Nickel-Catalyzed Coupling of Arenesulfonates with Primary Alkylmagnesium Halides

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Neopentyl arenesulfonates reacted with primary alkylmagnesium halides in the presence of $(PPh_3)_2NiCl_2$ to produce the corresponding alkylarenes. The efficiency of this coupling reaction considerably depends on the nature of catalyst and solvent. Highest yield was obtained by using three equivalents of Grignard reagent to a mixture of $(PPh_3)_2NiCl_2$ and arenesulfonate in refluxing Et_2O. This reaction represents a novel method allowing the efficient and creative substitution of sulfur-containing groups in aromatic compounds. It also shows that the alkyloxysulfonyl group might be a suitable alternative to halides and triflate in some circumstances.

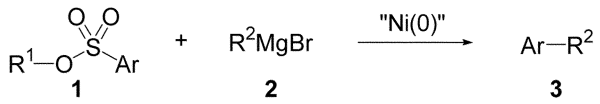
Key Words : Primary alkyl Grignard reagents, Arenesulfonates, Cross-coupling, Nickel catalyst

Introduction

Cross-coupling reaction of organometallic nucleophiles with organic electrophiles using transition metal catalysts is among the most useful processes for constructing carbon–carbon bonds.[1] The nickel- and palladium-catalyzed reactions of organoboronic acids,[2] organostannanes,[3] organozincs,[4] alkenes and alkynes,[5] and arylmagnesium halides[6] are most popular in this family. The repertoire of these reactions has recently increased in the area of solid-phase parallel synthesis/combinatorial chemistry[7] since Pd(0)-mediated C–C bond forming reactions were first explored on solid supports in the early 1990s.[8] However, the satisfactory electrophilic components of these reactions have been limited to organic halides and triflates in most reports in spite of the enormous effort to diversify the leaving group of the electrophiles.[9]

We recently reported that the alkyloxysulfonyl moiety attached onto aromatic compounds could act as an excellent leaving group in the nickel-catalyzed reactions with aryl and primary alkyl Grignard reagents.[10] Surprisingly, neopentyl arenesulfonates did not undergo the famous coupling reaction with arylmagnesium bromides via the displacement of the arenesulfonates under the standard reaction conditions. Moreover, alkyloxysulfonyl groups showed a good chemoselectivity by efficiently reacting with a nickel catalyst but not with palladium catalysts at all. Indeed, the stepwise palladium- and nickel-catalyzed reaction of bromobenzenesulfonates has been successfully demonstrated to be a promising and conceptually straightforward route for preparing unsymmetrical terphenyls.[11] However, in previous reports, the alkyl nucleophilic substrates were restricted to methyl and neopentylmagnesium bromides, which do not possess β-hydrogen to the metal.

While aryl nucleophiles have been thoroughly investigated and applied in most transition metal-catalyzed couplings, the use of unactivated alkyl nucleophiles has been less explored.[12] Only a limited number of methyl and primary alkyl Grignard reagents have been reported to undergo the coupling reactions with aryl or vinyl halides in moderate yields.[13] The reactions of secondary or tertiary alkylmagnesium halides have resulted in disappointing yields due to the isomerization of the alkyl groups.[14] Therefore, the development of a general coupling procedure utilizing unactivated sp^3 nucleophiles represents an interesting challenge in the field of organic synthesis.



R^1 : 2,2-dimethyl-3-phenyl-1-propyl
R^2 : ethyl, *n*-butyl, *n*-pentyl
Ar : toluene, naphthalene, biphenyls

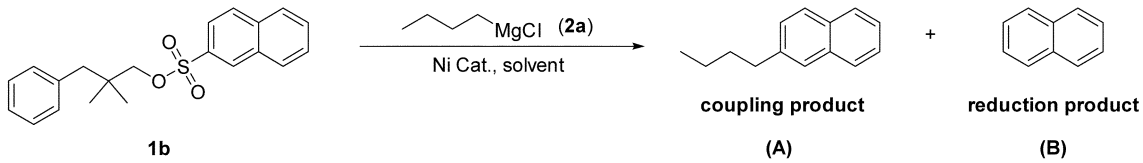
Scheme 1

In a program directed at the development of a cross-coupling reaction utilizing unactivated alkyl nucleophiles, we recently observed that arenesulfonates readily undergo nickel-catalyzed reactions with primary alkylmagnesium halides to produce the corresponding alkylarenes under the specific reaction conditions (Scheme 1). It was noteworthy that the reaction efficiency significantly depends on the nature of catalyst and solvent. The preliminary results of those coupling reactions between alkyloxysulfonylarenes and alkylmagnesium bromides are presented and discussed below.

