



## Reaction of Phthalic Anhydride and Ethylenediamine

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The reactions of phthalic anhydride and ethylenediamine were performed and the effect of solvents was investigated with a wide range of solvents in two groups (either containing H<sub>2</sub>O or without H<sub>2</sub>O). In H<sub>2</sub>O-containing media, phthalic ethylene ammonium salt was obtained with high yields; when the reaction was carried out in non-aqueous solvents, N,N'-diphthaloyl-1,2-ethylenediamine was formed at lower reaction rates and yields. All products were characterised and confirmed by a combination of analytical techniques. The use of water as solvent with a reasonably high product yield (80 %) suggests a green route for the synthesis of phthalic ethylene ammonium salts.

**Key Words:** Phthalic anhydride, Ethylenediamine, Phthalic ethylene ammonium salt, N,N'-Diphthaloyl-1,2-ethylenediamine, Structural characterization.

### INTRODUCTION

Imide compounds, which are commonly synthesized *via* the reaction of phthalic anhydride and ethylenediamine, are important industrial raw materials for the production of polyurethane foam plastics and white flame retardants. However, the products of the reaction can be complex mainly due to the fact that both phthalic anhydride and ethylenediamine, the typical representatives of dicarboxylic anhydride and aromatic (or aliphatic) diamine, possess two functional groups which could result in a number of products produced from the reactions of these two reactants. In addition, the variation of reaction conditions such as solvent composition, reaction temperature and heating method can also significantly affect the reaction process. Thus, there remain challenges to conduct the reaction in terms of reaction rate, product yield and selectivity. Consequently, much effort has been made to improve this reaction process.

Using aqueous acetic acid as solvent, Tarbit *et al.*<sup>1</sup>, developed a process for the reaction of tetrabromophthalic anhydride and ethylenediamine where a highly white N,N'-ethylene-*bis*(tetrabromophthalimide) was produced by precipitation. Hutchinson *et al.*<sup>2</sup>, synthesized the same reaction N,N'-ethylene-*bis*(tetrabromophthalimide) but in a higher temperature range of 140-200 °C, using tetrabromophthalic anhydride and a diamine, a diamine salt or their mixture; the product showed good thermal stability and resistance to UV degradation.

The application of alternative heating methods such as microwave dielectric heating has also been investigated. Seijas *et al.*<sup>3</sup>, examined the direct, efficient synthesis of imides from dicarboxylic acids with amines in a domestic microwave oven. Westaway *et al.*<sup>4</sup>, synthesized N-phenyl phthalimide in microwave by employing dimethyl formamide as solvent from the reaction of anhydride and isocyanate. Microwave radiation was also used to assist solvent-free catalytic synthesis of imides<sup>5</sup>. The study conducted by Vidal *et al.*<sup>6</sup>, showed that, however, some of these reactions required expensive catalysts and some products must be difficult to purify<sup>5</sup>. In addition, ionic liquids have been used as catalysts for the preparation of *bis*-imides under microwave heating conditions showing higher reaction rate and the yield<sup>7</sup>.

All processes described above have some limitations such as the use of considerable volumes of toxic solvents, low product selectivity, the use of expensive catalysts and difficult purification procedures. In the present study, we took a new approach by using water as the solvent for the reaction of phthalic anhydride and ethylenediamine. The effects of adding water to a range of organic solvents including were also examined. The reaction was further carried out in organic solvents without water for comparison. The synthesized compounds were characterized by several techniques including IR, <sup>1</sup>H NMR, HMBC, <sup>13</sup>C NMR, HSQC, DEPT, MS and elemental analysis.

## EXPERIMENTAL

Phthalic anhydride (AR) was provided by Xi'an Chemical Reagent Factory. Ethylenediamine (AR) was supplied by Tianjin Xinghua Chemical Reagent Factory. Other reagents (AR) were obtained from Xi'an Chemicals and used without further treatment.

The instruments employed included an infrared spectrometer (FT-IR 360, America Nicolet Instrument Corporation), a high performance liquid chromatography (Agilent 1100 series, America Agilent Technologies), an NMR (INOVA-400 MHz, America Varian Inc.), a High Performance Liquid Chromatography-Mass Spectrometry (Agilent 1100 series, America Agilent Technologies), an elemental analyzer (PE2400) and a digital melting point instrument (WRS-1A, Shanghai Precision Scientific Instrument Co. Ltd.).

