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Catalytic Sandmeyer cyanation as a synthetic pathway to aryl nitriles

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Abstract

Aryl nitriles ArCN were obtained by the Cu(I)/Cu(II) catalysed reactions of aryl diazonium salts with KCN in good yields.

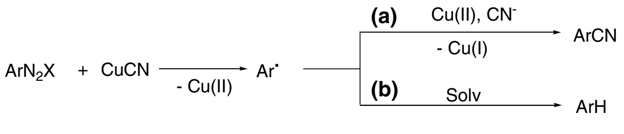
Keywords: Aryl nitrile; Aryldiazonium salts; Catalytic Sandmeyer cyanation; Copper(I) catalyst

Aryl nitriles are important class of organic compounds widely used in organic synthesis and in a production of pharmaceuticals, herbicides and dyes. The general ways to these compounds in a laboratory, until recently, were Rosenmund–von Braun reaction of ArHal with CuCN [1] and Sandmeyer reaction of ArN_2X with CuCN [2]. The first reaction is known in a catalytic version with CuI as a catalyst but it needs a huge amount of rather expensive ligand [3]. More recently, Ni- and Pd-catalysed reactions of ArHal with MCN ($M = K$, Na, Zn, $SiMe_3$) were developed which allow to perform a cyanation even of ArCl using $Pd(OAc)_2$-dppe system [4–6].

In this paper, we report for the first time the catalytic version of Sandmeyer reaction. The reaction of $p\text{-}FC_6H_4N_2BF_4$ with KCN catalysed by 10 mol% CuCN/phen in the presence of a phase transfer cocatalyst was chosen for the search of optimal conditions. The mechanism of Sandmeyer reaction proposed by Kochi [7] and supported by a subsequent study [8], involves two steps with a formation of aryl radicals on the first step.

The implementation of catalytic version of the reaction was hindered through a competition of two reactions (Scheme 1) of aryl radical: oxidation by Cu(II) with a formation of ArCN (**a**) and hydrogen abstraction from a molecule of solvent leading to arene (**b**). Formation of a variety of $Cu(CN)_n^{(n-1)}$ and $Cu(CN)_n^{(n-2)}$ complexes in the Cu(I)–Cu(II)–CN^- system with the ratio depending on the concentration of CN^- and with different reactivity [9] can cause further problems. Moreover, a noncatalytic formation of arylazocyanide **3** can take place (Scheme 2).

Varying the reaction conditions (Table 1) we have showed that the highest ratio of [ArCN]/[ArH] is observed in polar aprotic solvents such as MeCN or DMSO. Addition of crown ethers gives better results than the addition of R_4NX (Table 1, entries 3, 4, 10 vs 1, 2, 9). The nature of crown ether does not affect the



Scheme 1.

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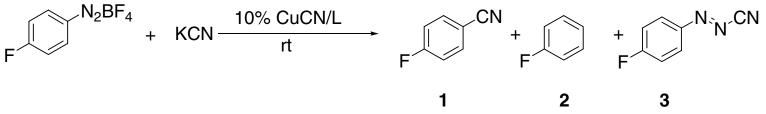
yield and the ratio of products (Table 1, entries 3, 4). The highest yield of *p*-fluorobenzonitrile **1** under these conditions is 61% (Table 1, entry 3). In nonpolar solvents such as benzene or CCl_4 the major product is arylazocyanide **3** due to a low solubility of Cu(I) catalyst (Table 1, entries 9–11).

Yield of nitrile **1** was raised up to 82% when $Cu(BF_4)_2$ was used as a co-catalyst (Table 1, entry 13). It should be noted, that this effect not due to increase of a catalyst concentration because a usage of 20% CuCN/phen leads only to a slight increase of the yield of the nitrile **1** (Table 1, entry 12). Presumably, the addition of $Cu(BF_4)_2$ accelerates the step (a). We used these conditions in the reactions of ArN_2BF_4 (3) with electron-withdrawing and electron-donating groups (Table 2) (see Scheme 3).

The reactions with diazonium salts with electron-withdrawing groups lead to formation of a corresponding nitrile in a high yield (Table 2, entries 2, 4, 7). The yield was lower for the compounds containing electron-donating groups (Table 2, entries 5, 6). It should be noted that, in the number of cases, aryldiazonium salts bearing electron-donating groups cannot be in-



Scheme 2.

