SUPPORTING INFORMATION

Facile and Highly Selective Conversion of Nitriles to Amides *via* Indirect Acid-Catalyzed Hydration using TFA or AcOH-H₂SO₄

Jarugu Narasimha Moorthy,* and Nidhi Singhal

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India.

SYNOPSIS TOC:

Both aliphatic and aromatic nitriles are conveniently and selectively converted in a single step, via an indirect acid-catalyzed hydration, into the corresponding amides in 1-8 h using TFA-H₂SO₄ mixture as a reagent system. While the same reagent did not work for the sterically hindered nitriles such as mesitonitrile, the transformation could be accomplished by changing TFA to AcOH at higher temperatures (> 90 °C).

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¹H NMR and ¹³C NMR spectra of 2,5-dimethylterephthalamide, 1,1'-biphenyl-4,4'-dicarboxamide, spirobifluorene-tetraamide, and 2,3,5,6-tetramethylterephthalamide

S2-S9

1,1'-Biphenyl-4,4'-dicarboxamide. Yield 81%, mp > 250 °C; IR (KBr) cm^{-1} 1404, 1615, 1654, 3175, 3378; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.41 (s, 2H), 7.81 (d, $J = 8.0$ Hz, 4H), 7.98 (d, $J = 8.0$ Hz, 4H), 8.04 (s, 2H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) 126.7, 128.2, 133.6, 141.8, 168.5.

Spirobifluorenetetraamide. Yield 77%, mp > 280 °C; IR (KBr) cm^{-1} 1389, 1608, 1658, 3199, 3353; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.16 (s, 4H), 7.27 (s, 4H), 7.91 (s, 4H), 8.03 (d, $J = 8.0$ Hz, 4H), 8.21 (d, $J = 8.0$ Hz, 4H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) 65.2, 121.2, 122.8, 128.0, 134.3, 143.4, 148.2, 167.0.

2,3,5,6-Tetramethylterephthalamide. The solution of 2,3,5,6-tetramethylterephthalonitrile (5.0 mmol) in 8 mL of $\text{AcOH-H}_2\text{SO}_4$ (2:1, v/v) mixture was heated at reflux (120 °C). The progress of the reaction was monitored by TLC analysis. After completion of the reaction (1.5 h), the reaction mixture was poured into ice-cold water. The product precipitated out was filtered to obtain the amide in 90% yield as a colorless powdery material, mp > 280 °C; IR (KBr) cm^{-1} 1437, 1657, 3167, 3374; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 2.11 (s, 12H), 7.47 (s, 2H), 7.70 (s, 2H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) 16.3, 128.7, 139.1, 172.0.

2,5-Dimethylterephthalamide

NS443A-1H

NS472AA-13C

1,1'-Biphenyl-(4,4')-dicarboxamide

1,1'-Biphenyl-(4,4')-dicarboxamide

NS471A-13C

Spirobifluorenetetraamide

Spirobifluorenetetraamide

2,3,5,6-Tetramethylterephthalamide

NS476A-1H

2,3,5,6-Tetramethylterephthalamide