

Supporting Information

Tautomerism of α,β -Ethylenic Imines and their Reactivity towards Electrophilic Olefins

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EXPERIMENTAL

General: ¹H and ¹³C NMR spectra were recorded respectively at 200 and 50 MHz. Chemical shifts for hydrogen and carbon resonances are reported in ppm (δ) relative to TMS. Thin-layer chromatographies (TLC) were performed with aluminum plates (0.20 mm) precoated with fluorescent silica gel, using EtOAc/hexane as eluent. Reaction components were then visualized under UV light and dipped in a Dragendorff solution. Silica gel (230-400 mesh) was used for flash chromatography (FC) separations and EtOAc/hexane (% EtOAc given) was the eluent. Gas chromatography-mass spectrometry (GC-MS) was performed with a Hewlett-Packard 5890A GC apparatus (equipped with a 25 m capillary column) linked to a Model 5970 EIMS, at 90 °C for 2 min, then 10 °C/min up to 290 °C. IR spectra were recorded on a Perkin-Elmer IRFT Paragon 1000 apparatus. All extractions were usually followed by water and saturated NaCl aqueous solution washings, MgSO₄ drying, filtration and evaporation.

General Procedures for Ethylenic Imines (**2a-c** and **4**) Formation. Enones **1a-c** and **3** (1 eq.) and benzylamine (3 eq.) were dissolved under an inert atmosphere in anhydrous ether (3 mL/mmol of enone). To the stirred reaction mixture, TiCl₄ (0.5 eq) in solution in anhydrous pentane (1.5 mL/mmol of TiCl₄) was added slowly at 0 °C. After the addition was complete, the reaction mixture was stirred vigorously at room temperature for 4 hours. The resulting precipitate was removed by suction filtration, washed with toluene and the solvent evaporated under reduced pressure yielding the crude imines **2a-c** and **4** which were used without any further purification.

Preparation of Lactams **5** and **6**. Phenyl acrylate (4.53 g, 30.61 mmol) was added to crude imine **2a** (5.01 g) and the reaction mixture was heated at 70 °C under an inert atmosphere for 24 hours in the presence of a trace of hydroquinone. A GC-MS analysis of the reaction mixture revealed the presence of two signals at 16.427 min (lactam **5**, 22 %) and 17.185 min (lactam **6**, 78 %). Then 150 mL of ether and 50 mL of 1 M NaOH were added and the reaction mixture was stirred for 30 min. After ether extraction of the aqueous layer, the combined organic layers were washed with 10 % HCl. An usual work-up followed by a flash chromatography (10 % then 20 % and 30 %) yielded 1.80 g of a mixture of lactams **5** and **6** (28 % overall yield from enone **1a**). Flash chromatography fractions yielded analytical samples of lactams **5** and **6**.

Preparation of Lactam **7**. Phenyl acrylate (0.69 g, 4.66 mmol) was added to crude imine **2c** (0.99 g) and the reaction mixture was heated at 55 °C under an inert atmosphere for 16 hours in the presence of a trace of hydroquinone. A GC-MS analysis of the reaction mixture revealed the presence of a signal at 17.378 min (lactam **7**) besides a trace of unreacted starting imine **2c**. To the reaction mixture, 100 mL of ether and 30 mL of 1 M NaOH were added and the reaction mixture was stirred for 30 min. After ether extraction of the aqueous layer, the combined organic layers were washed with 10 % HCl. An usual work-up followed by a flash chromatography (30 %) gave 0.53 g (43 % overall yield from enone **1c**) of lactam **7**.

Preparation of Lactams **8** and **9**. Phenyl acrylate (1.67 g, 11.28 mmol) was added to crude imine **4** (2.00 g) and the reaction mixture was heated at 65 °C under an inert atmosphere for 24 hours in the presence of a trace of hydroquinone. A GC-MS analysis of the reaction mixture revealed the presence of two signals at 17.738 min (lactam **8**, 35 %) and 18.378 min (lactam **9**, 65 %). Then, 30 mL of ether and 20 mL of 1 M NaOH were added and the reaction mixture was stirred for 1 hour. After ether extraction of the aqueous layer, the combined organic layers were washed with 10 % HCl. An usual work-up followed by a flash chromatography (15 % and 25 %) afforded 1.45 g of a mixture of regioisomers **8** and **9** (58 % overall yield from enone **3**). Flash chromatography fractions yielded analytical samples of lactams **8** and **9**.

Preparation of Lactam **13**. A solution of maleic anhydride (1.10 g, 11.22 mmol) in 10 mL of anhydrous THF was slowly added under an inert atmosphere at - 78 °C to a solution of the crude imine **4** (2.00 g) in 10 mL of anhydrous THF. After the addition was complete, the reaction mixture was stirred at room temperature under an inert atmosphere for 16 hours. Then 10 mL of dry methanol, a trace of 4-(dimethylamino)pyridine and 1,3-dicyclohexylcarbodiimide (2.32 g, 11.24 mmol) were added and the reaction mixture was stirred under an inert atmosphere for 16 hours. A GC-MS analysis of the reaction mixture revealed the presence of a signal at 21.220 min (lactam **13**) besides signals corresponding to 1,3-dicyclohexylurea and unreacted 1,3-dicyclohexylcarbodiimide. After removal of the solvent under reduced pressure, addition of 30 mL of 10 % HCl to the resulting residue and CH₂Cl₂ extraction followed by the usual work-up, a flash chromatography (20 % and 30 %) yielded 0.98 g (32 % overall yield from enone **3**) of lactam **13**.