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Supporting Information

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One-Pot Lactams Synthesis from Cycloalkanes and *tert*-Butyl Nitrite Using *N*-Hydroxyphthalimide (NHPI) as Key Catalyst

Masaharu Hashimoto, Satoshi Sakaguchi and Yasutaka Ishii

Department of Applied Chemistry, Faculty of Engineering & High Technology Research Center, Kansai University, Suita, Osaka 564-8680, Japan.

*To whom correspondence should be addressed. E-mail: ishii@ipcku.kansai-u.ac.jp

General Procedures. All starting materials were commercially available and used without any 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 or 400 MHz and 67.5 or 100 MHz, respectively, in $CDCl_3$ with Me4Si as the internal standard.

Nitrosation of 1a with t-BuONO catalyzed by NHPI: To a solution of **1a** (5 mmol) and *t*-BuONO (1 mmol) in benzene (2 mL) and AcOH (0.5 mL) in a 20-mL Schlenk tube was added NHPI (0.5 mmol). The tube was cooled to liquid nitrogen temperature to freeze the solvent, and degassed in vacuo. The reaction mixture was allowed to stand at room temperature and then to react at 75 °C for 2 h. After the reaction, the NMR analysis was performed. The yield of 2a was estimated from the peak areas based on the internal standard technique using NMR.

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_3COOH (0.5 mL) under argon atmosphere at 80 ºC 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_3COOH (1 mL) under argon atmosphere at 80 ºC for 2 hours (standard conditions). After the reaction, volatile materials (CH_3COOH 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_3CN gave 0.08 mmol (13 mg) of NHPI

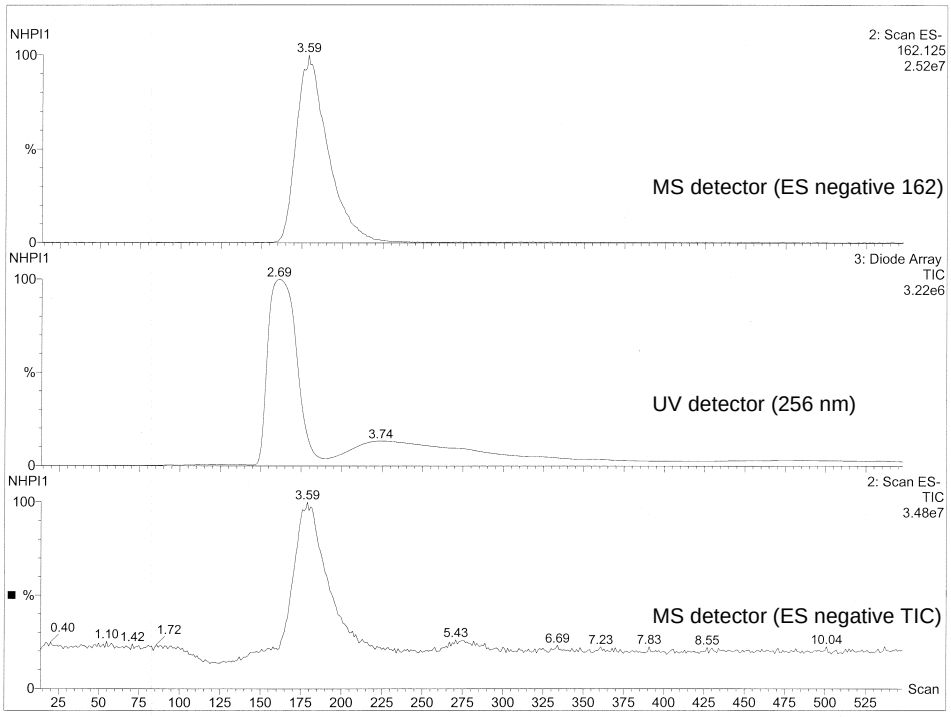

Fig. 1 The LC-MS analysis of the reaction mixture after the reaction of cyclohexane (**1a**, 4 mmol, 0.5 mL) with *tert*-butyl nitrite (**2**, 0.5 mmol) in the presence of NHPI (0.05 mmol) in CH_3COOH (0.5 mL) under argon atmosphere at 80 ºC for 2 hours (standard conditions).

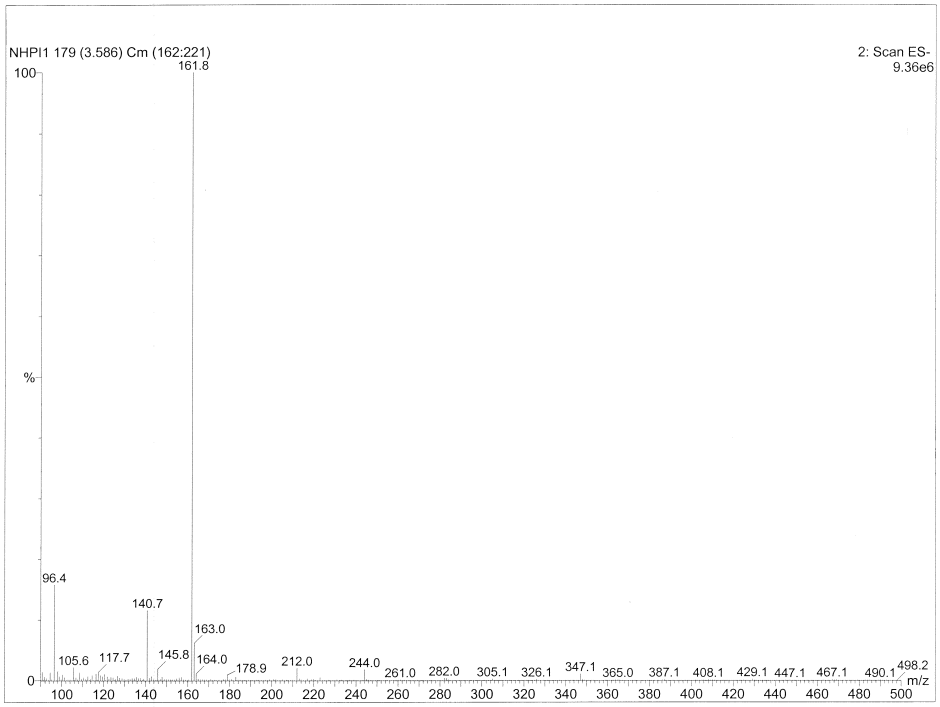

Fig. 2 The Mass spectra (ES negative) of the scan (162-221) in the LC-MS analysis in Fig. 1.

Transformation of 4a to 6a: To a solution of cyanuric chloride (0.005 mmol) in HFP (1 mL) in a

30-mL round-bottom flask was added **4a** (1 mmol). The reaction mixture was allowed to react under refluxing temperature for 2 h. The yield of 6a was estimated from the peak areas based on the internal standard technique using GC.

Preparation of 2,4,6-tris[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]-1,3,5-triazine (8): To a solution of HFIP (10 mL) were added cyanuric chloride (3 mmol), K_2CO_3 (10 mmol), and MS-3A (200 mg). The mixture was stirred at room temperature for 15 h. Removal of solids by filtration and evaporation under reduced pressure gave crude **8** in almost quantitative yield as a white solid: IR(KBr) 1590, 1397, 1289, 1230, 1200 cm^{-1}; MS (*m/z*) 579 (M^+), 560 $(M-F)^+$, 413, 262, 69 (CF_3^+).

Fig. 3 ^{1}H- and ^{13}C-NMR spectra of **8**