Results and Discussion

Alkyl arenesulfonates **1a** and **1b** were prepared by the reactions between 2,2-dimethyl-3-phenyl-1-propanol and arenesulfonyl chlorides.[9] Biphenylsulfonates **1c–1f** were prepared by the palladium-catalyzed coupling reactions of 2,2-dimethyl-3-phenyl-1-propyl 4-bromobenzenesulfonate with the corresponding arylboronic acids.[11,15] Neopentyl moiety was selected as the alkyl groups for the sulfonates in order to avoid the competitive substitution and elimination

Table 1. Effect of Varying Reaction Conditions on the Coupling of **1b** with **2a**



entry	catalyst	**2a** (equiv)	solvent	temperature	yield (%)[a]	
					A	**B**
1	$dppeNiCl_2$	3	THF	reflux	16	53
2	$dpppNiCl_2$	3	THF	reflux	16	53
3	$dppfNiCl_2$	3	THF	reflux	17	47
4	$(PPh_3)_2NiCl_2$	3	THF	reflux	46	27
5	$dppeNiCl_2$	3	Et_2O	reflux	16	53
6	$dppfNiCl_2$	3	Et_2O	reflux	15	47
7	$(PPh_3)_2NiCl_2$	3	Et_2O	reflux	85	11
8	$(acac)_2Ni$	3	Et_2O	reflux	11	52
9	$(PPh_3)_2NiCl_2$	3	DME	reflux	53	38
10	$(PPh_3)_2NiCl_2$	3	Et_2O	rt	69	14
11	$(PPh_3)_2NiCl_2$	3+2	Et_2O	reflux	85	12

[a]All yields were determined by GC analyses using biphenyl as an internal standard.

of arenesulfonate anions in the following reactions with alkyl nucleophiles. The displacement of the arenesulfonates and neopentyloxysulfonyl groups was not observed under the standard Suzuki–Miyaura reaction conditions.

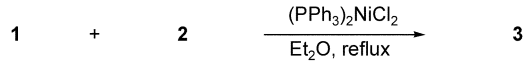
The cross-coupling reaction between 2-naphthalenesulfonate (**1b**) and *n*-butylmagnesium bromide (**2a**) was investigated first in order to uncover optimum reaction conditions (Table 1). The reactions performed in THF as the solvent generated more reduction product **B** than coupling product **A** in the presence of most nickel catalysts (entries 1–3). Only bis(triphenylphosphine)nickel dichloride produced the desired coupling product as the major product, although the efficiency was not good enough (entry 4). This nickel catalyst showed the great selectivity and conversion for **A** in refluxing diethyl ether (entry 7), while other catalysts still produced **B** more (entries 5, 6, and 8). DME was not a good solvent for this catalyst especially in terms of the selectivity (entry 9). This is interesting because THF is the best solvent for the reactions of aryl and methyl Grignard reagents.[9,11] The reaction requires an elevated temperature to overcome the relatively low reactivity of **1b**. Reaction conducted in Et_2O at room temperature could not be completed within 24 h (entry 10), while the reactions performed in refluxing Et_2O were finished within 12 h. Three equivalents of Grignard reagents are sufficient for the complete reaction. More addition of **2a** did not improve the reaction efficiency (entry 11). In summary, the optimization studies demonstrate that the highest yield is obtained by using three equivalents of **2a** to a mixture of $(PPh_3)_2NiCl_2$ and **1b** in refluxing Et_2O.

