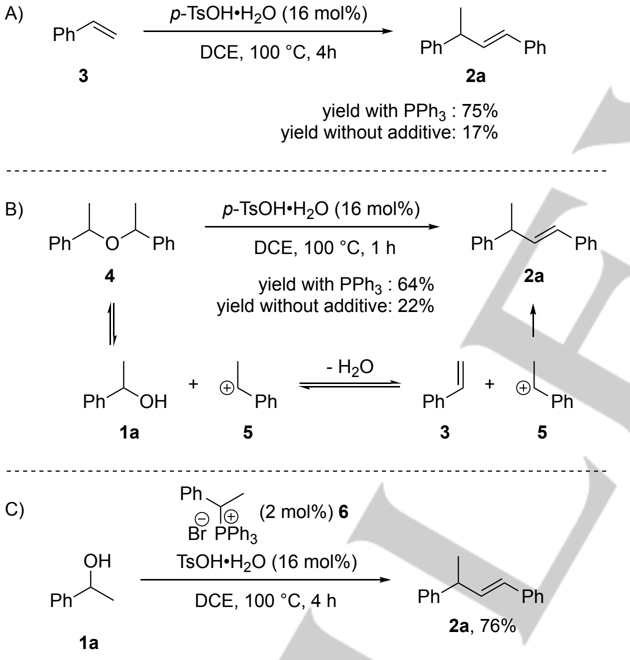


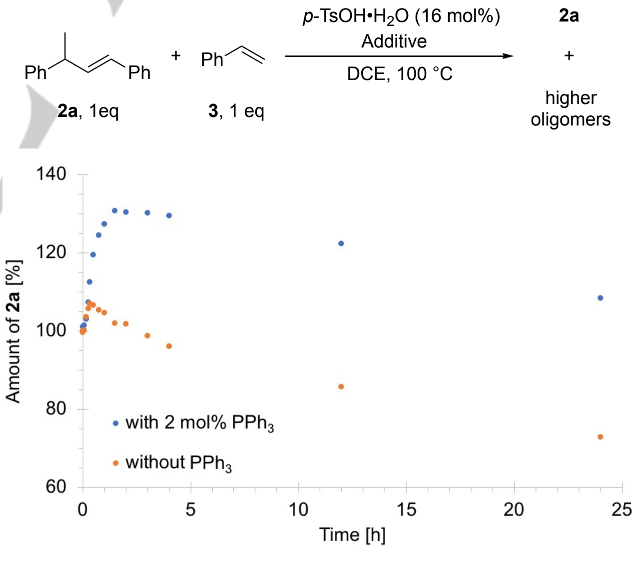
**Figure 1.** Reaction progress of the dehydrative coupling of **1a**. *General reaction conditions*: **1a** (1.0 mmol, 121 µL), *p*-TsOH•H₂O (16 mol%), PPh₃ (2 mol%), 1,2-dichloroethane (3 mL), 100 °C; Yields were determined *via* quantitative GC-FID.



**Scheme 2.** Mechanistic investigations. *General reaction conditions*: A) **3** (1.0 mmol, 115 µL), *p*-TsOH•H₂O (16 mol%), PPh₃ (2 mol%), 1,2-dichloroethane (3 mL), 100 °C; B) **4** (1.0 mmol, 113 mg), *p*-TsOH•H₂O (16 mol%), PPh₃ (2 mol%), 1,2-dichloroethane (3 mL), 100 °C; C) **1a** (0.5 mmol, 61 µL), *p*-TsOH•H₂O (16 mol%), **6** (2 mol%), 1,2-dichloroethane (1.5 mL); Yields were determined *via* quantitative GC-FID.

