Esterification of Several N,N-disubstituted Phthalamic Acids and Testing the Esters as Plastaziers for Poly (Vinyl Chloride) and Poly Styrene

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Abstract

Three N,N-disubstituted phthalamic acids were prepared by allowing phthalic anhydride to react with secondary amines. The prepared phthalamic acids were esterified directly or via their acid chlorides producing good yields of the corresponding esters. Some of the prepared esters were tested as plasticizers for poly (vinyl chloride) and the results were compared with Dioctyl phthalate (DOP), the universal plasticizers for P.V.C Results showed the new esters as effective plasticizers as DOP for PVC. The esters were also tested as plasticizers for polystyrene.

Introduction

Reactions of anhydrides with primary and secondary amines were well-documented \(^{1-3}\). The reaction is clean, fast, high yield and without any side products. Numerous uses for the phthalamic acid products are reported in literature \(^{4-6}\). The main use of amic-acid products is their cyclization to the corresponding cyclic imides. The unsaturated cyclic imides are used mainly as monomers or comonomers for polyimide synthesis. Recently, several esters of N-substituted amic acid esters were prepared in our laboratory and used to plasticizer polystyrene and poly(vinyl chloride) \(^{8}\). The following paper is a similar study in which novel phthalamic esters are prepared and used in plasticization of poly (vinyl chloride) and polystyrene.

Apparatus:

IR spectrum was recorded using PYE UNICAM PU a512, CHN analysis was carried out using Perkin-Elmer CHN-analyser.

Experimental

Preparation of N,N-Disubstituted phthalamic acids

Literature procedures were followed \(^{2,4}\) with few modification. The procedure for preparation of N,N-Dibenzylamine-phthalamic acid will be described as an example.

Reaction of phthalamic anhydride with ibenzylamine

In around bottom flask (100 ml) was dissolved 10 g (0.06 mole) of phthalic anhydride in 40 ml of acetone with stirring magnetically. A dropping funnel was charged with 8.5 ml (0.06 mole) of dibenzylamine and placed on top of the flask. The amine was allowed to add to the flask dropwise while stirring, a white precipitate was formed. The precipitate was filtered, washed with dilute (5%) HCl and dried.

The product was recrystallized from n-hexane and the crystals showed a m.p of 157-159\(^{0}\)C. The percent yields was 78%. Following the above procedures several-N,N-disubstituted phthalamic acids were prepared.

Table 1 lists the physical properties of three of the prepared phthalamic acids.
Table 1. Physical properties and yield of the prepared phthalamic acid

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>M.P</th>
<th>C₀</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>N,N-diethyl phthalamic acid</td>
<td>152-154</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>N,N-dibenzyl phthalamic acid</td>
<td>157-159</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>N,N-diphenyl phthalamic acid</td>
<td>140-142</td>
<td>90</td>
<td></td>
</tr>
</tbody>
</table>

Preparation of Esters from the prepared phthalamic acids
Preparation of Ethyl N,N-(diethyl) phthalamate

A) Preparation of N,N-(diethyl phthalamoyl) chloride
In a two necked round bottom flask (200 ml) was placed 10 g (0.04 mole) of N,N-(diethyl) phthalamic acid. Thionyl chloride, 0.6 ml (0.08 mole) was placed in a dropping funnel, and protected with CaCl₂ drying tube. The flask was provided with a reflux condenser, a steam bath, and a magnetic stirrer. The thionyl chloride was allowed to add dropwise to the flask while stirring and heating, the color was changed to yellow-brown, the reflux was continued for another hour. The apparatus was changed to distillation apparatus where the unreacted thionyl chloride distilled off. The residue (acid chloride) was solidified at room temperature and used in step (B) without further purification.

B) Reaction of N,N-(diethyl) phthalamoyl chloride with Ethanol
Ethanol (10ml) was added to the product residue in the round bottom in (A) and refluxed for two hours. The mixture was then added to (30ml) of distilled water placed in a separator funnel. The mixture was shaken and allowed to settle. Two layers were formed, the lower aqueous layer was extracted a couple of times with (10ml) of ether. The ether extracts were added to the oily layer, washed with (10ml) of water, and dried with anhydrous MgSO₄. The ether was allowed to evaporate, red crystals were left. The product was recrystallized from ccl₄, and pure crystals formed showing m.p of 53-55°C and percent yield was 57.7%.
Following the same procedure several other esters were prepared and their physical points are reported in table II.

