Nickel-Catalyzed Hydrogenolysis of Arenesulfonates Using Secondary Alkyl Grignard Reagents

Chul-Bae Kim, Chul-Hee Cho, and Kwangyong Park*

*School of Chemical & Materials Engineering, Chung-Ang University, Seoul 156-756, Korea. *E-mail: kypark@cau.ac.kr*
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Neopentyl arenesulfonates react with secondary alkylmagnesium chlorides in the presence of dppfNiCl$_2$ to produce the corresponding arenes *via* the reductive cleavage of carbon-sulfur bond. Highest yield is obtained by using three equivalents of Grignard reagent to a mixture of arenesulfonate and dppfNiCl$_2$ in Et$_2$O at room temperature. This reaction represents a novel method allowing the efficient hydrogenolysis of sulfur-containing groups in aromatic compounds.

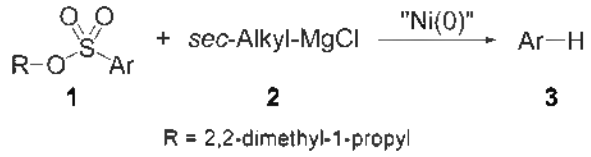
Key Words : Hydrogenolysis, Arenesulfonates, Homogeneous nickel catalyst, Secondary alkyl Grignard reagents

Introduction

Nickel- and palladium-catalyzed coupling reactions[1] of organoboronic acids,[2] organostannanes,[3] organozincs,[4] and organomagnesium halides[5] with organic electrophiles have established a fountainhead of the reliable regio- and chemoselective construction of carbon-carbon bonds. These reactions have recently gained high popularity in solid-phase parallel synthesis/combinatorial chemistry.[6] However, the 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.[7]

Since Wenkert and Takei demonstrated that nickel(0) can insert into the sp^2 carbon-sulfur bond of aryl or alkenyl sulfides and sulfones,[8] various sulfur-containing compounds, such as sulfoxides and sulfonamides have been investigated as the alternate 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] 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 in both solution and solid phase reactions.[11]

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] In a program directed toward the development of the coupling reaction of arenesulfonates with alkyl nucleophiles, we recently observed that arenesulfonates readily undergo the nickel-catalyzed reaction with secondary alkylmagnesium chlorides *via* the reductive C-S bond cleavage to generate the corresponding arene derivatives under the specific reaction conditions (Scheme 1). It was noteworthy that the reaction efficiency significantly depended on the nature of catalyst and solvent. Even though the reductive cleavage of vinyl halides by the nickel-catalyzed reaction with alkylmagnesium halides was known previously,[14] it has not been adopted as a useful reaction in organic synthesis due to the low yield primarily caused by the competition of the coupling reaction.



Scheme 1

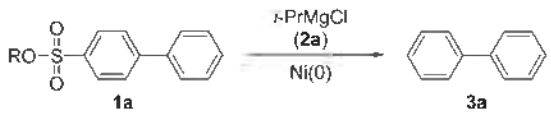
The carbon-sulfur bond in sulfur compounds, including thioethers, thiols, thiono esters, thioamides, sulfoxides, and thioacetals, has been known to be cleaved by photolysis or with reducing agents such as Raney nickel or tin hydrides.[15] Efficient desulfurization has been continuously investigated not only for the simple removal of sulfur moiety, but also for the generation of the desired product attached on the macromolecule.[16] However, the hydrogenolysis of C-S bond in sulfonates has not previously been reported to the best of our knowledge. The preliminary results of the nickel-catalyzed hydrogenolysis of alkyloxysulfonylarenes using alkylmagnesium chloride are presented and discussed below.

Results and Discussion

Neopentyl biphenylsulfonates **1a-1f** were prepared by the palladium-catalyzed coupling reactions of 2,2-dimethy-1-propyl bromobenzenesulfonate with the corresponding arylboronic acids.[17] Neopentyl moiety was selected as the alkyl groups for the sulfonates in order to avoid the competitive substitution and elimination of arenesulfonate anions in the following reactions with alkyl nucleophiles.