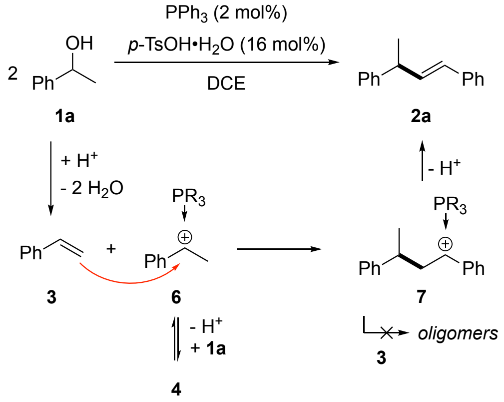
A similar observation was made, when looking at the transformation of **4** (Scheme 2B). Since **4** is acid labile, **2a** was obtained in 22% yield in the absence of PPh₃, with 82% conversion of **1a** and formation of **3** in 10%. This leads to the assumption that in the model reaction, formation of **4** is reversible and reformation of **1a**, dehydration and subsequent attack on the benzylic carbocation (**5**) generates **2a**. As observed before, the employment of PPh₃ resulted in an increase of yield. With this result in hand we concluded that PPh₃ has to interact with carbocation **5** by catalytically forming a phosphine salt which allows the attack of a single nucleophile but sterically prevents the attack of a further one and consequently supresses the formation of oligomers. In a subsequent experiment, phosphine salt **6** was applied in the reaction of **1a** to **2a** (Scheme 2C). As the yield is comparable to the model reaction (Table 1, entry 5), it supports the conclusion we have made before.

Furthermore, we followed the progress of the reaction of product **2a** with styrene (**3**, Scheme 3). Since the product itself is stable for at least 18 h under the given reaction conditions, we were wondering, if the addition of **3** would lead to oligomerization. In the experiment without additive, the amount of **2a** initially increased to 107% of the initially applied **2a** due to the dimerization of **3**. However, after only 15 minutes the amount of **2a** started to decline. After 24 h, the amount of **2a** was 30% lower than in the beginning. This means that vinylarene **3** indeed undergoes dimerization to **2a** within the first 15 minutes, but subsequently reacts with **2a** to generate higher oligomers. Contrary to that, **3** was consumed much slower in the presence of PPh₃ and 130% of **2a** was obtained after 4 hours. Even after 24 hours the amount of **2a** was not lower than at the start of the reaction. This proves that **3** is directly converted to **2a** and PPh₃ inhibits the further reaction of **2a** and **3**. Slow decrease in the amount of **2a** indicates, that the additive cannot completely suppress oligomerization over a longer period of time.



**Scheme 3.** Investigation of the oligomerization of **2a** with **3**. *General reaction conditions*: **1a** (0.5 mmol, 61 µL), **3** (0.5 mmol, 57 µL), *p*-TsOH•H₂O (16 mol%), PPh₃ (2 mol%), 1,2-dichloroethane (3 mL), 100 °C; Yields were determined *via* quantitative GC-FID.

Based on these observations, a plausible mechanism of the dehydrative coupling is depicted in Scheme 4. Unlike shown in previous publications,[20,21] we exclude the direct formation of **2a** from **4** by reaction with **3** since we could show the reversibility of the formation of **4** in acidic medium (Scheme 2B). Hence, we propose that dehydration of **1a** provides vinylarene **3** and carbocation **5** *in situ*, while **5** is stabilized by phosphine to give salt **6**. Formation of phosphonium salt **6** and subsequent formation of **7** was investigated in NMR studies (*see supporting information for further details*). This carbocation stabilization constitutes a plausible explanation for the reactivity in this reaction. **7** is considered as the determining cause for the prevention of oligomerization due to steric reasons. Proton abstraction from **7** then generates product **2a**.



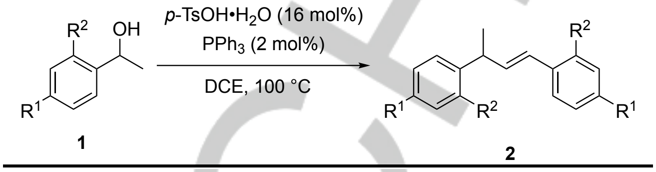
**Scheme 4.** Proposed mechanism for the dehydrative coupling.

With this mechanism, it is also possible to explain the trend in the phosphine screening (Table 1, entries 5–10). More electron-rich phosphines generally show slightly lower yields after 4 h but also higher amounts of **3** (entries 6,7). This leads to the assumption that a stronger C-P bond in intermediate **6** slows the reaction with **3**. Application of triphenylphosphine oxide (table 1, entry 10) shows a faster oligomerization since styrene (**3**) is completely consumed. However, a weak coordination to the carbocation is also possible with the oxide and allows to generate **2a** in lower amounts.

