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NOTE

One-pot Synthesis of Imides from Anhydrides in Solid Phase

AVAT (ARMAN) TAHERPOUR*†, ARAZ ABRAMIAN†
AND HANIYEH KARDANYAZD†
Faculty of Science, Islamic Azad University, Sanandaj Branch
P. O. Box 618, Sanandaj, Iran
E-mail: avat_1@yahoo.co.uk

In this study a simple synthesis of imides by the use of anhydrides and thioacetamide (CH_3-CS-NH_2) in solid phase is reported.

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

Imides are interesting functionality, due to their varied presence in the natural products and in the pharmacologically active compounds. Second order amides (with methylene —CH_2— group adjacent to —NH— function of amide bond) and lactams, which need not be N-substituted, can be converted to imides by oxidation with a hydroperoxide or peracid and a transition metal salt[1, 2]. The metal ion catalyzed decomposition of organic peroxy acids has been long known. The oxidation of amides to imides with air and transition metal ions has been reported, although the yields are quite low and the time of oxidation reactions would be very long[3–16].

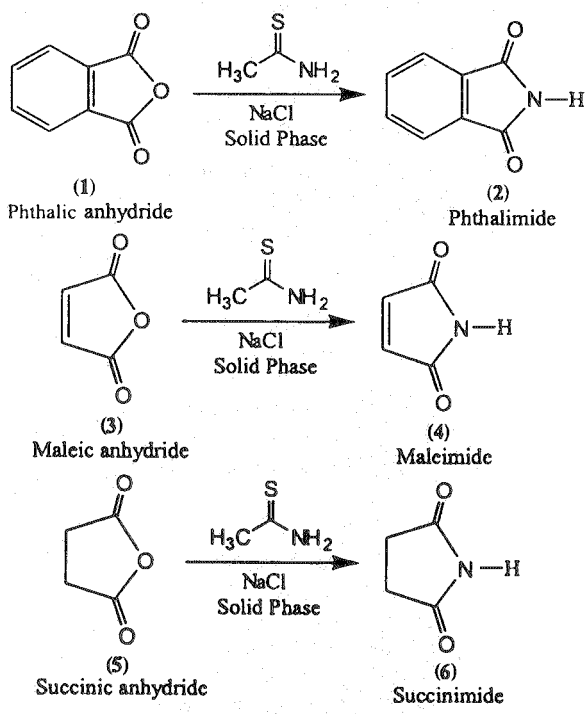
The conversion of lactams, without any N-substitution, to cyclic imides by oxidation with an oxidative agent such as peracetic acid or *t*-butyl hydroperoxide and a transition metal salt such as Mn(II) or Mn(III) salts under irradiation of microwave was reported[17,18].

There are a few important and nice syntheses of imide derivatives from anhydride compounds[19–22]. Some of these methods were used for synthesis of important compounds such as phthalimide, glutarimide and thalidomide (antiangiogenesis-active in multiple myeloma) by the use of urea and thiourea under microwave irradiation[20, 21]. The synthesis of 2,3-dimethyl maleimide in solid phase by the use of urea was reported[22].

In this study, one-pot conversion of anhydrides **1**, **3** and **5** to imides **2**, **4** and **6**, respectively, in solid phase (NaCl) are reported, by the use of thioacetamide (CH_3-CS-NH_2). There is nothing about by-products and only final products have been considered. Good purification allows excellent products recovery.

The simple imides that were synthesized (**2**, **4** and **6**) are known compounds and those physical data, infrared and ^{1}H NMR spectra were essentially identical with those of authentic samples[23–25]. The FTIR spectra were recorded as KBr pellets on a Shimadzu FTIR 8000 spectrometer. ^{1}H NMR spectra were recorded on a 300MHz Brüker spectrometer.

†Chemistry Department, Graduate Faculty, Islamic Azad University, Arak Branch, P.O. Box 38135-567, Arak, Iran.



Selected data of **1–8** (FTIR in cm^{-1}, ^1H NMR in ppm and melting point in °C) are given below. Solvent for all products in ^1H NMR was DMSO-d_6.

Phthalic anhydride (1) : m.p. 131–133°C; ^1H NMR : 8.2 (s, 4H); FTIR: 3050–3130 ν(Ar(C—H), *str.*); 2800–2950 ν(C—H); 1760 and 1852 ν(C=O, sym. and asym.); 1110–1250 ν(C—O, *str.*).

Phthalimide (70%) (2): m.p. 233–238°C; ^1H NMR : 7.78 (s, 4H); 10 (N—H, br); FTIR: 3200 ν(N—H), 3066–3100 ν(Ar(C—H), *str.*); 1690, 1750 ν(CO=O, sym. and asym.); 1055 and 1310 ν(C—N, *str.*).

Maleic anhydride (3): b.p. = 54–56°C; ^1H NMR: 7.2 (s, 2H); FTIR: 3050–3130 ν(=C—H, *str.*); 1753 and 1820 ν(C=O, sym. and asym.); 1120–1280 ν(C—O, *str.*).

Maleimide (75%) (4): m.p. 92–95°C; ^1H NMR: 6.78 (s, 2H); FTIR: 3197 ν(N—H), 3055–3100 ν(=C—H, *str.*); 1670, 1775 ν(C=O sym. and asym.); 1105 and 1295 ν(C—N, *str.*).

Succinic anhydride (5): m.p. 125–127°C; ^1H NMR: 3.0 (s, 4H); FTIR: 2800–2950 ν(C—H); 1780 and 1860 ν(C=O, sym. and asym.); 1050–1280 ν(C—O, *str.*).

Succinimide (60%) (6): m.p. 119–121°C; ^1H NMR : 2.6 (s, A_4 sys.); FTIR: 3150 ν(N—H), 2850–2920 ν(C—H), 1710, 1770 ν(C=O); 1195 and 1300 ν(C—N, *str.*).

For safety reasons, all the experiments should be performed in an efficient hood in order to avoid the contact of vapours. It should be noted that a limited amount of solvent is required for this experiment.

Typical procedure: As a typical reaction procedure, maleic anhydride (1.6 g, 16.7 mmol), thioacetamide (1.4 g, 18.6 mmol) and sodium chloride (1.25 g, 21.3 mmol) were mixed. For achieving a uniform mixture the materials were pulverized by pestle and mortar. The powder was heated by a heater with stirring at 100°C in a three-necked flask. The flask was fitted with an air condenser. Heating was

continued for 15 min. An orange-yellow mixture was obtained. Then, almost 40 mL boiling water was added to the flask and the mixture after mixing with water was cooled. Ethyl acetate (50 mL) in two or three times was added to the mixture. Almost 20 mL saturated NaCl (aq.) solvent was added. The ethyl acetate layer was separated and dried with $CaCl_2$. The solvent was evaporated by a rotary evaporator. Residue was an orange-yellow solid. By a plate of silica gel (TLC) and ethyl acetate-petroleum ether, the layer of the product was separated. Then, the silica gel layer (product) was scraped. Toluene (20 mL) was added and the silica gel separated. Maleimide as a colourless crystalline solid (1.2 g, 75%) was obtained by evaporation of the solvent.

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