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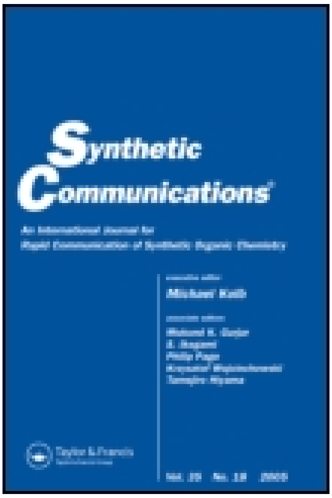

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Triflic Salt-Catalyzed Coupling: Iron Triflate-Catalyzed Homocoupling of Aryl Bromides in the Presence of Metallic Magnesium

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TRIFLIC SALT–CATALYZED COUPLING: IRON TRIFLATE–CATALYZED HOMOCOUPLING OF ARYL BROMIDES IN THE PRESENCE OF METALLIC MAGNESIUM

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In the presence of metallic magnesium, the homocoupling reaction of aryl bromides catalyzed by iron triflate was carried out readily in one pot. The catalyst was used successfully in this coupling reaction without preparation of Grignard reagent in advance. Meanwhile, the catalyst was recovered easily and reused smoothly with only a little loss of its activity.

Keywords: Aromatic bromide; homocoupling; iron triflate

INTRODUCTION

Transition metal–catalyzed coupling reaction of halogen compounds is one of the most important methods in organic synthesis[1–12] and is widely applied in pharmaceutical chemistry[13] where palladium and nickel complexes are more often used as the catalysts.[14,15]

However, many auxiliary reagents, which were used in the reaction to improve catalytic effect, are generally toxic, not environmentally friendly, expensive, or sensitive to oxygen and moisture. In 1975, Kochi et al.[16–21] reported that coupling reaction of halogen compounds with Grignard reagents could be catalyzed smoothly by iron salt, a cheap and ecofriendly compound. Since then, a large number of studies were reported about iron salt–catalyzed coupling reactions.[22–38]

Although the methods are better than their earlier efforts for the synthesis of symmetrical biaryls, there were obvious drawbacks: (1) Grignard reagents had to be prepared before the coupling reaction, (2) the toxic 1,2-dihalogen ethane was used as the oxidant, and (3) some iron salts such as $Fe(acac)_3$ and $Fe(dbm)_3$ are apt to

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dissolve in organic solvents, which made the workup procedure of the reaction mixtures more complex and tedious.

Therefore, the developing of a more efficient synthetic methodology for carbon–carbon bond formation is still in demand.

Metal triflates, which were confirmed to be ecofriendly and water-incompatible catalysts, could be recovered and reused with only a little loss of their activity in various kinds of reactions.[39–42] These encouraged us to try the aryl–aryl coupling reactions using triflate as a catalyst.

RESULTS AND DISCUSSION

The homocoupling reaction of aryl bromide was investigated in the presence of magnesium strips and a catalytic amount of transition-metal salt. Thus, the reaction of 1 mmol bromobenzene with 2 mmol magnesium strips in presence of 5 mol% catalytic transition metal was carried out in anhydrous solvent. The results are shown in Table 1.

As shown in Table 1, compared with other iron compounds such as $FeCl_3$, $Fe(acac)_3$, and $Fe(dbm)_3$ (entries 1–4), $Fe(OTf)_3$ gives a better yield (entry 5). It seems that the catalytic effect of the coupling reaction was improved by triflate, which induced us to investigate the catalytic effect of a series of transition-metal triflates on this reaction system. However, the results were not satisfying (entries 6–11). Meanwhile, $Fe(OTf)_3$ is a comparatively excellent catalyst with many advantages, such as environmental friendliness and water incompatibility, and it also can be recovered and reused with only a little loss of its activity after several runs.

The effect of different solvents on this coupling reaction was studied (entries 5 and 12–14), in which tetrahydrofuran (THF) was found to be the best solvent in this reaction.