In subsequent investigations, substrate scope and limitations of the reactions were studied (Table 2). In general, electron donating substituents like methoxygroups in *ortho-*, *meta-* and *para*-position of phenyl, as well as 1-(2-napthyl)ethanol and heteroaromatic compounds led to inseparable mixtures of various regioisomeric C-C coupling products. This can be explained by the fact that the higher electron density in benzylic position generates a reactive benzylic cation, which cannot provide the desired head-to-tail dimer selectively. On the other hand, strongly electron withdrawing substituents as trifluoromethyl (table 2 entry 10) or nitro-groups (entry 11) deactivate the benzylic position and no product formation takes place.

Nevertheless, halogenated substrates were suitable for this protocol, due to their “chameleon-like” inductive electron withdrawing (–I) and mesomeric electron donating (+M) effects. Halides in *para*-position gave good to excellent yields (entries 3-7). A chloro-substituent in *ortho*-position however, only provided 27% yield of **2g** (entry 6). Interestingly, also 1-(4-biphenyl)ethanol (**1b**) as well as *ortho-* and *para*-methylsubstituted phenylethanols (**1h**, **1i**) appear to be reactive and selective enough to generate the C-C coupling products (entries 2, 9 and 10). Thus, the reactivity of benzylic alcohols in the homocoupling seems to correlate to substituents constants, however a precise kinetic analysis is beyond the scope of this work.

**Table 2.** Homocoupling of benzylic alcohols: substrate screening.



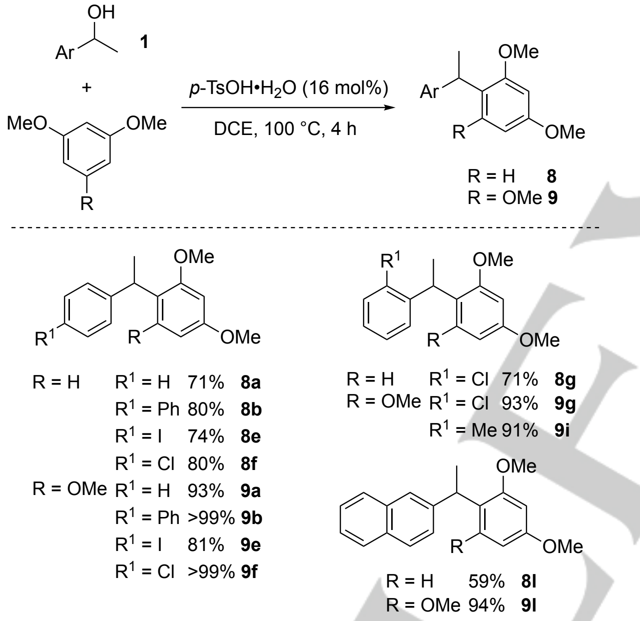
| Entry | $R^1$ | $R^2$ | Product | Time [h] | Yield [%][a] |
|---|---|---|---|---|---|
| 1 | H | H | **2a** | 4 | 80 |
| 2 | Ph | H | **2b** | 4 | 77 |
| 3 | Br | H | **2c** | 18 | 63 |
| 4 | F | H | **2d** | 4 | 75 |
| 5 | I | H | **2e** | 18 | 91 |
| 6 | Cl | H | **2f** | 12 | 77 |
| 7 | H | Cl | **2g** | 18 | 27 |
| 8 | Me | H | **2h** | 4 | 75 |
| 9 | H | Me | **2i** | 4 | 81 |
| 10 | $CF_3$ | H | **2j** | 4 | 0 |
| 11 | $NO_2$ | H | **2k** | 4 | 0 |

*General reaction conditions*: substrate (1.0 mmol), p-$TsOH•H_2O$ (16 mol%, 30 mg), $PPh_3$ (2 mol%, 5 mg), DCE (3.0 mL), 100 °C; [a] Isolated yields.

