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THE CYANATION OF VINYL HALIDES CATALYZED BY NICKEL(0) COMPLEX GENERATED *IN SITU*

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Nickel(0) species generated *in situ* from $NiBr_2(PPh_3)_2$-Zn-PPh_3 catalyzed the formation of unsaturated nitriles from vinyl halides and potassium cyanide. The reaction proceeded under very mild conditions and was stereoselective.

The difficulty of nucleophilic substitution at an sp^2 carbon atom by conventional organic techniques is overcome by using transition metals. Previously we have reported the cyanation of aryl halides by KCN catalyzed by Pd(II)[1] and Ni(0).[2] Now, with the cyanation of vinyl halides, some metal cyanides such as $NaCu(CN)_2$,[3] CuCN,[4] and $K_4Ni_2(CN)_6$[5] are known to be effective for stoichiometric synthesis of cinnamonitriles from β-bromostyrenes. Recently, it was reported that $Pd(PPh_3)_4$-crown ether[6] and $K_3Co(CN)_4$, which was generated *in situ* from $CoCl_2$-KCN-KOH-H_2,[7] catalyzed the cyanation of vinyl halides by KCN. On the other hand, it is stated that $Ni(PPh_3)_3$, though known as an effective catalyst for the cyanation of aryl halides, cannot be used for catalytic transformation of vinyl halides into acrylonitrile, because the nitrile strongly binds to nickel phosphine complex.[8] In this communication we wish to report a new procedure for the preparation of unsaturated nitriles from vinyl halides and KCN by use of a catalytic amount of $NiBr_2(PPh_3)_2$-Zn-PPh_3 which generates Ni(0) phosphine complex *in situ*.

$$>C=C<_{X} + KCN \xrightarrow{NiBr_2(PPh_3)_2\text{-}Zn\text{-}PPh_3} >C=C<_{CN} + KX \qquad X=Br,\ Cl$$

We firstly found that (E)-β-bromostyrene was cyanated catalytically at low temperature in the presence of $NiBr_2(PPh_3)_2$-Zn-PPh_3 (1:3:2 molar ratio) in DMF. The cyanation proceeded fairly smoothly even at 40°C in DMF which was the most suitable solvent and the best yield (96%) was obtained at 50°C; further raising of temperature lowered the yield. Here, it is noted that the Pd catalyst is not active in solvents such as DMF and CH_3CN.[6] DMSO showed a fairly slower reaction rate than that of DMF. HMPA, CH_3CN, THF, and EtOH gave only poor yields compared with DMF and DMSO. With these four solvents, the formation of (E,E)-1,4-diphenyl-1,3-butadiene as a by-product was remarkable, especially in CH_3CN. NaCN also could be used in the place of KCN.

A typical experimental procedure is as follows: To a mixture of $NiBr_2(PPh_3)_2$ (740 mg, 1.0 mmol), Zn powder (200 mg, 3.0 mmol), PPh_3 (520 mg, 2.0 mmol), and KCN (2.2 g, 34 mmol) was added a solution of (E)-β-bromostyrene (5.5 g, 30 mmol) and dibenzyl ether (400 mg, internal standard) in DMF (8 ml). The mixture was degassed

Table 1. Nickel-catalyzed cyanation of vinyl halides[a)]

Vinyl halide (mmol)	$NiBr_2(PPh_3)_2$ mmol	DMF ml	Temp °C	Time h	Conversion %	Selectivity %	E/Z(molar ratio)
(E)-PhCH=CHBr(30)	1	8	50	16	100	96	95/5
(Z)-PhCH=CHBr(30)	1	8	50	8	93	79	12/88
BuC(Br)=CH_2(15)	0.5	4	60	4	64	81	
BuC(Br)=CH_2(15)[b)]	0.5	4	60	16	100	90	
(E)-BuCH=CHCl(10)	0.5	4	50	8	71	70	100/0
(E)-BuCH=CHBr(15)[b)]	0.5	4	50	8	77	90	98/2
(Z)-BuCH=CHBr(15)[b)]	0.5	4	50	16	85	98	14/86
(E)-EtC(Cl)=CHEt(10)	0.5	4	50	4	100	20	100/0
(Z)-EtC(Br)=CHEt(5.4)	0.5	4	50	8	95	28	31/69
-Cl (15)	0.5	4	50	16	99	92	
CH_2=CHBr[c)] (15)	0.5	4	60	4	—	20[d)]	

a) The reactions of vinyl halides with KCN (1.1 equivalent amount) were carried out in the presence of $NiBr_2(PPh_3)_2$-Zn-PPh_3 (1:3:2 molar ratio). b) The vinyl halide was added after keeping the mixture of the catalyst, KCN, and DMF at the specified reaction temperature for 30 min. c) The reaction was carried out in a pressure bottle. d) Yield based on the amount of vinyl bromide used.

by evacuation at -70°C, flushed with nitrogen, and then heated at 50°C for 16 h with vigorous stirring. The reaction mixture was shaken with aq NaCl-CH_2Cl_2. The GLC analysis of the organic layer showed the formation of cinnamonitrile (E:Z=95:5) in 96% yield. The results of the cyanation of several vinyl halides in DMF are summarized in Table 1.

All examined vinyl halides, except for 3-halo-3-hexenes, afforded the corresponding nitriles in fair to excellent yields. Contrary to the Co catalyst,[7)] the Ni catalyst showed high activity also for the cyanation of vinyl halides containing phenyl group without the formation of the corresponding saturated nitriles as by-products. With 3-halo-3-hexenes having an internal double bond, the selectivities were low because of the formation of polymeric materials with nitrile group. However, 1-chloro-1-cyclohexene having a double bond in a ring was cyanated satisfactorily. Vinyl bromide also underwent the catalytic cyanation. In general, the reaction was stereoselective; nitriles being formed with a stereoselectivity higher than 95% for the (E)-isomers and in a range of 69-88% for the (Z)-isomers.

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