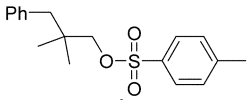
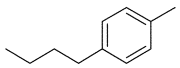
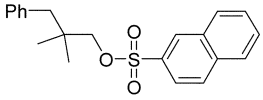
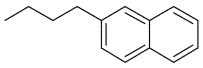
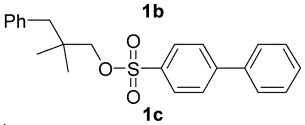
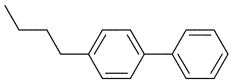
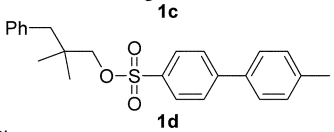
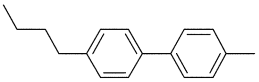
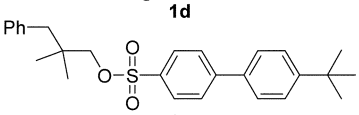
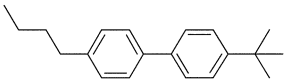
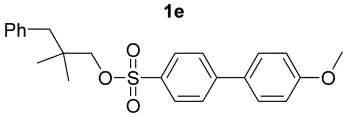
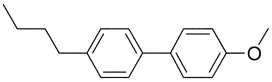
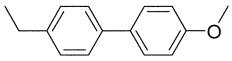
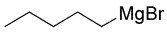
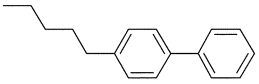
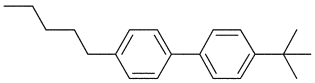
The results of cross-coupling reactions between the various arenesulfonates **1** and the primary alkylmagnesium bromides **2**, performed in the presence of 5 mol % of $(PPh_3)_2NiCl_2$ in refluxing Et_2O, are summarized in Table 2. The arenesulfonates underwent the reaction with **2a** to give the corresponding *n*-butylarenes, **3a–3f**, in good yields within 12 h (entries 1–6). Most of the reactions showed the good selectivity for the coupling products **A** under the standard reaction conditions. The reaction of benzenesulfonate **1a** required more time than those of naphthalenesulfonate (**1b**) and biphenylsulfonates (**1c–1f**) as the faster reaction of the more conjugated arenesulfonates has been consistently observed in these reactions.[9-11] The isolated yield of 4-*n*-butyltoluene (**3a**) was relatively low due to its volatility, although its GC yield was reasonable. Methoxybiphenylsulfonate **1f** also gave comparable yields without undergoing any secondary cross-coupling reaction with excess Grignard reagents via the cleavage of the carbon–oxygen bonds (entries 6 and 7).[16] Ethyl- (**2b**) and *n*-pentylmagnesium bromides (**2c**) underwent the cross-coupling reactions well enough to produce the corresponding biphenyls **3g–3i** in good yields (entries 7–9).

Conclusions

In summary, neopentyl arenesulfonates were reacted with primary alkylmagnesium halides in the presence of $(PPh_3)_2NiCl_2$ to produce the corresponding alkylarenes. To our knowledge, the study reported above is the first general exploration of transition metal-catalyzed cross-coupling reactions of alkyloxysulfonyl arenes with typical primary alkyl nucleophiles. The application of optimum combination of the reaction conditions was very important for the successful result, because the efficiency of this coupling reaction considerably depends on the nature of catalyst and solvent. This reaction represents a novel method allowing the efficient and creative substitution of sulfur-containing groups in aromatic compounds. It also shows that the

Table 2. Cross-coupling of sulfonates **1** with alkylmagnesium halides **2**[a]



Entry	Sulfonate **1**	Grignard reagent **2**	coupling Product (**A**) **3**	product ratio (**A** : **B**)	Yield of **A**[b] (%)
1	 **1a**	**2a**	 **3a**	-	43 (73)[c]
2	 **1b**	**2a**	 **3b**	88 :12	61
3	 **1c**	**2a**	 **3c**	73 : 27	60
4	 **1d**	**2a**	 **3d**	74 : 26	57
5	 **1e**	**2a**	 **3e**	71 : 29	56
6	 **1f**	**2a**	 **3f**	68 : 32	51
7	**1f**	**2b**	 **3g**	72 : 28	54
8	**1c**	 **2c**	 **3h**	84 : 16	66
9	**1e**	**2c**	 **3i**	77: 23	65

[a]Reactions of sulfonates **1** (0.200 mmol) with **2** (0.600 mmol) were carried out at the refluxing temperature of Et_2O (6.0 mL) by using $(PPh_3)_2NiCl_2$ (0.010 mmol). [b]Isolated yields of the coupling product, A, based on **1**. [c]The value in parenthesis indicate GC yield based on **1**.

alkyloxysulfonyl group might be a suitable alternative to halides and triflate in some circumstances, especially when a chemoselective leaving group, which is inert toward palladium catalysts but reactive with nickel catalysts, is desirable.