Table 1. Optimization of catalyzed homocoupling reaction of bromobenzene[a]

Entry	Catalyst	Solvent	Time (h)	Yield[b] (%)
1	$FeCl_3$	THF	4	76
2	$FeCl_3/ClCH_2CH_2Cl$	THF	4	81
3	$Fe(dbm)_3$	THF	2	82[c]
4	$Fe(acac)_3$	THF	2	80[c]
5	$Fe(OTf)_3$	THF	2	88
6	$Yb(OTf)_3$	THF	4	51
7	$VO(OTf)_2$	THF	2	53
8	$Mn(OTf)_2$	THF	4	64
9	$Ni(OTf)_2$	THF	2	78
10	$Cu(OTf)_2$	THF	2	71
11	$Sc(OTf)_3$	THF	4	45
12	$Fe(OTf)_3$	Ether	2	73
13	$Fe(OTf)_3$	Benzene	4	51
14	$Fe(OTf)_3$	Toluene	4	50

[a] Reaction condition: 5 mol% catalyst, 1 mmol PhBr, 2 mmol Mg, 3 mL solvent, room temperature; dbm, dibenzoyl methane; acac, acetylacetonate.

[b] Isolated yield.

[c] Quoted from Ref. 38.

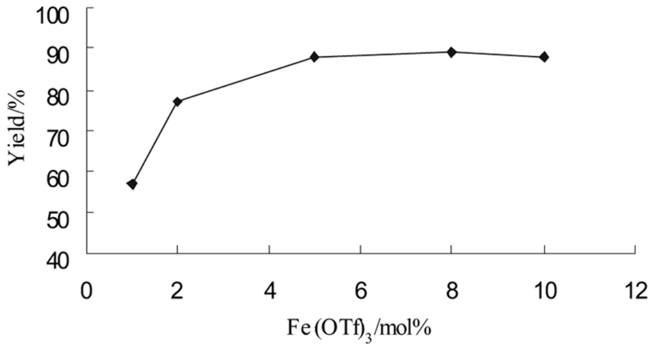

Figure 1. Effect of amount of catalysts on the homocoupling of bromobenzene.

Table 2. Catalyst recycling

Run	Recovery rate of catalyst (%)	Yield (%)
1	92	84
2	91	81
3	92	80

Notes. Reaction condition: 5 mol% Fe(OTf)$_3$, 1 mmol PhBr, 2 mmol Mg, 3 mL THF, room temperature, and reaction time: 4 h.

Table 3. Fe(OTf)$_3$-catalyzed homocoupling of aryl bromides[a]

$$\underset{\mathbf{1}}{\mathrm{RBr}} \xrightarrow[\text{2 mmol Mg, THF, r.t.}]{\text{5 mol\% } \mathrm{Fe(OTf)_3}} \underset{\mathbf{2}}{\mathrm{R\text{-}R}}$$

Entry	Aryl bromide **1**	Product	Yield[b] (%)
1	C_6H_5Br	**2a**	88
2	4-MeC_6H_4Br	**2b**	90
3	3-MeC_6H_4Br	**2c**	92
4	2,3-$Me_2C_6H_3Br$	**2d**	71
5	4-$MeOC_6H_4Br$	**2e**	93
6	4-ClC_6H_4Br	**2f**	82
7	3-$NO_2C_6H_4Br$	**2g**	70
8	4-$CF_3C_6H_4Br$	**2h**	63[c]
9	3,5-$(CF_3)_2C_6H_3Br$	**2i**	66[c]
10	3-Thienyl Br	**2j**	81
11	3-Pyridinyl Br	**2k**	78

[a] Reaction conditions: 5 mol% Fe(OTf)$_3$, 1 mmol aryl bromides, 2 mmol Mg, 3 mL anhydrous THF, room temperature, and standard reaction time: 4 h.

[b] Isolated yield.

[c] Reaction time: 6 h.

The effect of the amount of catalyst and reaction time on the homocoupling reaction was also investigated using 1 mmol PhBr, 2 mmol Mg, and 3 mL anhydrous THF.

