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Fast Oxidation of Lactams to Cyclic Imides Using Microwave Irradiation

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Since polar reactants can adsorb microwave irradiation, chemists can utilize the microwave oven for some organic reactions. In this paper, we report a rapid conversion of lactams to cyclic imides using peracetic acid (CH_3-CO_3H) and manganic chloride ($MnCl_2$) in ethyl acetate (CH_3-COOEt) as a solvent and under microwave irradiation (90 W, 5 min) in good yields.

Key Words: Oxidation, Lactams, Cyclic imides, Microwave irradiation, Peracetic acid

Introduction

Lactams, which need not be N-substituted, can be converted to cyclic imides by oxidation with a hydroperoxide or peracid and a transition metal salt[1,2]. The metal ion catalyzed decomposition of organic peroxyacids has long been known. The oxidation of amides to imides with air and transition metal ions has been reported, although the yields are quite low and the oxidation reactions are very long[3−15].

Lactams, without any N-substitution, can be converted to cyclic imides by oxidation with a peracid such as peracetic acid and a transition metal salt such as manganic chloride. The use of supported reagents in this reaction has attracted interest, because of improved selectivity and reactivity and the associated ease of manipulation. The solvent of this reaction is ethyl acetate. Microwave irradiation for one-pot synthesis of maleimides and phthalimides has been reported[16]. Microwave irradiation of the reaction vessel containing reactants improved the velocity, yield and selectivity of this reaction. No details are given about the by-products and only the final products are considered.

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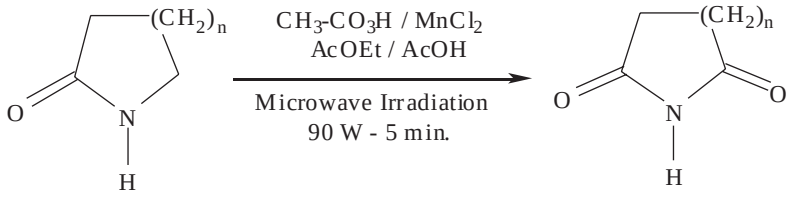


n = 1 : 2-Pyrolidinone (**1**)	Succinimide (70%) (**4**)
n = 2 : δ-Valerolactam (**2**)	Glutarimide (85%) (**5**)
n = 3 : ε-Caprolactam (**3**)	Adipimide (85%) (**6**)

With regard to the useful application of microwaves in organic synthesis and the popularization of using industrial microwaves, the reactions mentioned above can be carried out on an industrial scale and greater[17].

Cyclic imides are very useful materials in chemistry and the chemical industry. Some of these compounds such as succinimide are used as growth stimulants for plants and/or as starting materials for the synthesis of heterocycles[18].

Experiment

The simple cyclic imides synthesized (**4-6**) are known compounds and their physical data and infrared and ^{1}H-NMR spectra were essentially identical with those of authentic samples[19−21]. The FT-IR spectra were recorded as KBr pellets on a Shimadzu FT-IR 8000 spectrometer. ^{1}H-NMR spectra were determined on a 300 MHz Brüker spectrometer. All the reagents were purchased from Fluka.

It should be noted that a limited amount of solvent is required for this experiment. Therefore only a small quality of vapor is evolved during irradiation. The microwave oven was a Moulinex-245W.

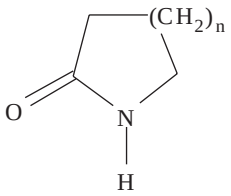
Caution

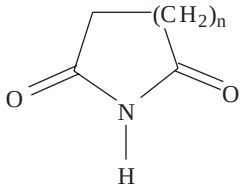
All domestic microwave ovens are equipped with fans that can efficiently remove vapors from the microwave cavity. For safety reasons all of the experiments should be performed in an efficient hood in order to avoid contact with vapors.

Typical procedure

A typical reaction procedure involved solutions of $MnCl_2$in ethyl acetate (10^{-5} mol in 10 mL of CH_3COOEt) and 2.85 g (0.025 mol) of ε-caprolactam in 20 mL of ethyl acetate. The solutions of $MnCl_2$ and ε-caprolactam (**3**) were mixed in an Erlenmeyer flask (100 mL), and cooled to 0-5 °C. Peracetic acid (15 g, 0.045 mol, 25% solution in ethyl acetate) was added dropwise (with caution, slowly), maintaining a temperature of 0-5 °C. After the addition of peracetic acid was completed, the reaction mixture was placed in a microwave oven and irradiated at 90 W power for 5 min. The solvent was removed under reduced pressure. Recrystallization from 2-propanol gave white crystals of adipimide **6** (85%, 2.7 g) (see Table).

Table. Selected data of **1-6** (FT-IR in cm^{-1}, ^{1}H-NMR in ppm and melting point in °C. All solvents in ^{1}H-NMR were ^{6}d-DMSO).





n = 1 : 2-Pyrolidinone (**1**)	Succinimide (70%) (**4**)
m.p. = 23-25	m.p. = 125-127
^{1}H-NMR: 1.5-2.5(m), 2.2-2.5 (m) 3.2-3.5 (m), 7.6 (Broad band).	^{1}H-NMR: 2.6 (s, A_4 sys.)
FT-IR: 3200 (N-H), 2800-2950 (C-H), 1660 (C=O), 1300-1480, 1260	FT-IR: 3150 (N-H), 2850-2920 (C-H), 1710,1770 (C=O),1350-1450.
n = 2 : δ-Valerolactam (**2**)	Glutarimide (85%) (**5**)
m.p. = 35-39	m.p. = 154-157
^{1}H-NMR: 1.5-2.5(m), 2.2-2.5 (m) 3.2-3.5 (m), 7.6 (Broad band).	^{1}H-NMR: 1.5-2.0(m), 2.3-2.5 (t)
FT-IR: 3200 (N-H), 2800-2950 (C-H), 1660 (C=O), 1300-1480, 1260	FT-IR : 3200 (N-H), 2900-2950 (C-H) 1680,1710 (C=O), 1380-1450.
n = 3 : ε-Caprolactam (**3**)	Adipimide (85%) (**6**)
m.p. = 68-92	m.p. = 167-172
^{1}H-NMR: 1.5-2.1(m), 2.3-2.7 (m) 3.0-3.5 (m), 7.7 (Broad band).	^{1}H-NMR: 1.5-1.7(m), 2.1-2.3 (t)
FT-IR: 3280 (N-H), 2800-2900 (C-H), 1660 (C=O), 1300-1450, 1220	FT-IR : 3280 (N-H), 2900-2950 (C-H) 1650, 1712 (C=O),1360-1455.

Conclusion

The reaction described here represents a simple and fast procedure to synthesize cyclic imides **4-6** from lactams **3-5**. Comparison of this procedure with other methods confirms the ease and rapidity of this method for the synthesis of cyclic imides (without N-substitution) from lactams.

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