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ULLMANN-TYPE COUPLING REACTION OF ARYL TRIFLUOROMETHANESULFONATES CATALYZED BY IN SITU-GENERATED LOW VALENT NICKEL COMPLEXES[1)]

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The low valent nickel complexes generated in situ from nickel(II) chloride, triphenylphosphine, sodium iodide, and zinc powder in dimethylformamide catalyze the Ullmann-type homo-coupling of aryl trifluoromethanesulfonates to biaryls under ultrasounds irradiation.

The metal promoted homo-coupling reaction of aryl halides has been accomplished by copper powder(Ullmann reaction)[2)] or by nickel(0) complexes.[3)] The latter method has been improved to use in situ-generated nickel(0) from a catalytic amount of nickel(II) salt, triphenylphosphine, potassium iodide, and zinc powder.[4)]

During the course of our studies on the ultrasounds-promoted reactions, we found the first examples of the homo-coupling reaction of aryl sulfonates, especially aryl trifluoromethanesulfonates(Ar-OTf), to afford biaryls(Ar-Ar) which was catalyzed by in situ-generated low valent nickel complexes. Although p-toluenesulfonate moiety is known to be a good leaving group in aliphatic nucleophilic substitution, only few reactions are known which involve aryl-oxygen bond fission of aryl sulfonates.[5)]

$$\text{Ar-OTf} \xrightarrow[\text{DMF, 60 °C, ultrasounds}]{\text{NiCl}_2\text{, Zn, PPh}_3\text{, NaI}} \text{Ar-Ar}$$

A typical procedure is described for the reaction of 1-naphthyl trifluoromethanesulfonate: Zn (5.0 mmol), $NiCl_2$ (0.27 mmol), NaI (2.0 mmol), PPh_3 (2.0 mmol), and dry DMF (20 cm^3) were sonicated at room temperature for 0.5 h under nitrogen atmosphere. 1-Naphthyl trifluoromethanesulfonate (3.4 mmol) was added and the mixture was sonicated at 60 °C for 4 h, and then filtered. The residue was washed with benzene. After the combined filtrates were treated with iodine to remove PPh_3 as PPh_3I_2 followed by the usual work-up procedure, 1,1'-binaphthyl was obtained in 67% yield (80% yield on GLC).

The results of homo-coupling of various aryl trifluoromethanesulfonates are summarized in Table 1.[6)] The reaction may proceed with ordinary stirring without sonication; however, the reaction rate decreases by 20-50%.[7)] The amount of $NiCl_2$ is not optimized, but the 0.08 molar ratio to the substrate is sufficient for the reaction. Without a large excess of NaI and PPh_3 over the nickel catalyst, the reaction stops with a lower yield. Aryl *p*-toluenesulfonates or methanesulfonates can be used instead of the trifluoromethanesulfonates, but the rate of reaction decreases significantly.

Table 1. Homo-coupling of aryl trifluoromethanesulfonates to biaryls catalyzed by low valent nickel complexes[a]

Ar-OTf Ar:	Reaction time/h	Yield/%[b] Ar-Ar	 Ar-H
4-methylphenyl[c]	1	38	5
4-methylphenyl	1	85	10
4-methylphenyl[d]	2	65	8
3-methylphenyl	1	82	13
2-methylphenyl	4	82	17
4-methoxyphenyl	2	95	trace
2,4,6-trimethylphenyl	4	no reaction	
1-naphthyl	4	80	14
2-methoxycarbonylphenyl[e]	4	67	trace

a) Molar ratio of Ar-OTf : Zn : $NiCl_2$: NaI : PPh_3 = 1 : 1.5 : 0.08 : 0.6 : 0.6, unless otherwise noted. For other reaction conditions, see a typical procedure in the text. b) Yields by GLC; the products were identified by the retention time of GLC and their mass spectra compared with the authentic samples. c) Molar ratio of NaI was 0.14. d) Molar ratio of PPh_3 was 0.30. e) Molar ratio of $NiCl_2$ was 0.24.

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