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One-Pot Microwave Assisted Solid Phase Synthesis of Cyclic Imides from Cyclic Anhydrides

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In this study, a simple one-pot microwave assisted solid phase synthesis of cyclic imides from cyclic anhydrides by the use of KBr as solid phase, urea and thiourea as reagents in good yield are reported.

Key Words: Microwave irradiation, One-pot synthesis, Solid phase, Cyclic imides, Anhydrides.

INTRODUCTION

The microwave synthesis is utilized as a powerful and effective technique to promote a group of chemical reactions. Among the microwave class reactions, the microwave-assisted solid phase synthesis has emerged as a powerful variety form[1-6]. Imides having interesting functionality, due to their various presences in the natural products and in the pharmacologically active compounds. There are a few important and effective synthesis of imide derivatives from anhydride compounds[7-10]. Some of this methods were used for synthesis of important compounds such as phthalimide, maleimide and thalidomide by the use of urea and thiourea under microwave irradiation[8,9]. The synthesis of 2,3-dimethylmaleimide in solid phase by the use of urea was reported[10]. Compound **3** was used as a reagent in synthesis of maleimides and as an amino group protecting agent for superoxide dismutase. Some of the maleimides have been prepared by reaction of the appropriate maleic anhydrides with either ammonium acetate or methyl ammonium acetate in boiling acetic acid[11].

Second order amides and lactams, which need not be N-substituted, can be converted to imides by oxidation with a hydrogen peroxide or peracid and a transition metal salt[12,13]. The metal ion catalyzed decomposition organic peroxyacids has been long known. The oxidation of amides to imides with air and transition metal ions have been reported, although the yields are quite low and the time of oxidation reactions is long[14-22].

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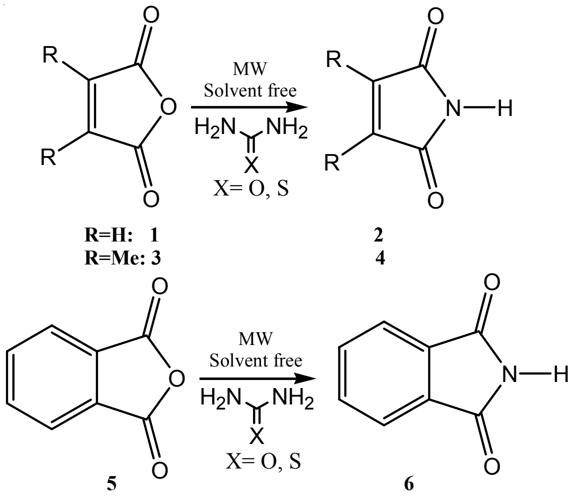

R=H: 1 **2**
R=Me: 3 **4**

5 **6**

The conversion of lactams, without any N-substitution, to cyclic imides by oxidation with an oxidative agent such as peracetic acid or *t*-butyl hydrogen peroxide and a transition metal salt such as manganic II or III salts under irradiation of microwave was reported[23-26].

In this study, we wish to report one-pot microwave assisted solid phase synthesis of cyclic imides **2**, **4** and **6** from cyclic anhydrides **1**, **3** and **5** using urea ($H_2N–CO–NH_2$) and thiourea ($H_2N–CS–NH_2$) in good yield. It is found that the various metallic halides such as $AlCl_3$[27], CuBr[28], $FeCl_3$[29], $BiCl_3$[30], $ZnCl_2$[31], $InCl_3$[32] and $TaCl_3$[33] have been apparently safely employed in microwave-assisted synthetic reactions[34]. For this study, KBr was used as solid phase for the reactions. There is no by-products and only final products have been considered. Good purification allows excellent products recovery.

EXPERIMENTAL

The simple imides synthesized (**2**, **4** and **6**) in present studies, are known compounds and those physical data, infrared and ^{1}H NMR spectra were essentially identical with those of authentic samples[35,36]. The FT-IR spectra was recorded as KBr pellets on a Shimadzu FT-IR 8000 spectrometer. ^{1}H NMR spectra was determined on a 300 MHz Brucker spectrometer.

Typical procedure: As a typical reaction procedure, a mixture of phetalic anhydride **5** (0.05 g, 33.78 mmol), urea (0.025 g, 41.17 mmol, 1 equiv.) and KBr (1.0 g) are ground by pestle and mortar to give a uniform mixture. The mixture was transferred to a dried heavy wall Pyrex tube. The tube was sealed and then exposed to microwave oven. The condition of microwave-irradiation was shown in Table-1. Boiling water (5-8 mL) is then added. Then was added $CHCl_3$ to the cooled mixture (10-15 mL). The combined organic layers are washed (NaCl sat. aq., 10 cm^3). After separation the organic layer was dried with $MgSO_4$. The solvent was evaporated under vacuum. The product as a white powder was remained. Purification by dry column vacuum chromatography[13] (eluting with 0-100 % EtOAc in 40-60 petroleum ether with increments of 10 %) gives phetalimide as a colourless crystalline solid **6** (0.038 g, 75 %) (Table-1).

TABLE-1
ANALYTICAL DATA AND MICROWAVE IRRADIATION CONDITIONS, FT-IR SPECTRUMS WERE RECORDED BY THE USE OF KBr PELLET, SOLVENT OF THE ^{1}H-NMR RECORD WAS $CDCl_3$

Compd. / m.f. / m.p. (ºC)	IR (cm^{-1})*	^{1}H NMR (δ ppm)*	Mass (m/z)*	CH_3-CO-NH_2 MW		Yield (%)	CH_3-CS-NH_2 MW		Yield (%)
				Time (min)	Power (W)		Time (min)	Power (W)	
2 $C_4H_3NO_2$ 91-93	3260, 3060, 1768, 1712, 1670, 1100-1350	10.5 (NH, br.) 6.7 (s, 2H, C=C)	97 (100), 98 (6), 69, 54	3	600	70	2	600	79
4 $C_6H_7NO_2$ 111-114	3253, 2950, 2880, 1774, 1710,1677, 1100-1350	10.2 (NH, br.), 1.9 (s, 2CH_3)	125 (100), 126 (4), 97, 82, 54	4	600	50	3	600	53
6 $C_8H_5NO_2$ 180-183	3266, 3100-3050, 1770, 1710, 1600, 1488, 1100-1350	10.5 (NH, br.) 7.9 (d, 2H), 7.4 (d, 2H)	147 (100), 148 (4), 104, 76, 66, 50	3	600	75	2	600	73

*See references.

Conclusion

The simple one-pot microwave assisted solid phase synthesis of cyclic imides from cyclic anhydrides described here to synthesize imides **2**, **4** and **6** from anhydrides **1**, **3** and **5**, respectively. Comparison this procedure with the other methods confirm the facility and rapidity of this method for synthesis of the imides from the appropriate anhydrides.

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