**General procedure:** To a solution of phthalic anhydride (0.05 M) in selected solvent within a standard three-necked flask (100 mL) was added the ethylenediamine solution (0.05 M) through a dripping funnel at appropriate speeds. The reaction was stirred at a given temperature while monitored by TLC. The solvents compositions, reaction temperature and times used are summarized in Table-1. Once reactions were completed and cooled to room temperature, the reaction mixtures were filtered and the solids obtained were washed thoroughly. The product was further purified by re-crystallization using ethanol/water (1:1 v/v) and dried in a vacuum oven at 100 °C.

## RESULTS AND DISCUSSION

Table-1 summarises the products and yields from the reaction of phthalic anhydride and ethylenediamine under different conditions including solvent composition, reaction time and reaction temperature.

It can be seen that two main products (I and II) were obtained which corresponded to the two groups of solvents, respectively, with and without water indicating the significant effect of water. In the water-containing media the yield of product I varied ranging from 45.7-92.4 % with the variation of the solvent composition. It was interesting to note that the reaction resulted in a reasonably high yield (80 %) of product I in water suggesting a green synthetic route for the production of imides in aqueous media. No significant effect was observed

of temperature in the operational range on the yield of product I. The variation of phthalic anhydride/ethylenediamine ratio had no significant effects on the product selectivity, whilst its yield decreased when the molar ratio was increased. The phthalic anhydride/ethylenediamine molar ratio of 1:1 gave the highest yield of product I.

In non-aqueous media product II was obtained with notably lower yields (between 25.5 and 36.4 %), even at higher temperatures and longer reaction times. Similarly, varying phthalic anhydride/ethylenediamine ratios had no significant effects on the product selectivity and its yield decreased when the molar ratio was increased. The best molar ratio of phthalic anhydride/ethylenediamine was also found to be 1:1.

**Product I:** White crystals, m.p. 214.3-214.8 °C, <sup>1</sup>H NMR (400 Hz, D<sub>2</sub>O): δ: 3.28 (s, 4H, CH<sub>2</sub>-CH<sub>2</sub>-), 7.41 (d, 2H, *J* = 3.27 Hz), 7.47 (d, 2H, *J* = 3.44 Hz). <sup>13</sup>C NMR (100 Hz, D<sub>2</sub>O) δ: 180.1 (C=O), 139.9, 131.6, 129.8, 39.3. IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3023, 2708, 1631, 1607, 1516, 1445, 1571, 1549, 1381, 1244, 766. MS (EI): *m/z* 226.2 (the molecular ion peak did not appear, but M<sub>1</sub><sup>+</sup>-NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>=M<sub>1</sub>-61 = 165.2). Anal. calcd (%) for C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>: C, 53.09; H, 6.24; N, 12.39. Found. (%): C, 53.09; H, 6.24; N, 12.38.

Product I in 3540-3180 cm<sup>-1</sup> region had no absorption peaks indicating that there were no amino groups, but quaternary ammonium existed. Based on the mass spectrometry (M<sub>1</sub> = 226.2) and elemental analysis results from product I, its formula can be drawn as C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>.

**Product II:** m.p. 237.8-238.2 °C, (literature data<sup>8</sup>: 237.5-239.9 °C. <sup>1</sup>H NMR (400 Hz, D<sub>2</sub>O) δ: 3.85 (s, 4H, -CH<sub>2</sub>-), 7.82 (s, 8H, Ar-H). <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>) δ: 167.7 (C=O), 134.5, 131.3, 123.1, 36.5. IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3459, 3050, 2813, 1715, 1632, 1464, 1445, 1190, 723. MS (EI): *m/z* 321 (M + H). Anal. calcd. (%) for C<sub>18</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub>: C, 67.50; H, 3.78; N, 8.75. Found (%): C, 67.46; H, 3.81; N, 8.78. Based on the results from mass spectrometry (M<sub>II</sub> = 320) and elemental analysis from product II, the formula can be drawn, C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>.

**Reaction mechanism:** As discussed above, the reaction of phthalic anhydride and ethylenediamine can result in a number of products. By analysing the chemical structures of these two reactants with two functional groups theoretically, we found that there are 14 compounds which may be produced from the reactions of phthalic anhydride and ethylenediamine (Fig. 1).

