Arene Functionalization

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Calcium-Catalyzed Friedel–Crafts Alkylation at Room Temperature

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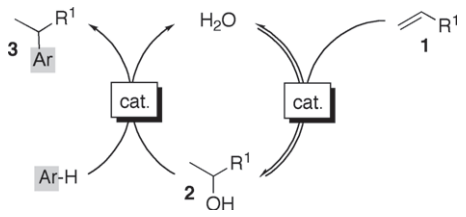
Friedel–Crafts reactions are among the oldest and most efficient C–C bond-forming processes for the functionalization of aromatic compounds.[1] A vivid interest in the synthesis of polycyclic aromatics, core structures of innumerable, biologically active natural products having continuing industrial and academic impact, has recently revived the research field of Friedel–Crafts reactions.[2] Most of the original Friedel–Crafts procedures have now been replaced by environmentally more compatible catalytic approaches. An additional step on the way towards ecologically and economically beneficial arylations was the use of alcohols as electrophiles, wherein water is the only by-product accompanying the transformation of these readily available substrates.[3] Ideally, a coupled catalytic process as depicted in Scheme 1 would be a conceivable reaction.



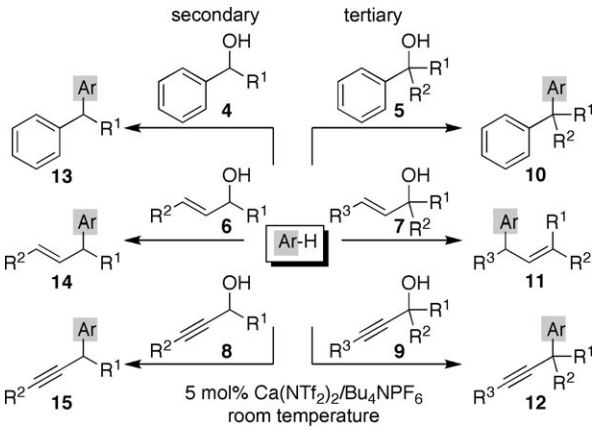
Scheme 1. Coupled catalytic arylation of inactivated olefins.

In a first reaction step, an equilibrium between the olefin **1** and the Markovnikov product **2** would be established by a Lewis acid catalyzed addition of water to an olefinic double bond.[4] As these equilibria often provide only minor amounts of the alcohol **2**, a coupled catalytic process seems ideal for a synthetically useful application of this reaction. In the next step, the same catalyst would then account for the functionalization of the arene with alcohol **2**. Therefore, water would be no more than a mediator, present only in negligible amounts, and olefins that were previously unreactive in Friedel–Crafts reactions may be activated. On the way towards the envisioned coupled catalysis, we needed to identify a broadly applicable Lewis acid for the functionalization of arenes with alcohols.

On the basis of the lanthanoid-catalyzed transformations of secondary α-aryl alcohols to diarylmethanes by Ishii and co-workers,[5] a series of transition metal based catalyst systems[3,6,7] were published within the last couple of years. Transition metal free procedures were realized by the means of aluminum,[8] indium,[9] bismuth,[10] iodine,[11] and Brønsted acid[12,13] catalysis. Transformation of propargylic and allylic alcohols, not activated by an additional aryl substituent in the α-position to the hydroxy group, has been scarce in intermolecular Friedel–Crafts reactions.[7,12,14,15] Palladium-[16] and molybdenum-catalyzed[17] processes are not included here, as they proceed through a different mechanism. The transformation of a tertiary allylic alcohol was, to our knowledge, thus far unsuccessful. Arylation of tertiary benzylic[18] and tertiary propargylic[14] alcohols have not yet been realized under mild reaction conditions. A central drawback of Friedel–Crafts-type additions remains the low functional group tolerance, because even modern procedures generally suffer from the necessity of rather harsh reaction conditions.