The hydrogenolysis of 4-biphenylsulfonate (**1a**) using 2-

Table 1. Effect of Varying Reaction Conditions on the reaction of **1a** with **2a**[a]

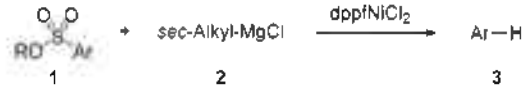


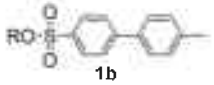
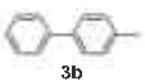
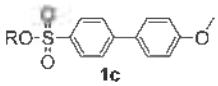
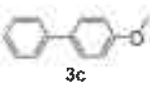
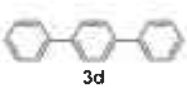
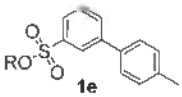
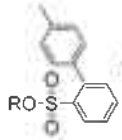
entry	catalyst	solvent	temperature	yield (%)[b]
1	$dppfNiCl_2$	THF	rt/reflux	48/52
2	$dppeNiCl_2$	THF	rt/reflux	47/51
3	$Ni(acac)_2$	THF	rt/reflux	40/46
4	$dppfNiCl_2$	Et_2O	rt/reflux	93/90
5	$dppeNiCl_2$	Et_2O	rt/reflux	76/81
6	$Ni(acac)_2$	Et_2O	rt/reflux	90/86
7	$(PPh_3)_2NiCl_2$	Et_2O	rt	52
8	$dppfNiCl_2$	DME	rt	8
9	$dppfNiCl_2$	toluene	rt/reflux	48/56
10	$dppeNiCl_2$	toluene	reflux	48
11	$Ni(acac)_2$	toluene	reflux	53

[a]Reactions of sulfonate **1a** (0.300 mmol) with **2a** (0.900 mmol) were carried out in the presence of the indicated nickel catalyst (0.015 mmol) in Et_2O (6.0 mL) for 12 h at the indicated temperature. [b]All yields were determined by GC analyses using naphthalene as an internal standard.

propylmagnesium chloride (**2a**) was preliminarily investigated in order to determine optimum reaction conditions (Table 1). All reactions were performed using three equivalents of **2a** for **1a** at the indicated temperature for 12 h. THF, which gave a best result for the nickel-catalyzed cross-coupling of **1** with methyl and neopentyl Grignard reagents,[10a] was proved to be not appropriate for this reaction. No matter what temperature the reaction was performed at, reactions in THF did not give a satisfactory result primarily due to the slow reaction rate (entries 1-3). A brief solvent survey indicated that the reaction efficiency is highest when Et_2O is used as solvent in the presence of most nickel catalysts (entries 4-7). [1,1'-Bis(diphenylphosphino)-ferrocene]dichloronickel ($dppfNiCl_2$) proved to be best for the hydrogenolysis among selected nickel catalysts. While an increase of the reaction temperature did not give a meaningful change for the result, room temperature seemed to be slightly more efficient than refluxing temperature for the reaction in Et_2O (entries 4-6). Room temperature was preferred for our purpose to apply this approach in solid-phase organic reactions and selected as the optimum reaction temperature, although the elevated temperature slightly increased the reaction rate for the reactions in Et_2O. DME was not a proper solvent for this reation at all (entry 8). While the previous report showed that the reactions of aryl sulfonamides with 2-propylmagnesium chloride underwent the cross-coupling reaction in refluxing toluene in the presence nickel catalyst,[9a] the reactions of aryl sulfonates with 2-propylmagnesium chloride did not show any evidence of the cross-coupling reaction but the hydrogenolysis under the standard reaction conditions (entries 9-11). However, the yield of the reactions in toluene was not as high as that in ether. In summary, the optimization studies demonstrated that the highest yields were obtained using $dppfNiCl_2$ in Et_2O at room temperature.