TABLE-1  
REACTION CONDITIONS AND RESULTS

No.	Solvent	Reaction time (min)	Reaction temperature (°C)	Product	Yield (%)
1	H <sub>2</sub> O	60	95	I	80.0
2	H <sub>2</sub> O:Ethanol = 1:1	60	70	I	92.4
3	H <sub>2</sub> O:Tetrahydrofuran = 1:1	60	60	I	63.3
4	H <sub>2</sub> O:1,4-Dioxane = 1:1	60	90	I	82.4
5	H <sub>2</sub> O:Pyridine = 3:2*	60	95	I	90.1
6	H <sub>2</sub> O:Toluene = 5:3*	60	100	I	91.4
7	H <sub>2</sub> O:Trichloromethane = 1:1	60	70	I	45.7
8	Tetrahydrofuran	150	60	II	26.1
9	1,4-Dioxane	150	90	II	28.8
10	Pyridine	120	108	II	36.4
11	Toluene	120	90	II	28.9
12	Trichloromethane	120	55	II	25.5

\*Highest concentrations under the reaction conditions stated.

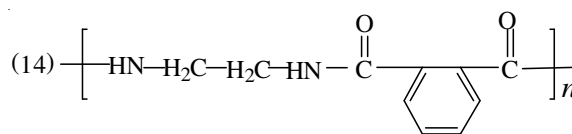
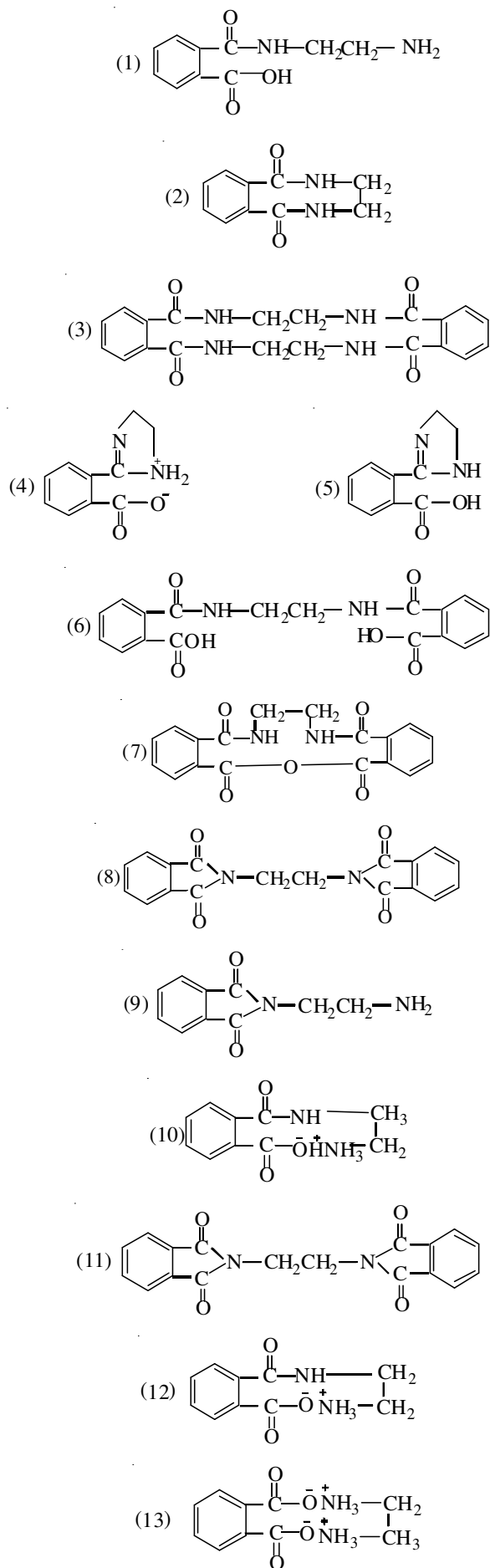
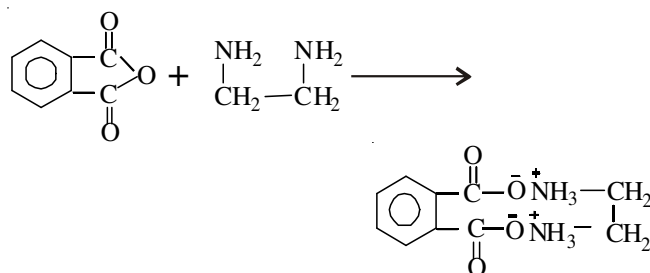