In the last couple of years sustainable metal catalysis has emerged, complementing the concept of organocatalysis. An exponentially growing number of publications have showed that iron complexes provide efficient alternatives to the precious transition-metals Pd, Rh, and Au.[19] Bismuth salts have exhibited growing importance as ecologically benign Lewis acids.[20] Remarkably, the catalytic activity of the nontoxic alkaline earth metals is almost unexplored despite excellent availability and the low cost of these potential, sustainable metal catalysts.[21] Among the alkaline earth metals calcium appears particularly promising, as it displays similarities to the lanthanoids with regard to its chemical properties.[22] Furthermore, first applications of this main group metal as a catalyst have been recently realized.[23]

Herein we present a calcium-based catalyst system for the alkylation of electron-rich arenes using secondary and tertiary benzylic, allylic, and propargylic alcohols at room temperature (Scheme 2). The new catalyst system allows the general arylation of allylic and propargylic alcohols, without neces-



Scheme 2. Calcium-catalyzed arylation of alcohols.

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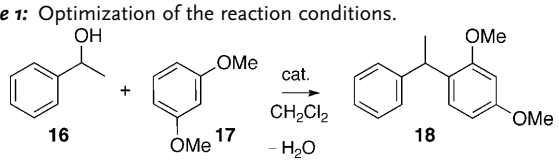
Table 1: Optimization of the reaction conditions.

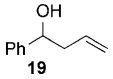
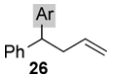
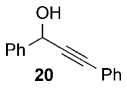
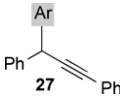
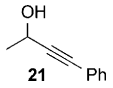
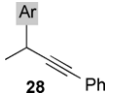
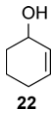
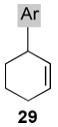
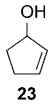
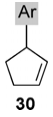
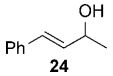
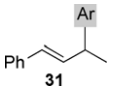
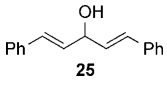
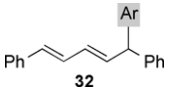


16 **17** **18**

Entry[a]	Catalyst (mol%)	Additive (mol%)	*t* [h]	Yield [%][b]
1	$LiNTf_2$ (10)	Bu_4NPF_6 (5)	16	68
2	$Mg(NTf_2)_2$ (5)	Bu_4NPF_6 (5)	16	–
3	**$Ca(NTf_2)_2$ (5)**	**Bu_4NPF_6 (5)**	**1**	**85**
4	$Ca(NTf_2)_2$ (5)	NH_4PF_6 (5)	2	82
5	$Ba(NTf_2)_2$ (5)	Bu_4NPF_6 (5)	16	22
6	$Ca(NTf_2)_2$ (5)	–	16	–
7	$Ca(OTf)_2$ (5)	Bu_4NPF_6 (5)	16	47
8	$Ca(BF_4)_2$ (5)	Bu_4NPF_6 (5)	16	25
9	$HNTf_2$ (5)	Bu_4NPF_6 (5)	20	5
10	$HNTf_2$ (0.1)	Bu_4NPF_6 (0.1)	23	–
11	HOTf (5)	Bu_4NPF_6 (5)	23	3

[a] Reaction conditions: Alcohol **16** (0.5 mmol) and arene **17** (1.5 mmol) were dissolved in CH_2Cl_2 (1 mL). Both the additive and (Lewis-) acid were added at room temperature and then stirred for the time indicated. [b] Yield of isolated product.

Table 2: Addition of different secondary alcohols to arene **17**.