Experimental Section

^{1}H NMR (300 or 500 MHz) and ^{13}C NMR (75 or 125 MHz) were registered in $CDCl_3$ or acetone-d_6 as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in δ units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.2 ppm. All coupling constants (J) are reported in hertz (Hz). Column chromatography was performed on silica gel 60, 70−230 mesh. Analytical thin-layer chromatography (TLC) was performed using Merck Kieselgel 60 F_{254} precoated plates (0.25 mm) with a fluorescent indicator and visualized with UV light (254 and 365 nm) or by iodine vapor staining. GC analysis was performed on a bonded 5% phenylpolysiloxane BPX 5 capillary column (SGE, 30 m, 0.32 mm i.d.). Electron impact (EI, 70 eV) was used as the ionization method for the mass spectrometry. Melting points were obtained using a Barnstead/Thermolyne MEL-TEMP apparatus and are uncorrected. Solvents were distilled from an appropriate drying agent prior to use: THF and DME from sodium−benzophenone ketyl, and Et_2O from calcium hydride. $DppfNiCl_2$ was prepared according to a literature procedure.[17] $DppeNiCl_2$, $dpppNiCl_2$, $(PPh_3)_2NiCl_2$ and $(acac)_2Ni$

were purchased. *n*-Butyl- **2a** (2.0 M, THF), *n*-ethyl- **2b** (1.0 M, THF), and *n*-pentylmagnesium bromide **2c** (2.0 M, Et_2O) were also purchased, and used as received.

General Procedure for Cross-Coupling Reaction. To a stirred solution of sulfonates **1** (0.200 mmol) and $(PPh_3)_2NiCl_2$ (0.010 mmol) in dry Et_2O (6 mL) was added primary alkyl Grignard reagents **2** (0.600 mmol) at room temperature under Ar atmosphere. The resulting mixture was heated at reflux for ca. 12 h. The mixture was then allowed to cool to room temperature, diluted with Et_2O (30 mL), and quenched by the addition of a 1% HCl (20 mL). The organic layer was washed with water (3 × 20 mL) and saturated brine (20 mL), dried over $MgSO_4$, filtered, and concentrated under vacuo. The crude product was purified by an appropriate chromatography to give pure compound **3**.

1-Butyl-4-methylbenzene (3a) was prepared by the reaction of **1a** (63.7 mg, 0.200 mmol) with **2a** (0.300 mL, 0.600 mmol) in the presence of $(PPh_3)_2NiCl_2$. The crude compound was purified by silica gel chromatography (Et_2O : *n*-hexane = 1 : 20) to give **3a** (38.4 mg, 43%) as a colorless oil: TLC R_f 0.61 (Et_2O : *n*-hexane = 1 : 4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 3H), 1.32−1.37 (m, 2H), 1.54−1.60 (m, 2H), 2.31 (s, 3H), 2.56 (t, J = 7.7 Hz, 2H), 7.07 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 21.0, 22.5, 33.9, 35.4, 128.6 (× 2), 129.2 (× 2), 135.1, 140.1; HRMS (EI, 70 eV) calcd for $C_{11}H_{16}$ (M^+), 148.1252, found 148.1254.

2-Butylnaphthalene (3b) was prepared by the reaction of **1b** (70.9 mg, 0.200 mmol) with **2a** (0.300 mL, 0.600 mmol) in the presence of $(PPh_3)_2NiCl_2$. The crude compound was purified by preparative HPLC (CH_3CN) to afford **3b** (67.6 mg, 61%) as a colorless oil: TLC R_f 0.61 (Et_2O : *n*-hexane = 1 : 4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, J = 7.31 Hz, 3H), 1.31−1.46 (m, 2H), 1.63−1.74 (m, 2H), 2.77 (t, J = 7.64 Hz, 2H), 7.30−7.47 (m, 3H), 7.61 (s, 1H), 7.73−7.82 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.5, 33.6, 35.9, 125.2, 126.1, 126.6, 127.7, 127.7, 127.9, 128.0, 132.2, 134.0, 140.7; HRMS (EI, 70 eV) calcd for $C_{14}H_{16}$ (M^+), 184.1252, found 184.1304.