Table 1
Dependence of a yield and a ratio of products of the reaction of *p*-$FC_6H_4N_2BF_4$ with KCN[a] catalysed by CuCN/phen on reaction conditions

N	Phase transfer catalyst	Solvent	L	Time (min)	Conversion (%)[b]	Yield (%)[b]		
						1	2	3
1	Et_4NBr	CH_3CN	Phen[c]	60	80	40	28	–
2	Et_3BnNCl	CH_3CN	Phen	30	100	51	34	–
3	Dibenzo-18-crown-6	CH_3CN	Phen	20	100	61	32	–
4	Dicyclohexyl-18-crown-6	CH_3CN	Phen	20	100	60	31	–
5	Dibenzo-18-crown-6	CH_3CN	–	20	100	30	65	–
6	Dibenzo-18-crown-6	DMSO	Phen	10	100	50	31	–
7	–	DMSO	Phen	10	100	52	26	–
8	–	DMSO	–	10	100	50	45	–
9	Et_3BnNCl	C_6H_6	Phen	240	100	–	–	54
10	Dibenzo-18-crown-6	C_6H_6	Phen	240	100	24	–	42
11	Dibenzo-18-crown-6	CCl_4	Phen	240	100	9	–	62
12[d]	Dibenzo-18-crown-6	CH_3CN	Phen	20	100	65	29	–
13[e]	Dibenzo-18-crown-6	CH_3CN	Phen	120	100	82	14	–

[a] Reaction conditions: 1.0 mmol *p*-$FC_6H_4N_2BF_4$, 1.5 mmol KCN, 10% mol CuCN/phen, 10% mol phase transfer catalyst, 4 ml of solvent, room temperature, 20 min.

[b] ^{19}F NMR data.

[c] 1,10-phenantroline.

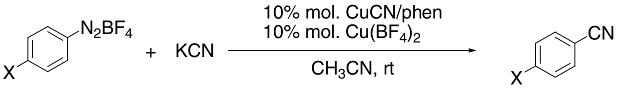
[d] 20% CuCN/phen.

[e] In the presence of 10% $Cu(BF_4)_2$.

Table 2
The reaction of ArN_2BF_4 with KCN in acetonitrile catalysed by CuCN/phen/$Cu(BF_4)_2$ [11]

N	ArN_2BF_4	ArCN	Yield[a] (%)
1	PhN_2BF_4	PhCN	72
2	4-$NO_2C_6H_4N_2BF_4$	4-$NO_2C_6H_4CN$	93
3	4-$FC_6H_4N_2BF_4$	4-FC_6H_4CN	79
4	4-$AcC_6H_4N_2BF_4$	4-AcC_6H_4CN	88
5	4-$MeC_6H_4N_2BF_4$	4-MeC_6H_4CN	66
6	4-$MeOC_6H_4N_2BF_4$	4-$MeOC_6H_4CN$	52
7	3-Me-4-$BrC_6H_4N_2BF_4$	3-Me-4-BrC_6H_4CN	74

[a] Isolated yield.



Scheme 3.

volved in such reactions even with stoichiometric amounts of copper salt [10]. However, the influence of the nature of substituent on the ratio and the yield of ArCN/ArH requires further investigations.

In conclusion, we accomplished the catalytic version of Sandmeyer reaction for a number of aryl diazonium salts with a good yield of corresponding aryl nitriles. This result is of a particular interest for contemporary studies in catalytic organic synthesis that tend to replace the expensive Pd with Cu in Ullman-type reactions of formation of carbon–carbon and carbon–heteroatom bonds.

References

[1] (a) K.W. Rosenmund, E. Struck, Ber. 52 (1919) 1749;
(b) J. von Braun, G. Manz, Ann. 488 (1931) 111.

[2] (a) T. Sandmeyer, Berichte 17 (1884) 1633;
(b) T. Sandmeyer, Ber. 23 (1890) 1880.

[3] (a) W.R.H. Hurtley, J. Chem. Soc. (1929) 1870;
(b) J.X. Wu, B. Beck, R.X. Ren, Tetrahedron Lett. 43 (2002) 387.

