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Nickel(0) or Palladium(0)-catalyzed Cyanation of Aryl Triflates1)

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Aryl triflates readily participated in a nickel(0) or palladium(0)-catalyzed nucleophilic displacement with cyanide anion, thereby providing a new convenient method for the preparation of aryl cyanides.

Hitherto, there have been no convenient ways for converting a phenolic oxygen into a cyano group, mainly because of the difficulty of nucleophilic displacement at sp^2 carbon centers.2) However, in certain cases, such difficulty is overcome by using a transition-metal catalyst as exemplified by a palladium or nickel-catalyzed cyanation of non-activated aryl halides.3) In view of the facts that 1) aryl triflates (ArOTf, aryl trifluoromethanesulfonates) are prepared easily from phenols4) and 2) their carbon-oxygen bonds are cleaved readily by transition metals,5) the application of aryl triflates to the catalytic cyanation was undertaken. In this paper, we will communicate facile syntheses of aryl cyanides from aryl triflates and potassium cyanide by means of a nickel or palladium catalyst.

$$\mathrm{ArOTf} + \mathrm{KCN} \xrightarrow{\mathrm{Ni(0)\ or\ Pd(0)\ catalyst}} \mathrm{ArCN} + \mathrm{KOTf}$$

As shown in Table 1, the reaction of phenyl triflate with cyanide anion took place in the presence of 2 mol% of nickel(0), generated in situ from dibromobis(triphenylphosphine)nickel(II) ($NiBr_2(PPh_3)_2$), triphenylphosphine (PPh_3), and zinc powder as reducing agent, in 1-methyl-2-pyridone (NMP) or acetonitrile (AN) at 60 °C. Benzonitrile was obtained in an excellent yield, not accompanied by phenol.6) In the cyanation, aryl triflates containing electron-donating groups required more severe conditions than did ones containing electron-withdrawing groups. That is, a larger amount of potassium cyanide (Run 5) or 1,1'-bis(diphenylphosphino)ferrocene (dppf) ligand instead of the conventional PPh_3 ligand and higher temperature (Run 6) were necessary to complete the reactions. An in-situ generated palladium(0) from tris(dibenzylideneacetone)(chloroform)-di-palladium(0) ($Pd_2(dba)_3 \cdot CHCl_3$) and dppf, though less reactive than the nickel(0), was an effective (Run 8) and, in one case not as nickel(0), chemoselective catalyst (Run 9). It is to be noted that an ortho substituent in the aryl triflate did not affect the reaction, so that even 2,6-dimethylphenyl triflate afforded the desired product in a good yield (vide infra). Thus, aryl triflates are revealed to be effective and unique

Table 1. Synthesis of Aryl Cyanides[a)]

Run	Aryl triflate $R-C_6H_4-OTf$ R	Catalyst	Solvent	Time h	Yield/%[b)] $R-C_6H_4-CN$
1	H	$Ni-PPh_3$	NMP	3	98
2	H	$Ni-PPh_3$	AN	3	92
3	$p-CH_3CO$	$Ni-PPh_3$	AN	2	(89)
4	p-Cl	$Ni-PPh_3$	AN	3	60[c)]
5[d)]	$p-CH_3$	$Ni-PPh_3$	AN	3	(85)
6[e)]	$p-CH_3O$	Ni-dppf	AN	10	(89)
7	$o-CH_3$	$Ni-PPh_3$	AN	3	92
8	H	Pd-dppf	NMP	8	94
9	p-Cl	Pd-dppf	NMP	3	94

a) Every run was carried out at 60 °C under nitrogen. Molar ratio of each component ($ArOTf/KCN/NiBr_2(PPh_3)_2/PPh_3/Zn$ or $ArOTf/KCN/Pd_2(dba)_3 \cdot CHCl_3/dppf$) was 1.0/1.1-2.0/0.02/0.04/0.04 (Runs 1-7) or 1.0/2.0/0.02/0.08 (Runs 8 and 9).

b) Yields were determined by GLC. Yields in parentheses were isolated ones.

c) 1,4-Dicyanobenzene was obtained in a yield of 31%.

d) Run using 6.0 equivalents of potassium cyanide.

e) Run at 80 °C.

substrates in the catalytic cyanation, which provides a new convenient method for the preparation of aryl cyanides.

A typical procedure is as follows: A mixture of 2,6-dimethylphenyl triflate (254 mg, 1.0 mmol), KCN (130 mg, 2.0 mmol), $NiBr_2(PPh_3)_2$ (26.2 mg, 0.035 mmol), PPh_3 (21.0 mg, 0.08 mmol), zinc powder (5.2 mg, 0.08 mmol), and AN (0.5 cm^3) was stirred at 80 °C for 5 h under nitrogen. The resulting mixture was chromatographed on a silica-gel column using hexane-ethyl acetate as an eluent, affording 110 mg of 2,6-dimethylbenzonitrile (84%). Mp 89.5-90 °C (lit,[7)] 90-91 °C).

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