Entry[a]	Alcohol	Product[b]	*t* [h]	Yield [%][c]
1	 **19**	 **26**	1	87
2	 **20**	 **27**	1	83
3	 **21**	 **28**	4	76
4	 **22**	 **29**	5	68
5	 **23**	 **30**	5	77
6	 **24**	 **31**	4	80
7	 **25**	 **32**	4	88

[a] Reaction conditions: The alcohol (0.5 mmol) and arene **17** (1.5 mmol) were dissolved in CH_2Cl_2 (1 mL). 5 mol% Bu_4NPF_6 and 5 mol% $Ca(NTf_2)_2$ were added at room temperature and then the reaction mixture was stirred for the time indicated. [b] Ar = *o*,*p*-dimethoxyphenyl; regioselectivity determined by NMR and GC analysis. [c] Yield of isolated product.

sitating activation of the alcohol by an additional aryl substituent in α-position (R^1) to the hydroxy group.

Our investigations began with the optimization of the reaction conditions for the model reaction shown in Table 1. A catalyst loading of 5 mol% $Ca(NTf_2)_2$ in the presence of 5 mol% Bu_4NPF_6 afforded the desired product **18** within one hour at room temperature. Multiple functionalizations of the arene were suppressed in the presence of just three equivalents of this reaction partner. The regioselectivity of the transformation was found to be remarkable; substitution of the arene was observed exclusively in *o*,*p*-position relative to the two methoxy groups of resorcinol dimethyl ether (**17**).[24] The reaction succeeded only in aprotic, noncoordinating solvents such as dichloromethane, 1,2-dichloroethane, or *n*-hexane. $LiNTf_2$, $Mg(NTf_2)_2$, $Ba(NTf_2)_2$, $Ca(OTf)_2$, and $Ca(BF_4)_2$ displayed none or very little catalytic activity (Table 1, entries 1, 2, 5, 7, and 8). No transformation of the model substrates occurred with any of the examined Lewis acids in the absence of the hexafluorophosphate salt. Similar to the observations made by Shibasaki for a $Bi(OTf)_2/MPF_6$-based catalyst system,[25] the choice of the counter cation to the hexafluorophosphate additive had little to no influence upon the reaction outcome (Table 1, entry 4). This finding possibly points towards the formation of a more reactive $CaNTf_2{\cdot}PF_6$ species.

Alternative calcium sources such as $Ca(OiPr)_2$, $Ca(OAc)_2$, $Ca(TFA)_2$, or calcium halogenides showed no reactivity even in the presence of the hexafluorophosphate. By using 5 mol% of either $HNTf_2$ or HOTf ($Tf = CF_3SO_2$; Table 1, entries 9–11) full conversion of phenylethanol **16** was achieved in the presence of the additive, but the reactions were sluggish. Reaction did not occur either in the absence of Bu_4NPF_6, or when a catalyst loading as little as 1 or 0.1 mol% of the acid/additive pair was applied (Table 1, entry 10).

Having the optimized reaction conditions in hand, resorcinol dimethyl ether (**17**) was reacted with a series of secondary alcohols (Table 2). The secondary benzylic alcohols **19** and **20** were arylated within one hour in excellent yields. Conversion of the propargylic alcohol **21**, as well as the cyclic alcohols **22** and **23**, occurred readily to give the corresponding products **28**–**30**. As far as we know substrates **21**–**23** have never been transformed in a reaction of this type employing any of the previously published catalyst systems. Likewise, linear allylic alcohols **24** and **25** were arylated smoothly. The reaction times were significantly longer when there were no α-aryl substituents to activate the alcohol for the ionization step (Table 2, entries 3–7). Nevertheless, the high reactivity of the catalyst system accounted for full conversion of the alcohlol in just 4–5 hours at room temperature. As observed for the transformation of phenylethanol **16** (Table 1), substitution of the arene occurred exclusively in *o*,*p*-position to the two methoxy groups of the resorcinol dimethyl ether (**17**) in all cases.[25]