[4] (a) For Ni-catalyzed cyanation of aryl halides and triflates, see: L. Cassar, M. Foa, F. Montanari, G.P. Marinelli, J. Organomet. Chem. 173 (1979) 335;
(b) Y. Sakakibara, F. Okuda, A. Shimoyabashi, K. Kirino, M. Sakai, N. Uchino, K. Takagi, Bull. Chem. Soc. Jpn. 61 (1988) 1985;
(c) Y. Sakakibara, Y. Ido, K. Sasaki, M. Sakai, N. Uchino, Bull. Chem. Soc. Jpn. 66 (1993) 2776;
(d) M.R.I. Chambers, D.A. Widdowson, J. Chem. Soc., Perkin Trans. 1 (1989) 1365.

[5] (a) For Pd-catalyzed cyanation of aryl halides and triflates, see: T. Okano, J. Kiji, Y. Toyooka, Chem. Lett. (1998) 425;
(b) P.E. Maligres, M.S. Waters, F. Fleitz, D. Askin, Tetrahedron Lett. 40 (1999) 8193;
(c) M. Alterman, A. Hallberg, J. Org. Chem. 65 (2000) 7984;
(d) K. Takagi, T. Okamoto, Y. Sakakibara, A. Ohno, S. Oka, N. Hayama, Bull. Chem. Soc. Jpn. 49 (1976) 3177;
(e) K. Takagi, K. Sasaki, Y. Sakakibara, Bull. Chem. Soc. Jpn. 64 (1991) 1118;
(f) B.A. Anderson, E.C. Bell, F.O. Ginah, N.K. Harn, L.M. Pagh, J.P. Wepsiec, J. Org. Chem. 63 (1998) 8224;
(g) Y. Anderson, B. Langstrom, J. Chem. Soc., Perkin Trans. 1 (1994) 1395;
(h) Y. Akita, M. Shimazaki, A. Ohta, Synthesis (1981) 974;
(i) T. Okano, M. Iwahara, J. Kiji, Synlett (1998) 243;
(j) U. Drechsler, M. Hanack, Synlett (1998) 1207;
(k) H. Kubota, K.C. Rice, Tetrahedron Lett. 39 (1998) 2907;
(l) T. Erker, S. Nemec, Synthesis 1 (2004) 23.

[6] (a) For metal-catalyzed cyanation of aryl chlorides, see: M. Sundermeyer, A. Zapf, M. Beller, J. Sans, Tetrahedron Lett. 42 (2001) 6707;
(b) F. Jin, P.N. Confalone, Tetrahedron Lett. 41 (2000) 3271;
(c) M. Sundermeyer, A. Zapf, S. Mutyala, W. Baumann, J. Sans, S. Weiss, M. Beller, Chem. Eur. J. 9 (2003) 1828;
(d) Y. Sakakibara, K. Sasaki, F. Okuda, A. Hokimoto, T. Ueda, M. Sakai, K. Takagi, Bull. Chem. Soc. Jpn. 77 (2004) 1013;
(e) R.K. Arvela, N.E. Leadbeater, J. Org. Chem. 63 (2003) 9122.

[7] J.K. Kochi, J. Am. Chem. Soc. 79 (1957) 2942.

[8] (a) C. Galli, J. Chem. Soc., Perkin Trans. 2 (1984) 897;
(b) C. Galli, J. Chem. Soc., Perkin Trans. 2 (1981) 1459;
(c) C. Galli, J. Chem. Soc., Perkin Trans. 2 (1982) 1139.

[9] P. Hanson, S.C. Rowell, A.B. Taylor, P.H. Walton, A.W. Timms, J. Chem. Soc., Perkin Trans. 2 (2002) 1126.

[10] D.J. Adams, A. Goddard, J.H. Clark, D.J. Macquarrie, J. Chem. Soc., Chem. Commun. (2000) 987.

[11] General procedure: 3.0 mmol of ArN_2BF_4, added stepwise to a stirred mixture of 293 mg (4.5 mmol) of KCN, 108 mg (0.3 mmol, 10% mol) dibenzo-18-crown-6, 27 mg (0.3 mmol, 10% mol) CuCN 54 mg (0.3 mmol, 10% mol) phen and 71 mg (0.3 mmol, 10% mol) $Cu(BF_4)_2$ in 10 ml of dry MeCN under inert atmosphere at room temperature. A final mixture was stirred at room temperature during 2 h and poured into 50 ml of ether. A solid was filtered and washed twice by ether. The ether solution was evaporated and a crude mixture was purified by column chromatography on silica (eluent hexane or hexane/EtOAc, 8:2) to afford the corresponding nitrile. ^1H and ^{13}C NMR spectra of all synthesized nitriles are identical to those of the authentic compounds.