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FACILE SYNTHESIS OF ARYL CYANIDES FROM IODIDES CATALYZED BY PALLADIUM TRIPHENYLPHOSPHINE COMPLEX

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Cyanogenation of iodobenzene with potassium cyanide has been found to proceed smoothly in tetrahydrofuran in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0). The reaction involves an intermediate, iodo(phenyl)bis(triphenylphosphine)palladium(II), which acts as a retracing species in the catalytic reaction path.

The oxidative addition of halobenzenes to tetrakis(triphenylphosphine)palladium (0) [1] has been known to give halo(phenyl)bis(triphenylphosphine)palladium(II).[1,2] Displacement of the halogen ligand of this adduct with a nucleophile, followed by a reductive elimination, appears to be of synthetic significance for the nucleophilic substitution of unactivated halobenzenes. We have found a new substitution reaction of iodobenzene with potassium cyanide which is catalyzed by 1. This aromatic cyanogenation is entirely different, in catalyst and conditions, from the recently reported one[3] using palladium(II)acetate in dimethylformamide at high temperature.

For example, in a solution of 0.35 g (0.3 mmol) of 1 and 6.1 g (30 mmol) of iodobenzene dissolved in 30 ml of tetrahydrofuran (THF), 2.3 g (36 mmol) of powdered potassium cyanide was suspended and the mixture was refluxed with stirring under nitrogen for 9 hours. After removing the resulting insoluble potassium iodide, the filtrate was concentrated. The residual liquid was treated with petroleum ether to remove a small amount of insoluble material and subjected to a distillation under reduced pressure to give 2.9 g (93%) of benzonitrile.

$$\mathrm{PhI} + \mathrm{KCN} \xrightarrow[\mathrm{THF}]{\text{cat. } \mathrm{Pd(PPh_3)_4} \quad [1]} \mathrm{PhCN} + \mathrm{KI}$$

By a similar procedure p-iodotoluene was likewise converted into p-cyanotoluene in a yield of 91%.

Increasing the amount of 1 was found to be unfavorable to the yield of benzonitrile. For instance, when 1/5, 1/10 and 1/100 molar amounts of 1 were used, the yields by glc. analysis were 82%, 94% and 98% respectively.

Further the yields were influenced markedly by the solvents used. The results of a number of runs which were carried out using several kinds of solvents under a settled condition are shown in Table 1.

Table 1 The Formation of Benzonitrile from Iodobenzene in Various Solvents

Solvent	Reaction Temp. (°C)	Yield of PhCN (%)
Ether	reflux	0
THF	reflux	82
Diglyme	75	65
Chloroform	reflux	9
Benzene	reflux	14
Anisole	85	20
Dioxane	75	51
DMF	75	43
DMSO	75	53

A mixture of PhI (1.5 mmol), KCN and 1 in 1 : 1.5 : 0.2 molar ratio and the solvent (3 ml) was heated for 8 hours. The yields were determined by glc. analysis using tetralin as an internal standard.

The formation of iodo(phenyl)bis(triphenylphosphine)palladium(II) [2], as the first step of this reaction was confirmed by the isolation of this complex by the reaction of iodobenzene with 1 in THF. This complex 2 was then conceived as the actual catalyst which can retrace in the reaction path. This is supported by the fact that, when a mixture of 2, potassium cyanide, and iodobenzene in 1 : 1 : 1 molar ratio was refluxed with THF, benzonitrile was obtained in 80% yield. Further runs revealed a strong catalytic effect of 2, for instance, with its 1/50 molar amount of 2, benzonitrile was afforded in a yield of 97%. Therefore, at present, the following path can be written.

$$PhI + Pd(PPh_3)_4 \longrightarrow (PPh_3)_2Pd(Ph)I + 2\,PPh_3$$

$$PhI + KCN \xrightarrow[THF]{\text{cat. } (PPh_3)_2Pd(Ph)I \quad [2]} PhCN + KI$$

On the other hand, refluxing a solution of 2 in THF suspended with equimolar amount of potassium cyanide resulted in a precipitation of palladium black. On addition of two molar amount of triphenylphosphine in the above reaction, no formation of 1, but recovery of 2 was resulted. This fact suggests that 1 is not a retracing species in the catalytic reaction path.

Bromobenzene was much less reactive for this cyanogenation. For instance, with 1/50 molar amount of bromo(phenyl)bis(triphenylphsphine)palladium(II), bromobenzene in THF gave benzonitrile only in a poor yield (12%).

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