As shown in Fig. 1, with the same reaction time, the more catalyst was employed, the better the yield, and the reaction yield reached the maximum value of 88% when 5 mol% of catalyst was employed.

Meanwhile, the catalyst was recovered from the aqueous layer during the workup after the reaction and was reused in subsequent reactions for three times. The activity was still maintained at a desirable level as shown in Table 2.

A diverse array of biaryls from aryl bromides were efficiently synthesized under the standard reaction condition (Table 3).

As shown in Table 3, all of the aryl bromides gave their corresponding products in moderate to good yields under the standard conditions. Aromatic bromide substituted with electron-donating groups (methyl, methoxy, etc.) at the *m*- or *p*-position gave good yields. It is noteworthy that the present reaction system is tolerant of strong electron-withdrawing groups such as trifluoro-methyl and nitro, and the desired products were obtained in moderate yields. Heteroaryl bromides such as 2-bromothiophene and 3-bromopyridine also work well in this system.

CONCLUSION

In summary, the homocoupling reaction of aryl bromides catalyzed by an eco-friendly catalyst, $Fe(OTf)_3$, was carried out readily in one pot, in which it is not necessary to prepare Grignard reagent in advance.

EXPERIMENTAL

General

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring. Tetrahydrofuran (THF) was distilled from a benzophenone–sodium adduct and stored over sodium wires. ^{1}H NMR spectra were measured on a Varian Plus-400 (400-MHZ) apparatus ($CDCl_3$ solution); MS spectra were found on an AEI MS-902 apparatus. Melting points were determined on X-4 micromelting-point apparatus.

Homocoupling Reaction Catalyzed by $FeCl_3$

The general synthetic process is as follows: 1 mmol PhBr, 3 mL anhydrous THF, and 1 mmol Mg strips were added to a 50-ml, three-necked, round-bottom flask equipped with dropping funnel and condenser, the top of which was connected to a calcium chloride drying tube, and then stirred at reflux temperature until the Mg strips disappeared. Then 1.2 mmol 1,2-dihaloethane and 5 mol% $FeCl_3$ were added. The mixture was then stirred at reflux temperature for 1 h and quenched with 1 mol/L HCl. The solvent was evaporated, and the residue was extracted with Et_2O (3×10 mL). The organic extracts were combined, dried with $MgSO_4$, concentrated, and then purified by column chromatography on silica gel (300–400 mesh) with hexane as eluant to give the pure homocoupling product.

Homocoupling Reaction Catalyzed by Fe(OTf)$_3$ and Recovery of Fe(OTf)$_3$

The general synthetic process is as follows: 1 mmol PhBr, 3 mL anhydrous THF, 5 mol% Fe(OTf)$_3$, and 2 mmol Mg strips were added to a 50-ml, three-necked, round-bottom flask equipped with dropping funnel and condenser, the top of which was connected to a calcium chloride drying tube. The whole reaction mixture was stirred for 2–6 h at room temperature and quenched with 1 mol/L HCl. The solvent was evaporated, and the residue was treated with Et$_2$O (10 ml) and water (15 ml). The organic phase was separated, and the aqueous layer was washed with Et$_2$O (2×10 ml). Concentration of the combined organic layer, dried over MgSO$_4$ in advance, afforded the crude product, which was further purified by column chromatography on silica gel (300–400 mesh) with hexane as eluant to give the pure homocoupling product.

The aqueous layer containing Fe(OTf)$_3$ in the workup procedure was evaporated under reduced pressure, and the reside was extracted with ethyl acetate (2×10 ml). The organic phases were combined, evaporated under reduced pressure, and dried at 70 °C for 2 h to give pure Fe(OTf)$_3$ in 92% recovery. The recovered catalyst was reused for the next run in the same way.

Selected Data

Biphenyl 2a. Mp 68–71 °C (lit.[38] 68–71 °C); ^{1}H NMR δ: 7.35–7.47 (6H, m), 7.58–7.62 (4H, m); MS (EI): *m/z* (%): 154 (M$^+$, 100), 153 (35), 152 (20), 115 (3), 76 (13), 51 (4).