Fig. 1. Products of the reaction of phthalic anhydride and ethylenediamine

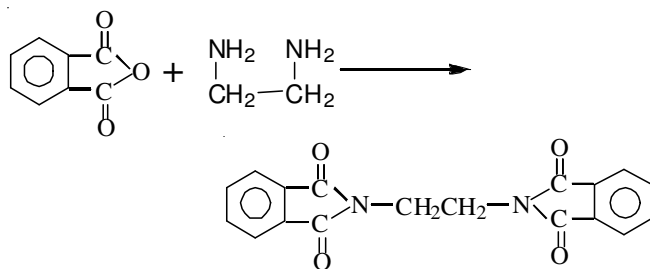
It was found that the formula of product I,  $C_{10}H_{14}N_2O_4$ , matched one of the 14 possible product structures (compound **13** in Fig. 1), which was named phthalic ethylene ammonium salt. It was also found that the formula of product II,  $C_{18}H_{12}N_2O_4$ , corresponded to the structure of compound **11** (Fig. 1), namely, N,N'-diphthaloyl-1,2-ethylenediamine. Both structures were confirmed by  $^1H$  and  $^{13}C$  NMR.

As shown in Table-1, the presence or absence of  $H_2O$  in the solvents determined the main product selectivity. This observation is in line with other researchers' results<sup>8</sup>. When the reaction was carried out in the  $H_2O$ -containing solvent, the reaction of phthalic anhydride and water could occur first to form carboxylic acid. Carboxylic acid then reacted with ethylenediamine resulting in product I, phthalic ethylene ammonium salt. Thus, the synthetic route in aqueous solution can be represented by **Scheme-I**.



Scheme-I

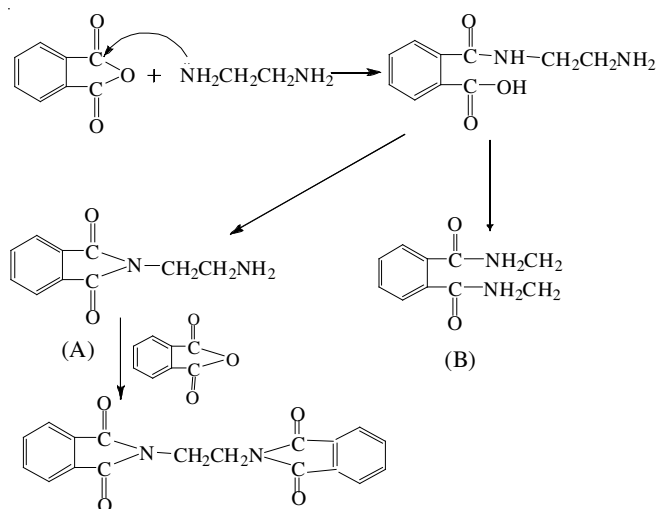
In non-aqueous solvents where phthalic anhydride was dissolved and reactions between phthalic anhydride and ethylenediamine occurred directly and product II, N,N'-diphthaloyl-1,2-ethylenediamine was produced (**Scheme-II**). There might be different intermedia (A and B) produced in this route (**Scheme-III**) where A had a more stable structure than B. Therefore, product II was likely formed through A.



Scheme-II

## Conclusion

The reactions of phthalic anhydride and ethylenediamine were conducted and significant effects of solvents were observed with 12 types of solvents in two groups (either containing or without  $H_2O$ ) used. In  $H_2O$ -containing media, phthalic ethylene ammonium salt was obtained with high yields. When the reaction



was carried out in non-aqueous solvents, N,N'-diphthaloyl-1,2-ethylenediamine was formed at lower reaction rates and yields. All products were characterised and confirmed by a combination of analytical techniques. The use of water as solvent with a reasonably high product yield (80 %) suggests a green route for the synthesis of phthalic ethylene ammonium salts although their applications are still under developments.

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