Using the same very mild reaction conditions, the transformation of tertiary alcohols resulted in high product yields and good selectivity (Table 3). Notably, reaction times were generally shorter compared to those observed for conversion of secondary alcohols. Benzylic (Table 3, entry 1) and propargylic alcohols (Table 3, entries 2–5) gave branched reaction products **44** and **45**–**48**, respectively. In contrast, allylic alcohols reacted to give the linear products **49**–**53** (Table 3, entries 6–11). A tertiary allylic alcohol such as **39** displayed no reactivity because the substituent in the allylic position might

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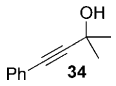
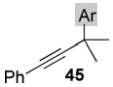
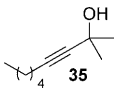
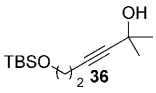
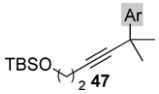
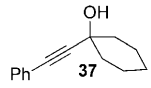
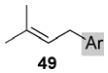
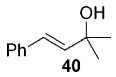
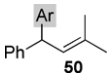
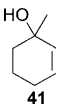
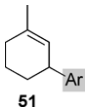
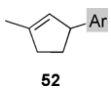
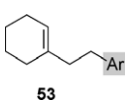
Table 3: Addition of different tertiary alcohols to arene **17**.

Entry[a]	Alcohol	Product[b]	*t* [h]	Yield [%][c]
1	 **33**	 **44**	1	90
2	 **34**	 **45**	2	87
3	 **35**	 **46**	2	79
4	 **36**	 **47**	2	71
5	 **37**	 **48**	2	82
6	 **38**	 **49**	2	72
7	 **39**	–	–	–
8	 **40**	 **50**	2	88
9	 **41**	 **51**	1	70
10	 **42**	 **52**	1	81
11	 **43**	 **53**	4	70

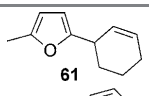
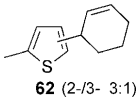
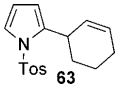
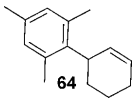
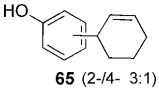
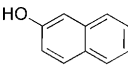
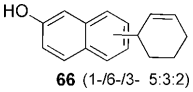
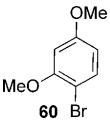
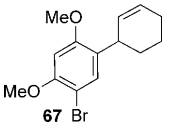
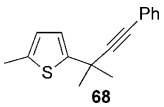
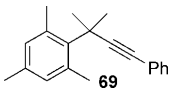
[a] Reaction conditions: Alcohol (0.5 mmol) and arene **17** (1.5 mmol) were dissolved in CH_2Cl_2 (1 mL). 5 mol% Bu_4NPF_6 and 5 mol% $Ca(NTf_2)_2$ were then added at room temperature and the resulting reaction mixture was stirred for the time indicated. [b] Ar = *o*,*p*-dimethoxyphenyl; regioselectivity determined by NMR and GC analysis. [c] Yield of isolated product.

sterically hamper an attack by the nucleophile (Table 3, entry 7). The successful transformation of propargylic alcohol **36** demonstrated once more the mildness of the reaction conditions employed, as the acid labile TBS ether in **36** remained intact. Interestingly, the exocyclic double bond generated during the arylation of the allylic alcohol **43** isomerized under the reaction conditions to form the endocyclic double bond in **53**. This rearrangement goes to 50% at full conversion of the alcohol **43** and is then complete after an additional three hours.

Furthermore, we were interested in the reactivity towards different arenes and heteroarenes (Table 4). A series of electron-rich aromatic compounds (**54**–**60**) was alkylated readily, at room temperature with the allylic alcohol **22** and the tertiary propargylic alcohol **34**, respectively. The data show that the electron-rich arenes were alkylated at room temperature, resulting in good to excellent product yields. The reaction with both alcohols (**22** and **34**) resulted in similar regioselectivity as that seen in the reaction with resorcinol dimethyl ether (**17**). The electrophilic attack of the cation, generated from the secondary allylic **22**, upon the arene substrates **55**, **58**, and **59** resulted in poorer regioselectivity than that seen with **17** (Table 4, entries 2, 5 and 6). In these cases the substituents on the arene were less directing than those in **17**. The tertiary propargylic alcohol **34** reacted with all the tested aromatic compounds in the same high regioselectivity as previously observed (Table 4, entries 8–11).

