Supporting Information

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A New Route to Lactam Precursors from Cycloalkanes: Direct Production of Nitrosocycloalkanes or Cycloalkanone Oximes with tert-Butyl Nitrite Assisted by N-Hydroxyphthalimide

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General Procedures. All starting materials were commercially available and used without further purification. GLC analysis was performed with a flame ionization detector using a 0.2 mm x 25 m capillary column (OV-1). $^1$H- and $^{13}$C-NMR were measured at 270 MHz and 67.5 MHz, respectively, in CD$_3$COOD with Me$_4$Si as the internal standard. LC-MS analysis was performed with Waters ZQ Mass 2000 detector and UV (256 nm) detector using CH$_3$CN / 10M-NH$_4$OAc aq. (2 / 8) eluent.

Fig. 1 shows the LC-MS analysis of the reaction mixture after the reaction of cyclohexane (1a, 4 mmol, 0.5 mL) with tert-butyl nitrite (2, 0.5 mmol) in the presence of NHPI (0.05 mmol) in CH$_3$COOH (0.5 mL) under argon atmosphere at 80 °C for 2 hours (standard conditions). Fig. 2 shows the Mass spectra (ES negative) of the scan between 162 and 221 in the LC-MS analysis in Fig. 1. These results indicates that most of the NHPI catalyst exists in the reaction mixture without decomposition after the reaction. In fact, 80% of the NHPI catalyst used could be recovered from the reaction mixture by the following procedure.

Procedure for Recovery of the NHPI Catalyst. Cyclohexane (1a, 8 mmol, 1 mL) was allowed to react with tert-butyl nitrite (2, 1 mmol) in the presence of NHPI (0.1 mmol) in CH$_3$COOH (1 mL) under argon atmosphere at 80 °C for 2 hours (standard conditions). After the reaction, volatile materials (CH$_3$COOH and 1a unreacted etc.) were removed by rotary evaporation under reduced pressure to give the yellow solid. The solid obtained was filtrated off, washed with diisopropyl ether. The recrystallization from CH$_3$CN gave 0.08 mmol (13 mg) of NHPI.
Fig. 1 The LC-MS analysis of the reaction mixture after the reaction of cyclohexane (1a, 4 mmol, 0.5 mL) with tert-butyl nitrite (2, 0.5 mmol) in the presence of NHPI (0.05 mmol) in CH₃COOH (0.5 mL) under argon atmosphere at 80 ºC for 2 hours (standard conditions).

Fig. 2 The Mass spectra (ES negative) of the scan (162-221) in the LC-MS analysis in Fig. 1.