Table 2. Hydrogenolysis of sulfonates **1** using secondary alkylmagnesium chlorides **2**[a]



entry	sulfonate **1**	Grignard reagent **2**	product **3**	yield (%)[b]
1	**1a**	**2a**	**3a**	90
2	 **1b**	**2a**	 **3b**	92
3	 **1c**	**2a**	 **3c**	95
4	 **1d**	**2a**	 **3d**	90
5	 **1e**	**2a**	**3b**	78
6	 **1f**	**2a**	**3b**	92
7	**1a**	 **2b**	**3a**	81
8	**1b**	**2b**	**3b**	89
9	**1c**	**2b**	**3c**	84
10	**1d**	**2b**	**3d**	77
11	**1a**	 **2c**	**3a**	31
12	**1b**	**2c**	**3b**	28
13	**1a**	 **2d**	**3a**	62
14	**1b**	**2d**	**3b**	56

[a]Reactions of sulfonates **1** (0.300 mmol) with **2** (0.900 mmol) were carried out in the presence of $dppfNiCl_2$ (0.015 mmol) in Et_2O (6.0 mL) at room temperature. [b]Isolated yields based on **1**.

The results of reactions between various arenesulfonates **1** and secondary alkylmagnesium bromides **2** are summarized in Table 2. Arenesulfonates **1a-1f** underwent the reaction with **2a** to produce arene derivatives, **3a-3d**, in good yields within 12 h (entries 1-6). The corresponding cross-coupled products were not detected in the standard GC and TLC analyses for the entire reactions. *m*-Substituted biphenylsulfonate **1e** showed the less reactivity than *p*-substituted biphenylsulfonate **1b** or *o*-substituted biphenylsulfonate **1f** under the standard reaction condition (entries 2, 5, and 6). 2-Butylmagnesium chloride **2b** also reacted with **1a-1d** with slightly less efficiency (entries 7-10). Cycloalkyl Grignard reagents did not undergo the reaction as efficient as normal alkyl nucleophiles. Reactions using cyclohexylmagnesium chloride **2c** and cyclopentylmagnesium chloride **2d** generated the desired product in less yields (entries 11-14).

Conclusions

In summary, neopentyl arenesulfonates reacted with secondary alkylmagnesium chlorides in the presence of $dppfNiCl_2$ to produce the corresponding arenes *via* the reductive cleavage of carbon-sulfur bond. To our knowledge, the study reported above is the first general exploration of the hydrogenolysis of alkyloxysulfonyl moiety from aromatic compounds. The 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. The application of this reaction toward various compounds is currently under investigation and will be reported in due course.

Experimental Section

^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) were registered in $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in δ units (ppm) by assigning TMS resonance in the ^1H 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 from sodium-benzophenone ketyl, and Et_2O and toluene from calcium hydride. $DppfNiCl_2$ was prepared according to a literature procedure.[18] $DppeNiCl_2$, $(PPh_3)_2NiCl_2$ and $Ni(acac)_2$ were purchased from Sigma-Aldrich Company. 2-Propyl- **2a** (2.0 M, Et_2O), 2-butyl- **2b** (2.0 M, Et_2O), cyclohexyl- **2c** (2.0 M, Et_2O), and cylclopentylmagnesium chloride **2c** (2.0 M, Et_2O) were also purchased, and used as received. Neopentyl bromobenzenesulfonates, intermediates for the preparation of arenesulfonates **1**, were prepared according to a literature procedure.[10b]

General Procedure for the Preparation of Neopentyl Biphenylsulfonates (1). To the solution of bromobenzenesulfonate (5.22 mmol) and $Pd(PPh_3)_4$ (0.157 mmol) in toluene (12.0 mL) was added 2.0 M aqueous Na_2CO_3 (6.0 mL) under Ar atmosphere. To the resulting mixture was added arylboronic acid (5.74 mmol), which was dissolved in ethanol (3.0 mL). The reaction mixture was heated at reflux for 6 h with vigorous stirring. To the resulting mixture was added 30% hydrogen peroxide (0.3 mL) to oxidize the residual boronic acid. The mixture was stirred at room temperature for 1 h and diluted with EtOAc. The organic layer was washed with water and brine; dried over $MgSO_4$; filtrated through a small pad of silica gel in a sintered glass filter; and concentrated in vacuo. The crude compound was purified by recrystallization from *n*-hexane to give **1** as a white solid.[19]

