One-Pot Tandem Reactions with a Bifunctional Solid Catalyst

**Significance:** A mesoporous silica catalyst 3 bearing both Brønsted base and acid groups was prepared by immobilization of 3-aminopropyltriethoxysilane [(EtO)3Si(CH2)3NH2] and phosphotungstic acid (H3PW12O40) to a mesoporous silica. Catalyst 3 drove the tandem deacetalization–Henry reaction and deacetalization–Knoevenagel reaction of 4 with nitromethane and malononitrile to give trans-1-nitro-2-phenylethylene 5 and benzylidene malononitrile 6 in 92% and 91% yield, respectively.

**Comment:** The acid/base properties were controlled by the ratio and surface concentration of an amino group and phosphotungstate. Catalyst 3 was characterized by XANES (X-ray absorption near-edge structure spectrum), BET, BJH, 31P NMR, 29Si and 13C CP-MAS NMR spectroscopy and GC-MS. Catalyst 3 was recovered by filtration and reused several times without significant loss of catalytic activity (4th use: 5 in 90% isolated yield, 6 in 91% isolated yield).

**Reaction pathway:**

1. Preparation of mesoporous silica catalyst 3:
   - (EtO)3Si(CH2)3NH2 (AP)
   - H3PW12O40 (HWP)
   - mesoporous silica pore diameter = 4.9 nm, surface area = 870 m²g⁻¹

2. Reaction pathway:
   - acid-catalyzed base-catalyzed

3. Selected results:
   - 4 (1 mmol)
   - H2O
   - MeNO2 (10 mL)
   - 50 °C, 12 h
   - tandem deacetalization–Henry reaction
   - >98% conversion, 91% isolated yield

4. H2O
   - MeNO2 (10 mL)
   - 50 °C, 12 h
   - tandem deacetalization–Knoevenagel reaction
   - 98% conversion, 92% isolated yield