The scope of this reaction was further expanded to C-C heterocoupling with electron-rich arenes. Similar hydroarylations of benzylic alcohols and vinylarenes have been shown with catalysts like gold,[24] calcium,[25] zinc,[26] graphene oxide[27] and iron (III) porphyrin complexes.[28] In the past, the main focus in the acid catalyzed heterocoupling of benzylic alcohols was put on vinylarenes or 1,3-dicarbonyl compounds as nucleophiles. However, acid-catalyzed dehydrative hydroarylation of benzylic alcohols with electron-rich arenes is rare. For example, fluorinated aryl boronic acids were developed as catalysts for this transformation.[29] In few reports using simple and available sulfonic acids, either the scope was narrow or a large excess of nucleophile were used.[30] On the other hand, the Brønsted-acid catalyzed hydroarylation of vinylarenes with electronrich arenes was reported.[31]

Thus, electron rich 1,3-dimethoxybenzene (DMB) and 1,3,5-trimethoxybenzene (TMB) were used as nucleophiles to react with benzylic alcohols. As expected and also as shown in literature, it is not necessary to add a phosphine or any other additive. This is due to the fact that TMB and DMB are both very good C-nucleophiles, which react much faster with the generated carbocation, than an *in-situ* formed vinylarene. This inhibits the oligomerization as side reaction kinetically. Hence, the aryl compounds were added in excess under the reaction conditions applied in the previously described homocoupling reactions just without the additive (Scheme 5).

Dehydrative hydroarylation starting from 1-phenylethanol (**1a**) with TMB yielded the respective product **9a** in very good yield (93%), whereas coupling with DMB gave product **8a** in 71% yield (entry 2), which could be explained by the higher nucleophilicity of TMB provided by the three electron donating methoxy groups. This is a general trend which is also visible when applying benzylic alcohols substituted on the aryl ring. In contrast to the homocoupling, the hydrooarylation of 1-(2-napthyl)ethanol (**1l**) to **8l** and **9l** was carried out in moderate to very good yields, even though **1l** was too reactive in the homodimerization. On the other hand, methoxy-substituted substrates still underwent various side reactions due to their higher electron density. Halogenated substrates worked well, generating the products in good to excellent yields (**8e**,**f**,**g** and **9e**,**f**,**g**). Unfortunately, other C-C-heterocoupling approaches with C-nucleophiles like indoles, *N*-methylpyrroles, norbornene or vinylarenes, could not yield the respective products selectively under these reaction conditions.



**Scheme 5.** Dehydrative hydroarylation. *General reaction conditions*: alcohol (0.5 mmol), arene (1 mmol) *p*-TsOH•H₂O (16 mol%, 15 mg), DCE (3.0 mL), 100°C, 4 h, isolated yields.

## Conclusion

In conclusion, we developed a simple, direct pathway to substituted olefins from benzylic alcohols *via* an acid catalyzed dehydrative homocoupling. An interesting promotive effect of phosphine as Lewis basic co-catalyst was observed and investigated. A plausible explanation is its interaction with carbocationic intermediates to inhibit oligomerization. The use of easy to handle and commercially available, inexpensive reagents, relatively low catalyst loadings and the avoidance of toxic waste provided an attractive route for the formation of new $sp^3$-$sp^2$ C-C bonds. Furthermore, the dehydrative hydroarylation of benzylic alcohols with electron-rich arenes led to a variety of substituted 1,1-diarylylethanes.

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**Keywords:** benzylic alcohols • direct dehydrative coupling • acid catalyzed • $sp^3$-$sp^2$ C-C bond formation• metal-free

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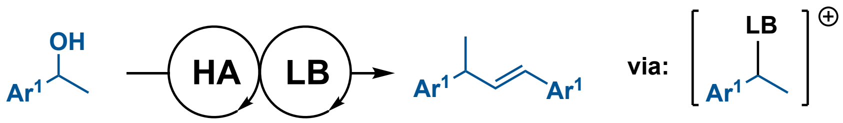
# Entry for the Table of Contents

## COMMUNICATION



A combination of Brønsted acid and Lewis base catalyse dehydrative transformations of benzylic alcohols: homocoupling and hydroarylation.

**Acid Catalysis**

*Marlene Böldl, Ivana Fleischer**

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**Dehydrative Coupling of Benzylic Alcohols Catalyzed by Brønsted Acid/Lewis Base**