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PHASE-TRANSFER CATALYSIS IN THE NICKEL-CATALYZED CYANATION OF ARYL HALIDES

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Summary

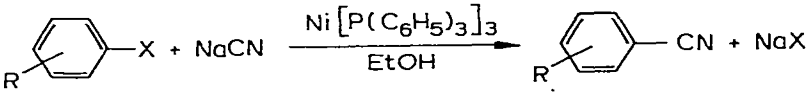
The nickel-catalyzed cyanation of aromatic halides under phase-transfer conditions is reported. Both liquid—liquid and solid—liquid techniques have been used, the former giving better yields and a higher catalyst turnover. The method provides a convenient and versatile route to aromatic nitriles.

Introduction

The possibility of using phase transfer techniques in the homogeneous catalysis with transition metal complexes has been recently shown to have some interesting features [1]. We report below the application of this technique to the transformation of aromatic halides into aromatic nitriles.

Results and discussion

The cyanation of aryl halides has been shown to occur with NaCN in the presence of $Ni[P(C_6H_5)_3]_3$ or σ-arylNi$[P(C_6H_5)_3]_2Cl$ as catalysts under very mild conditions [2].



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Some aspects of the mechanism of this catalytic transformation have been clarified [3]. We have found that the reaction can be conveniently carried out using two-phase systems:

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TABLE 1

RESULTS OF PHASE-TRANSFER CATALYSIS IN NICKEL-CATALYSED CYANATION OF ARYL HALIDES

Substrate (mmol)	Temperature (°C)	Nickel catalyst [a]	$P(C_6H_5)_3$ (mmol)	Phase-transfer catalyst (mmol)	$NaCN/H_2O$ (ml)	KCN (mmol)	Time (h)	Product	Yield [f] (%)
Bromobenzene (67)	55	0.54	—	Aliquat 336 [b] (0.2)	7.6 (33% solution)	—	9	C_6H_5CN	88 (98)
Bromobenzene (67)	55	0.27	0.57	Aliquat 336 (0.1)	7.6 (33% solution)	—	7.5	C_6H_5CN	81 (90)
Bromobenzene (67)	55	0.54	1.1	Teba [c] (0.44)	9 (29% solution)	—	8	C_6H_5CN	85 (94)
Bromobenzene (67)	55	0.54	1.1	Dicyclohexyl-18-crown-6 (0.43)	8.5 (29% solution)	—	9	C_6H_5CN	81 (90)
Bromobenzene (67)	55	0.54	1.1	—	4.5 (29% solution)	—	7	C_6H_5CN	41 (45)
Bromobenzene (67)	45	0.54	0.76	Aliquat 336 (0.2)	9 (29% solution in 0.01 *N* NaOH)	—	9	C_6H_5CN	89 (99)
Bromobenzene (67)	45	0.54	0.76	—	9 (29% solution in 0.01 *N* NaOH)	—	14	C_6H_5CN	88 (98)
Chlorobenzene (25)	45	2 [d]	2.5	Dicyclohexyl-18-crown-6 (0.43)	—	25	17	C_6H_5CN	81 (90)

Chlorobenzene (25)	45	2 [d]	2.5	—	—	25	17	—	—
1-Chloronaphthene (67)	55	0.54	1.1	Aliquat 336 (0.2)	9 (29% solution)	—	12.5	1-Cyanonaphthalene	(96)
2-Chloronaphthene [c] (67)	55	1.1	2.2	Aliquat 336 (0.2)	9 (29% solution)	—	16	2-Cyanonaphthalene	(90)
p-Chlorotoluene (67)	45	0.54	1.1	Aliquat 336 (0.2)	7 (29% solution)	—	10.5	*p*-Cyanotoluene	63 (70)
p-Chlorotoluene (50)	55	2 [d]	2.5	Dicyclohexyl-18-crown-6 (0.42)	—	50	25	*p*-Cyanotoluene	77 (86)
p-$ClC_6H_4COCH_3$ (67)	55	1.1	2.2	Aliquat 336 (0.2)	9 (29% solution)	—	14	*p*-$CNC_6H_4COCH_3$	(96)
m-Dichlorobenzene [e] (34)	55	0.54	1.1	Aliquat 336 (0.2)	4.8 (29% solution)	—	4.5	*m*-Dicyanobenzene *m*-Cyanochlorobenzene	(50) (16)
o,p-Dichlorotoluene [c] (67)	55	1.1	2.2	Aliquat 336 (0.2)	7.2 (29% solution)	—	8	*o,p*-Dicyanotoluene *o*-Chloro-*p*-cyano- and *p*-Chloro-*o*-cyano-toluene	(37) (40)

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[a] *trans*-Chloro(1-naphthyl)bis(triphenylphosphine)nickel unless otherwise mentioned.

[b] Aliquat 336 = tricaprilylmethylammonium chloride.

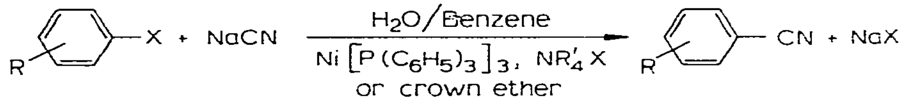
[c] Teba = triethylbenzylammonium chloride.

[d] The catalyst is tris(triphenylphosphine)nickel.

