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Nickel(0)-Catalyzed Reduction of Aryl Triflates with Zinc Powder and Methanol

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Deoxygenative reduction of aryl triflates was attained by using nickel(0)-dppp/PPh_3 catalyst with zinc powder and methanol as a hydrogen donor.

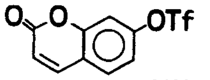
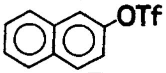
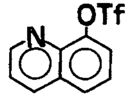
The deoxygenative reduction of phenols to the aromatic hydrocarbons is the most difficult transformations in organic synthesis because of the low reactivity of sp^2 carbon-oxygen bonds. However, such difficulty has been recently overcome by converting phenols into aryl triflates and allowing them to react with ammonium formate in the presence of palladium(0) catalyst.1) In this paper, we will report that the conversion of aryl triflates into the corresponding aromatic hydrocarbons is also achieved by the use of nickel(0)-dppp/PPh_3 (dppp=1,3-bis(diphenylphosphino)propane) complex as a catalyst and methanol as a hydrogen donor.

$$\text{Ar-OTf} \xrightarrow[\text{Ni(0)-dppp/PPh}_3\text{ catalyst}]{\text{MeOH (D), Zn}} \text{Ar-H (D)}$$

In the presence of nickel(0)-phosphine complex, generated in situ from nickel(II)-phosphine complex and zinc powder, the deoxygenative reduction of aryl triflates with alcohols (like methanol) or water took place smoothly. When zinc powder was used in excess, catalytic amount of nickel was sufficient for the proceeding of the reaction and, regarding turnovers of the catalyst, a binary ligand system composed of dppp and PPh_3 was found to be most favorable among the ligands examined. Thus, the reduction of p-tolyl triflate using 10 mol% of nickel(0)-complex generated in situ from $NiBr_2(PPh_3)_2$, dppp, KI2) and zinc powder (1.5 molar equivalent) in methanol/N,N-dimethylformamide mixed solvent at room temperature gave toluene in 97% yield. As shown in Table 1, various aryl triflates underwent the reaction readily to afford the corresponding reduction products (with intact functional group) in excellent to good yields.3)

It is to be noted that, in this nickel(0)-catalyzed reaction, the hydrogens, incorporated into aromatic hydrocarbons, come from the hyroxy-hydrogen of alcohols: in the reaction of 2-naphthyl triflate, use of MeOD in the place of MeOH gave naphthalene-2-d in D-content more than 95% (GC/MS). Thus, this catalytic procedure affords a new and convenient method for the deoxygenative reduction of various phenolic compounds and especially for the selective deuteration of the aromatic ring by the use of the readily available deuterium source as a reagent.

Table 1. Reduction of Various Aryl Triflate Catalyzed by Nickel Complex[a)]

$X\text{-}C_6H_4\text{-}OTf$ X	Temp/°C	Time/h	Yield/%[b)]
p-CH_3	20	16	(97)
p-CH_3	20	16	(85) [c)]
p-CH_3O	20	16	(88)
p-CH_3CONH	20	16	95
p-CH_3CO	20	16	(92)
p-CH_3OCO	20	16	85 (94)
p-CN	20	8	70 (82)
p-C_6H_5	20	12	(97)
p-(t-CH=$CHCOOCH_3$)	50	12	(90)
	50	4	98
	20	12	(98)
	20	16	78 (83)

a) Reactions using 2 mmol of aryl triflates in 2 ml of MeOH/DMF (1:4) solvent. Molar ratio of $ArOTf/NiBr_2(PPh_3)_2$/dppp/Zn/KI was 1.0/0.1/0.1/1.5/1.5.

b) Isolated yields. Yields in the parentheses were determined by GLC.

c) H_2O/DMF (1:20) solvent was used in the place of MeOH/DMF (1:4) solvent.

A typical procedure is as follows: A mixture of p-acetamidophenyl triflate (2.0 mmol), $NiBr_2(PPh_3)_2$ (0.20 mmol), dppp (0.20 mmol), KI (3.0 mmol), and Zn powder (3.0 mmol) in 2 ml of MeOH/DMF (1:4) solvent was stirred at 20 °C for 16 h under nitrogen atmosphere. The resultant mixture was chromatographed on a silica-gel column using hexane-ether (1:5) as an eluent, affording acetanilide (1.9 mmol, 95%).

References

1) W. J. Scott and J. E. McMurry, Acc. Chem. Res., 21, 47 (1988); S. Cacchi, P. G. Ciattini, E. Morera, and G. Ortar, Tetrahedron Lett., 27, 5541 (1986); Q. Y. Chen, Y. B. He, and Z. Y. Yang, J. Chem. Soc., Chem. Commun., 1986, 1452; Q. Y. Chen and Y. B. He, Synthesis, 1988, 896; L. R. Subramanian, A. G. Martinez, A. H. Fernandez, and R. M. Alvarez, ibid., 1984, 481.

2) The addition of KI was essential for successful reactions. The effect of KI in nickel-catalyzed reaction of aryl halides or aryl triflates has been reported: K. Takagi, N. Hayama, and K. Sasaki, Bull. Chem. Soc. Jpn., 47, 1887 (1984); I. Colon, J. Org. Chem., 47, 2622 (1982); J. Yamashita, Y. Inoue, T. Kondo, and H. Hashimoto, Chem. Lett., 1986, 407.

3) Palladium(0)-catalyzed reduction of aryl triflates is accompnied by a partial hydrogenation of alkenyl substituent. See Ref. 1.

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