4-*n*-Butylbiphenyl (3c) was prepared by the reaction of **1c** (76.1 mg, 0.200 mmol) with **2a** (0.300 mL, 0.600 mmol) in the presence of $(PPh_3)_2NiCl_2$. The crude compound was purified by preparative HPLC (CH_3CN) to afford **3c** (75.5 mg, 60%) as a colorless oil.[18]

4-*n*-Butyl-4'-methylbiphenyl (3d) was prepared by the reaction of **1d** (78.9 mg, 0.200 mmol) with **2a** (0.300 mL, 0.600 mmol) in the presence of $(PPh_3)_2NiCl_2$. The crude compound was purified by preparative HPLC (CH_3CN) to afford **3d** (77.3 mg, 57%) as a white solid.[18]

4-Butyl-4'-*tert*-butylbiphenyl (3e) was prepared by the reaction of **1e** (87.3 mg, 0.200 mmol) with **2a** (0.300 mL, 0.600 mmol) in the presence of $(PPh_3)_2NiCl_2$. The crude compound was purified by preparative HPLC (CH_3CN) to afford **3e** (89.5 mg, 56%) as a white solid.[19]

4-*n*-Butyl-4'-methoxybiphenyl (3f) was prepared by the reaction of **1f** (82.1 mg, 0.200 mmol) with **2a** (0.300 mL, 0.600 mmol) in the presence of $(PPh_3)_2NiCl_2$. The crude compound was purified by preparative HPLC (CH_3CN) to give **3f** (73.3 mg, 51%) as a white solid: TLC R_f 0.51 (Et_2O : *n*-hexane = 1 : 4); mp 69−70 °C (uncorrected); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, J = 7.30 Hz, 3H), 1.28−1.43 (m, 2H), 1.57−1.70 (m, 2H), 2.64 (t, J = 7.81 Hz, 2H), 3.82 (s, 3H), 6.97 (d, J = 8.70 Hz, 2H), 7.23 (d, J = 8.40 Hz, 2H), 7.45−7.53 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.5, 33.8, 35.4, 55.5, 114.4 (× 2), 126.8 (× 2), 128.2 (× 2), 129.1 (× 2), 134.1, 138.4, 141.7, 159.2; HRMS (EI, 70 eV) calcd for $C_{17}H_{20}O$ (M^+), 240.1514, found 240.1532.

4-Ethyl-4'-methoxybiphenyl (3g) was prepared by the reaction of **1f** (82.1 mg, 0.200 mmol) with **2b** (0.600 mL, 0.600 mmol) in the presence of $(PPh_3)_2NiCl_2$. The crude compound was purified by preparative HPLC (CH_3CN) to give **3g** (68.7 mg, 54%) as a white solid.[20]

4-Pentylbiphenyl (3h) was prepared by the reaction of **1c** (76.1 mg, 0.20 mmol) with **2c** (0.300 mL, 0.600 mmol) in the presence of $(PPh_3)_2NiCl_2$. The crude compound was purified by preparative HPLC (CH_3CN) to give **3h** (89.2 mg, 66%) as a pale yellow oil: TLC R_f 0.64 (Et_2O : *n*-hexane = 1 : 4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 6.72 Hz, 3H), 1.27−1.43 (m, 4H), 1.56−1.73 (m, 2H), 2.64 (t, J = 7.72 Hz, 2H), 7.24 (d, J = 8.56 Hz, 2H), 7.27−7.35 (m, 1H), 7.42 (t, J = 7.22, 7.72 Hz, 2H), 7.51 (d, J = 8.39 Hz, 2H), 7.55−7.61 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.7, 31.3, 31.7, 35.7, 127.2, 127.3 (× 2), 127.3 (× 2), 129.0 (× 2), 129.1 (× 2), 138.8, 141.5, 142.4; HRMS (EI, 70 eV) calcd for $C_{17}H_{20}$ (M^+), 224.1565, found 224.1604.

4-Pentyl-4'-*tert*-butylbiphenyl (3i) was prepared by the reaction of **1e** (87.3 mg, 0.200 mmol) with **2c** (0.300 mL, 0.600 mmol) in the presence of $(PPh_3)_2NiCl_2$. The crude compound was purified by preparative HPLC (CH_3CN) to give **3i** (110 mg, 65%) as a white solid: TLC R_f 0.65 (Et_2O : *n*-hexane = 1 : 4); mp 56−57 °C (uncorrected); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 6.63 Hz, 3H), 1.36 (s, 9H), 1.25−1.42 (m, 4H), 1.56−1.72 (m, 2H), 2.63 (t, J = 7.81 Hz, 2H), 7.23 (d, J = 8.22 Hz, 2H), 7.40−7.55 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.7, 31.3, 31.5 (× 3), 31.7, 34.6, 35.7, 125.9 (× 2), 126.9 (× 2), 127.1 (× 2), 129.0 (× 2), 138.6, 138.7, 142.1, 150.2; HRMS (EI, 70 eV) calcd for $C_{21}H_{28}$ (M^+), 280.2191, found 280.2182.

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