

THE PALLADIUM(0) CATALYZED SYNTHESIS OF VINYLNITRILES FROM VINYL HALIDES

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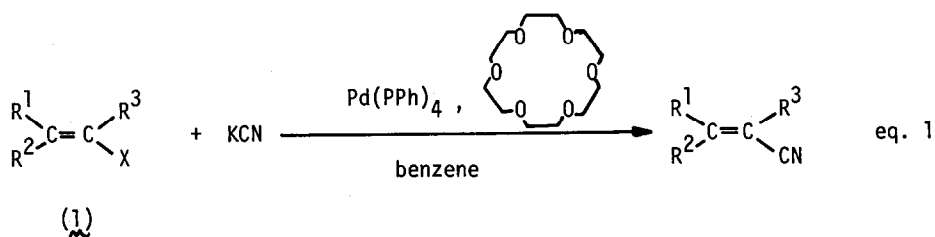
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Since the efficient nickel-catalyzed cross-coupling of vinyl halides with Grignard reagents was found by Kumada et al.¹, various methods for the carbon-carbon bond formation which include palladium catalyzed reactions of vinyl halides with organolithium² and organoaluminum compounds³ have been developed.

We now wish to report a convenient method for conversion of vinyl halides into the corresponding nitriles⁴(eq. 1). Treatment of a variety of vinyl halides with two molar equivalent of potassium cyanide in benzene in the presence of catalytic amount of palladium(0) complex and crown ether results in formation of vinylnitriles, which are hardly accessible, in an excellent yield and in a stereospecific manner. In the absence of crown ether, vinyl halides do not undergo



cyanation under even more forcing conditions employed for aryl halides⁵. The examples cited in Table 1 illustrate the synthesis of nitriles using the indicated reactants and reaction condition.⁶ Benzene is the best solvent⁷ because of facile isolation of both vinylnitriles and crown-ether⁸. For the cyanation with potassium cyanide, 18-crown-6 gave the best yield among the crown ethers examined such as dibenzo-18-crown-6 and Kryptofix 222. The higher temperature than 100° decreases the yield probably because of the formation of clusters⁹.

In a typical case, a mixture of trans- β -bromostyrene (10 mmol), potassium cyanide (20 mmol), tetrakis(triphenylphosphine)palladium(0.3 mmol) and 18-crown-6 (0.76 mmol) in 10 ml dry benzene was stirred at the ambient temperature for 20 min under nitrogen and heated 70-75°C for 2 hr. The resulting mixture was poured into 50 ml of water and 50 ml of ether. The organic layer was separated and concentrated in vacuum. Distillation (bp 132°C/2 mm Hg) gave β -cyanostyrenes in 94 % yield (3130 % yield based upon palladium). The GLC analysis showed that the relative ratio of trans and cis isomers was 97 vs 3.

Table 1. The Cyanation of Vinyl Halides (eq. 1)

Vinyl Halides (1)				Temp °C	Time hr	Yield ^a %	Isomeric Purity %
R ¹	R ²	R ³	X				
C ₆ H ₅	H	H	Br	70-75	2	94 (95) ^b	97 (97) ^b
C ₆ H ₅	H	H	Cl	95-100	15	84	97
H	C ₆ H ₅	H	Br	55-60	6	94	97
C ₄ H ₉	H	H	Br	100	12	96 ^c	99
H	C ₄ H ₉	H	Br	100	12	98 ^c	99
C ₆ H ₅	CH ₃	H	Br	90-95	10	93	92
C ₆ H ₅	C ₆ H ₅	H	Br	90-95	5	98	-
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	Br	90-95	15	85	-

a) Yields are of isolated products. b) NaCN and 15-crown-5 were used. c) GLC yields.

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- 4) A possibility of a stoichiometric cyanation was briefly reported, see E. J. Corey and L. S. Kcgedus, J. Am. Chem. Soc., **91**, 1233 (1969).
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- 6) Reaction products were identified by IR, NMR, and Mass spectra and elemental analyses and, for known compounds, comparison with authentic samples.
- 7) Pyridine also gave high yields; however, vinyl halides are unreactive in a solvent such as THF DMF, acetonitrile, acetone, alcohols.
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