4,4′-Dimethylbiphenyl 2b. Mp 119–120 °C (lit.[38] 119–120 °C); ^{1}H NMR δ: 2.56 (6H, s), 7.41 (4H, d, $J = 7.6$ Hz), 7.66 (4H, d, $J = 7.6$ Hz); MS (EI): *m/z* (%): 182 (M$^+$, 100), 167 (55), 152 (12), 89 (11), 76 (3).

3,3′-Dimethylbiphenyl 2c. Oil; 1H NMR δ: 2.42 (6H, s), 7.16 (2H, d, $J = 6.0$ Hz), 7.32–7.40 (6H, m); MS (EI): *m/z* (%): 182 (M$^+$, 100), 167 (33), 152 (12), 89 (8), 76 (4).

2,3,2′,3′-Tetramethylbiphenyl 2d. Mp 114–115 °C (lit.[43] 114–115 °C); ^{1}H NMR δ: 1.95 (6H, s), 2.33 (6H, s), 6.96 (2H, d, $J = 6.8$ Hz), 7.16–7.10 (4H, m); MS (EI): *m/z* (%): 210 (M$^+$, 93), 195 (100), 180 (25), 165 (19), 89 (11), 76 (3).

4,4′-Dimethoxydiphenyl 2e. Mp 177–179 °C (lit.[38] 177–179 °C); ^{1}H NMR δ: 3.84 (6H, s), 6.95 (4H, d, $J = 8.8$ Hz), 7.47 (4H, d, $J = 8.8$ Hz); MS (EI): *m/z* (%): 182 (M$^+$, 100), 167 (55), 152 (12), 89 (11), 76 (3).

4,4′-Dichlorobiphenyl 2f. Mp 149–150 °C (lit.[44] 146–148 °C); ^{1}H NMR δ: 7.40 (4H, d, $J = 8.0$ Hz), 7.48 (4H, d, $J = 8.0$ Hz); MS (EI): *m/z* (%): 222 (M$^+$, 100), 186 (15), 152 (51), 111 (5), 93 (7), 75 (9).

3,3′-Dinitrobiphenyl 2g. Mp 204–205 °C (lit.[45] 205 °C); ^{1}H NMR δ: 7.69–7.72 (2H, m), 7.96–7.98 (2H, m), 8.29–8.32 (2H, m), 8.50–8.51 (2H, m); MS (EI): *m/z* (%): 244 (M$^+$, 100), 202 (21), 152 (15), 96 (7), 76 (15), 62 (5).

4,4′-Bis(trifluoromethyl)biphenyl 2h. Mp 89–91 °C (lit.[46] 83–84 °C); ^{1}H NMR δ: 7.38 (4H, d, $J = 8.0$ Hz), 7.48 (4H, d, $J = 8.0$ Hz); MS (EI): m/z (%): 290 (M^+, 100), 271 (25), 240 (10), 219 (6), 201 (20), 152 (14), 145 (5).

3,5,3′,5′-Tetrakis(trifluoromethyl)biphenyl 2i. Mp 68–70 °C (lit.[38] 68–71 °C); ^{1}H NMR δ: 7.96 (2H, s), 8.04 (4H, s); MS (EI): m/z (%): 426 (M^+, 100), 407 (42), 357 (15), 337 (15), 287 (10), 213 (8).

3,3′-Bithienyl 2j. Mp 130–131 °C (lit.[45] 132–133 °C); ^{1}H NMR δ: 7.33–7.35 (4H, m), 7.37–7.38 (2H, m); MS (EI): m/z (%): 166 (M^+, 100), 83 (21).

3,3′-Bipyridinyl 2k. Mp 68–69 °C (lit.[45] 67 °C); ^{1}H NMR δ: 7.34–7.35 (2H, m), 7.80–7.82 (2H, m), 8.56–8.57 (2H, m), 8.76 (2H, s); MS (EI): m/z (%): 156 (M^+, 100), 152 (11), 72 (5), 66 (21).

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