Neopentyl 4-Biphenylsulfonate (1a) was prepared by the reaction of neopentyl 4-bromobenzenesulfonate (1.60 g, 5.22 mmol) with phenylboronic acid (0.70 g, 5.74 mmol) in the presence of $Pd(PPh_3)_4$ (0.181 g, 0.157 mmol) and 2 M aq. Na_2CO_3 (6.0 mL) by using toluene as solvent. The crude compound was purified by recrystallization from *n*-hexane to give **1a** (1.42 g, 80%) as a white solid: TLC R_f 0.51 (Et_2O : *n*-hexane = 1 : 1); ^1H NMR (300 MHz, $CDCl_3$) δ 0.93 (s, 9H), 3.73 (s, 2H), 7.45-7.49 (m, 3H), 7.62 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 8.7 Hz, 2H), 7.94 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.1 (×3), 31.8, 79.9, 127.6 (×2), 128.0 (×2), 128.6, 128.9 (×2), 129.4 (×2), 134.8, 139.3, 146.8; HRMS (EI, 70 eV) calcd for $C_{17}H_{20}O_3S$ (M^+), 304.1133, found 304.1141.

Neopentyl 4'-Methoxy-4-biphenylsulfonate (1c) was prepared by the reaction of neopentyl 4-bromobenzenesulfonate (1.60 g, 5.22 mmol) with 4-methoxyphenylboronic acid (0.87 g, 5.74 mmol) in the presence of $Pd(PPh_3)_4$ (0.181 g, 0.157 mmol) and 2 M aq. Na_2CO_3 (6.0 mL) by using toluene as solvent. The crude compound was purified by recrystallization from *n*-hexane to give **1c** (1.34 g, 77%) as a white solid: TLC R_f 0.53 (Et_2O : *n*-hexane = 1 : 1); mp 97-98 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (s, 9H), 3.71 (s, 2H), 3.88 (s, 3H), 7.02 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.94 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.1 (×3), 31.8, 55.6, 79.8, 114.8 (×2), 127.4 (×2), 128.7 (×2), 128.8 (×2), 131.7, 134.1, 146.4, 160.6; HRMS (EI, 70 eV) calcd for $C_{18}H_{22}O_4S$ (M^+), 334.1239, found 334.1228.

Neopentyl [1,1';4',1'']terphenyl-4-sulfonate (1d) was prepared by the reaction of neopentyl 4-bromobenzenesulfonate (1.60 g, 5.22 mmol) with biphenylboronic acid (1.14 g, 5.74 mmol) in the presence of $Pd(PPh_3)_4$ (0.181 g, 0.157 mmol) and 2 M aq. Na_2CO_3 (6.0 mL) by using toluene as solvent. The crude compound was purified by recrystallization from *n*-hexane to give **1d** (1.49 g, 75%) as a white solid: TLC R_f 0.66 (Et_2O : *n*-hexane = 1 : 1); mp 158159 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.94 (s, 9H), 3.74 (s, 2H), 7.14 (d, J = 7.3 Hz, 1H), 7.49 (t, J = 7.7, 7.3 Hz, 2H), 7.66 (d, J = 7.7 Hz, 2H), 7.72 (s, 4H), 7.82 (d, J = 8.7 Hz, 2H), 8.00 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.1 (×3), 31.8, 79.9, 127.6 (×2), 127.9 (×2), 128.0 (×3), 128.1 (×2), 128.7 (×2), 129.2 (×2), 134.7, 138.1, 140.5, 141.9, 146.3; HRMS (EI, 70 eV) calcd for $C_{23}H_{24}O_3S$ (M^+), 380.1446, found 380.1459.

General Procedure for the Hydrogenolysis of 1. To a stirred solution of sulfonate **1** (0.300 mmol) and $dppfNiCl_2$ (0.015 mmol) in dry Et_2O (6.0 mL) was added secondary alkyl Grignard reagent **2** (0.900 mmol) at room temperature under Ar atmosphere. The mixture was stirred at room temperature for 12 h. The mixture was diluted with Et_2O (100 mL). The organic layer was washed with water and

brine; dried over $MgSO_4$; and concentrated *in vacuo*. The crude compounds were purified by column chromatography (*n*-hexane : Et_2O = 8 : 1) to give **3** as white solids.

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