We have developed a general calcium-catalyzed functionalization that allows the selective alkylation of arenes using

Table 4: Addition of arenes to allylic alcohol **22** (entries 1–7) and propargylic alcohol **34** (entries 8–11).

Entry[a]	Arene	Product[b]	*t* [h]	Yield [%][c]
1	 **54**	 **61**	5	81
2	 **55**	 **62** (2-/3- 3:1)	5	74
3	 **56**	 **63**	5	80
4	 **57**	 **64**	5	82
5	 **58**	 **65** (2-/4- 3:1)	5	81
6	 **59**	 **66** (1-/6-/3- 5:3:2)	5	89
7	 **60**	 **67**	5	90
8	 **55**	 **68**	2	93
9	 **57**	 **69**	2	86
10	 **58**	**70**	2	78
11	**60**	**71**	2	91

[a] Reaction conditions: Alcohol (0.5 mmol) and the arene (1.5 mmol) were dissolved in CH_2Cl_2 (1 mL). 5 mol% Bu_4NPF_6 and 5 mol% $Ca(NTf_2)_2$ were added at to the reaction mixture at room temperature and then stirred for the time indicated. [b] Yield of isolated product; regioselectivity determined by NMR and GC analysis.

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secondary and tertiary benzylic, allylic, and propargylic alcohols. The scope of the reaction was broadened significantly, as the reactivity of the new catalyst system was sufficient to overcome the long standing limitation of this reaction to benzylic alcohols. Typical reactions proceed at room temperature, with no added strong acids or bases, and special precautions for exclusion of moisture or air are unnecessary. Functional groups such as phenolic hydroxy groups, primary TBS ethers, furans, and thiophenes are tolerated under the mild reaction conditions. Hence, calcium was identified as a suitable Lewis acid for the catalysis of our proposed arylation reaction. Additional developments in this transformation are currently underway in our laboratories.

Experimental Section

All reactions were carried out with no precautions taken for the exclusion of moisture and air. Arylation of phenylethanol: Compounds **16** (0.5 mmol) and **17** (1.5 mmol) placed in a reaction flask and dissolved in dichloromethane (1 mL). Bu_4NPF_6 (5 mol%) and $Ca(NTf_2)_2$ (5 mol%) were then added, and the reaction mixture for 1 h at RT. For the isolation of the product, 5 mL sat. $NaHCO_3$ solution was added to the reaction mixture, the aqueous phase was then extracted with dichloromethane, and the combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatography (silica, *n*-hexane/Et_2O 50:1) yielded 85% of analytically pure **18**. ^{1}H NMR (300 MHz; $CDCl_3$): $\delta = 7.26$–7.24 (m, 1H) 7.22–7.19 (m, 3H), 7.16–7.11 (m, 1H), 7.05–7.01 (m, 1H), 6.46–6.41(m, 2H), 4.47 (q, $J = 7.2$ Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 1.54 ppm (d, $J = 7.2$ Hz, 1H); ^{13}C NMR (90 MHz; $CDCl_3$): $\delta = 159.0$, 157.7, 146.7, 128.0, 127.9, 127.6, 125.6, 125.5, 103.9, 98.6, 55.5, 55.4, 37.1, 21.2 ppm; MS (EI): *m/z* (%): 242.1 (70), 227.1 (100), 165.1 (15), 91.1 (64); IR (film): $\tilde{\nu} = 3466, 3025, 2962, 2931, 2836, 1611, 1586, 1502, 1456, 1293, 1207, 1036\ cm^{-1}$.

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