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A Simple and Regioselective Conversion of Terminal Acetylene into 2-Substituted Acrylonitrile

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Abstract: Treatment of terminal acetylene with *in situ* generated hydrogen iodide and followed by the reaction with cuprous cyanide provided a simple and regioselective transformation of acetylene into 2-substituted acrylonitrile in fair to good yields.

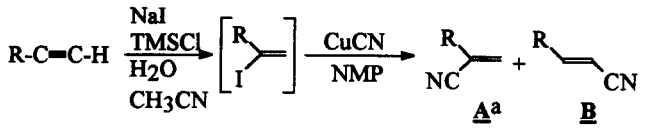
The addition of hydrogen cyanide to alkynes catalyzed by transition metal complexes to form α,β-unsaturated nitriles are potentially useful in organic synthesis.[1-3] Although hydrogen cyanide can be generated *in situ* from acetone cyanohydrin to avoid the use of the poisinous hydrogen cyanide,[4] one or two moles of hydrogen cyanide may add to a triple bond, since the initial product is a Michael-type substrate which may easily undergo the second addition reaction. Moreover, the transition metal catalyzed addition of hydrogen cyanide to phenylacetylene will give 3-substituted acrylonitrile as the major product.[1,2] The use of palladium- and nickel-catalyzed addition of trimethylsilyl cyanide or trimethylgermyl cyanide to acetylenes to form β-cyano alkenyl-silanes or germanes may be an alternative route to form 2-substituted acrylonitriles.[5-8] However, it tends to form cyclic pyrrole derivatives severely limiting its application as an alternative reagent in the approach to the hydrocyanation of alkynes.[6,7] Recently, a highly regioselective synthesis of 2-iodo-1-alkenes from terminal alkynes by using hydrogen iodide, generated *in situ* from TMSCl/NaI/H_2O in acetonitrile, has been reported.[9,10] In addition, cuprous cyanide has been reported to react with aryl halides to yield nitriles in the absence or presence of solvents.[11,12] Based on these works, we now report a simple and one-pot method for the regioselective conversion of terminal acetylenes into 2-substituted acrylonitriles in fair to good yields. As representative terminal alkynes, arylacetylenes, 1-alkynes, and other propargyl ether, sulfide, and ester were chosen. The results are shown in Table I. It is noted that terminal acetylene with various kinds of functional group and aryl bromide (entry 9) may be tolerated under these reaction conditions. The 3-substituted regioisomers were detected only in low yields by ^{1}H-NMR spectral analysis..

In a typical procedure, CH_3CN (5 mL), TMSCl (0.55 g, 5 mmol), H_2O (45 μL, 2.5 mmol) and phenylacetylene (0.51 g, 5 mmol) were sequentially added to a dry flask containing NaI (0.75 g, 5 mmol) under a nitrogen atmosphere at room temperature. After 0.5 h, a hypodermic syringe is used to transfer a solution containing dry CuCN (1.80 g, 20 mmol) and dry *N*-methyl-2-pyrrolidinone (NMP, 25 mL) into the reaction mixture at room temperature. The reaction mixture was then heated under a nitrogen atmosphere at 100°C for another 3 h. After being cooled, the mixture was poured into ether and was stirred vigorously with 40 mL of a solution containing 2.5 g of ferric chloride and 4.5 mL of 3 M HCl to remove cuprous ion complexes with the

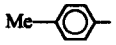
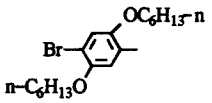
nitrile group. The organic extract was washed with brine to remove the remaining NMP, dried ($MgSO_4$), concentrated, and chromatography (hexanes/ether = 4/1) to give 0.50 g (78% yield) of 2-phenyl acrylonitrile.

Thus, we have developed a simple and one-pot conversion of terminal acetylene into 2-substituted acrylonitrile. The application of 2-substituted acrylonitriles in the preparation of poly(phenylene-vinylene) with electroluminescent property is under investigation in our laboratory.

Table I. Regioselective One-Pot Conversion of Terminal Acetylene into 2-Substituted Acrylonitrile.



A[a] B

Entry	R =	Iso. Yield (%)	Ratio of A:B[b]
1	Ph-	78	99:1
2	Me- 	63	98:2
3	Ph-CO_2-CH_2-	58	98:2
4	*n*-C_5H_{11}-	61	92:8
5	*n*-C_6H_{13}-	69	94:6
6	*n*-C_8H_{17}-	72	97:3
7	Ph-O-CH_2-	52	97:3
8	Ph-S-CH_2-	47	97:3
9		72	98:2

[a] All compounds have been fully characterized by ^1H- and ^{13}C-NMR, IR, and MS spectroscopy. [b] Based on crude ^1H-NMR spectral analysis.

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