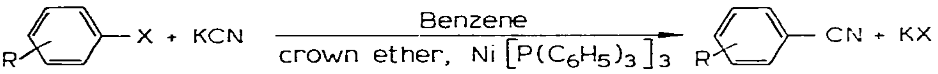
[e] Benzene as solvent (10 ml).

[f] Yields of isolated products are based on introduced aryl halides. Yields in parentheses are determined by GLC.

Method A

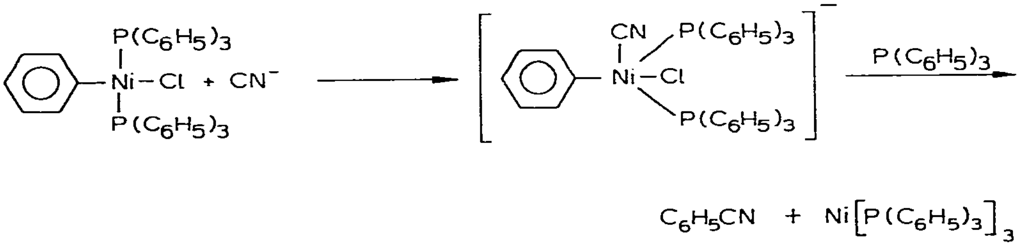


Method B



The main advantages of this new method are the high catalyst turnover and the ease of work-up, which make it very useful in the laboratory scale and for industrial production. In method A the reaction is carried out by mixing water, the organic halide, either alone or dissolved in an aromatic solvent, the ammonium salt or the crown ether, and the nickel complex, and then slowly adding an aqueous solution of NaCN. The rate of addition of NaCN to the reaction mixture is very important since excess of NaCN destroys the catalyst by transforming it into inactive species. The concentration of NaCN in the aqueous phase cannot be much higher than 0.1 mol/l.

In the absence of the nickel catalyst, even with a concentrated NaCN aqueous solution in the presence of the phase transfer catalyst at 100° C, the reaction does not occur for the aryl halides reported in Table 1. In the presence of the nickel catalyst the reaction does occur in the absence of the phase transfer catalyst, but at a slower rate. The reaction can also be carried out very well under alkaline conditions (pH 11.5) (see Table 1), which rules out the possibility that HCN is the species transferred into the organic phase. Then we think that cyanide ion is the reactive species, and that it react with the σ-arylnickel complexes at the interface on an irreversible step, according to equation 2. This assumption is supported by the very high reactivity of the intermediate σ-arylnickel complex towards cyanide ions.



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In the presence of phase-transfer catalyst (ammonium salt or crown ether) it is very likely that the reaction occurs in the organic phase in accordance with the well-known phase transfer catalysis mechanism [4]. In method B controlled addition of cyanide is not necessary but a less satisfactory catalyst turnover is obtained. The presence of the crown ether and of the nickel catalyst is necessary for the reaction. In this case the lipophilic crown ethers are more efficient than the onium salts, as previously reported for solid-liquid phase-transfer catalysis [5].

Table 1 lists several examples of the new method.

Experimental

Materials

All reagents were commercially available and were used without further purification. Solvents were deoxygenated by the vacuum-nitrogen technique. $Ni(PPh_3)_3$ was prepared by treating $Ni(PPh_3)_2(C_2H_4)$ with excess of phosphine [6]; *trans*-chloro(1-naphthyl)bis(triphenylphosphine)nickel was prepared as previously reported [3].

Gas chromatography

Samples were analyzed on 2 m of diethyleneglycol succinate polyester on a Chromosorb column. Known samples of the products were commercially available.

General procedure for synthesis of benzonitrile, Method A

Bromobenzene (10.5 g), *trans*-chloronaphthylbis(triphenylphosphine)nickel (0.2 g), $P(C_6H_5)_3$ (0.15 g), tricaprilylmethylammonium chloride (0.05 g), and H_2O (5 ml) were placed under nitrogen in a 100 ml flask equipped with magnetic stirrer, thermometer and water-cooled condenser. The mixture was kept at 55° C and 155 portions (50 μl each) of a solution of NaCN (4 g) in water (8 ml) were added during 7.5 hours, the additions being made every 2—6 minutes as the colour of the organic phase became red. For the work-up the mixture was added to aqueous HCl and the organic material was extracted with diethyl ether. Gas-chromatographic analysis showed that there had been 90% conversion to the benzonitrile. Distillation of the ether extract gave bromobenzene (1 g) and benzonitrile (5.3 g). The yield was 90% based on unrecovered bromide.

General procedure for synthesis of p-toluonitrile, Method B

p-Chlorotoluene (6.3 g), $Ni[P(C_6H_5)_3]_3$ (1.9 g), $P(C_6H_5)_3$ (0.65 g), KCN (1.6 g) and dicyclohexyl-18-crown-6 (0.1 g), were placed under nitrogen in a 20 ml flask equipped with magnetic stirrer, thermometer and water cooled condenser. The mixture was warmed to 45° C and stirred for 25 h. Aqueous hydrochloric acid was then poured in and the product extracted with diethyl ether. The gas chromatographic analysis showed that there has been 86% conversion into *p*-toluonitrile. Distillation of ether extract gave *p*-chlorotoluene (0.7 g) and *p*-toluonitrile (4.5 g). The yield was 90% based on unrecovered chloride.

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