Table (2): Physical properties and yield of the prepared phthalamate

<table>
<thead>
<tr>
<th>Ester</th>
<th>M.P</th>
<th>B.P</th>
<th>% yield</th>
<th>Color of product</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image4.png" alt="Ester 1" /></td>
<td>53-55</td>
<td></td>
<td>80</td>
<td>Reddish</td>
</tr>
<tr>
<td>Ester</td>
<td>M.P C°</td>
<td>B.P C°</td>
<td>% yield</td>
<td>Color of product</td>
</tr>
<tr>
<td>-------</td>
<td>---------</td>
<td>--------</td>
<td>---------</td>
<td>------------------</td>
</tr>
<tr>
<td><img src="image1.png" alt="Ester" /></td>
<td>103-105</td>
<td>—</td>
<td>62</td>
<td>White</td>
</tr>
<tr>
<td><img src="image2.png" alt="Ester" /></td>
<td>55-57</td>
<td>—</td>
<td>53</td>
<td>White-gray</td>
</tr>
<tr>
<td><img src="image3.png" alt="Ester" /></td>
<td>93-95</td>
<td>—</td>
<td>56</td>
<td>Green</td>
</tr>
<tr>
<td><img src="image4.png" alt="Ester" /></td>
<td>54-56</td>
<td>—</td>
<td>65</td>
<td>Yellow</td>
</tr>
<tr>
<td><img src="image5.png" alt="Ester" /></td>
<td>106-108</td>
<td>—</td>
<td>40</td>
<td>White</td>
</tr>
<tr>
<td><img src="image6.png" alt="Ester" /></td>
<td>60-62</td>
<td>—</td>
<td>45</td>
<td>Gray</td>
</tr>
<tr>
<td><img src="image7.png" alt="Ester" /></td>
<td>105-107</td>
<td>—</td>
<td>61</td>
<td>Gray</td>
</tr>
<tr>
<td><img src="image8.png" alt="Ester" /></td>
<td>55-57</td>
<td>—</td>
<td>36</td>
<td>Green</td>
</tr>
<tr>
<td><img src="image9.png" alt="Ester" /></td>
<td>63-65</td>
<td>—</td>
<td>45</td>
<td>Gray</td>
</tr>
</tbody>
</table>
Use of the new esters as plasticiser for PVC.
Three different methods were employed in order to test some of the prepared esters for plasticisation of poly (vinyl chloride).

**Method A.**
one gram of poly (vinyl chloride) was mixed with certain amount of dioctyl phthalate (obtained from the Iraqi plastic company, Zafarania, Baghdad) the unplasticised PVC had a M.wt of 10000 gm/mol, and was dissolved in 15 ml of THF in a 200 ml beaker. A thin film of the viscous solution was prepared and allowed to dry before measuring its softening point. Three different percentages of DOP in PVC were prepared and tested their softening point in order to prepare a standard curve for comparison with effects of the prepared esters.
One gram of the unplasticised PVC was dissolved in 15 ml of THF in a small beaker. In another beaker 0.1 g of the amic ester was dissolved in 5.0 ml of THF. The two solutions were mixed well and used to prepare a thin film on a clean slide of glass. After complete dryness the film was removed and its softening point was determined.

**Method B**
Three milliliters of the liquid ester (amic ester) was placed in a conical flask and heated to 130-140°C. Preweighed amount of powdered PVC was gradually added to the ester with stirring, until a homogenous mixture was obtained. The mixture was added to water. The solidified material was dried before determining its softening point.

**Method C**
In an agar mortar 1.0 g of unplasticised PVC was mixed with the exact weight of one of the prepared amic ester, grounded well until forming a homogenous mixture; the softening point was determined.

**Results and Discussion**
Literature procedures were followed to prepare the new N – substituted phthalamic acids. The reactions were

<table>
<thead>
<tr>
<th>Ester</th>
<th>M.P C⁰</th>
<th>B.P C⁰</th>
<th>% yield</th>
<th>Color of product</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="ester1" /></td>
<td>137-139</td>
<td>57</td>
<td>Violet</td>
<td></td>
</tr>
<tr>
<td><img src="image2" alt="ester2" /></td>
<td>45-47</td>
<td></td>
<td>51</td>
<td>Violet</td>
</tr>
<tr>
<td><img src="image3" alt="ester3" /></td>
<td>54-56</td>
<td></td>
<td>42</td>
<td>Green</td>
</tr>
<tr>
<td><img src="image4" alt="ester4" /></td>
<td>159-161</td>
<td></td>
<td>37</td>
<td>Violet</td>
</tr>
<tr>
<td><img src="image5" alt="ester5" /></td>
<td>110-112</td>
<td></td>
<td>30</td>
<td>White</td>
</tr>
<tr>
<td><img src="image6" alt="ester6" /></td>
<td>310-312</td>
<td></td>
<td>43</td>
<td>Yellow</td>
</tr>
</tbody>
</table>
straight forward and the yields were high. Table I lists structures names and melting points of the prepared amic acids. It is important to notice that all the employed amines that were allowed to react with phthalic anhydride were secondary amines and not primary. This was to avoid cyclization of the amic acids to from the corresponding imides during heating or treatment with thionyl chloride prior to esterification. The yields of the esters obtained by direct reaction of the alcohol with the amic acids using sulfuric acid as catalyst gave low yields of the corresponding esters. However, indirect esterification via converting first the amic acids to their corresponding acid chlorides followed by reaction with the alcohols gave fair to good yields of the esters. Table II lists the structures, melting points or boiling points, percent yields and colours of the prepared esters. Structures of the esters were proved by I.R analysis and hydroxamic acid test of esters. The I.R spectra of the esters in (KBr) showed carbonyl absorptions of the ester and amides. Table III lists major I.R absorptions and Elemental analysis of some of the prepared esters.

Table III Major I.R. Absorption of the prepared Esters and their Elemental Analysis

<table>
<thead>
<tr>
<th>Ester</th>
<th>V c=0cm$^{-1}$</th>
<th>V c=0cm$^{-1}$</th>
<th>C.H.N. Anal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ester</td>
<td>Amide</td>
<td>Cald %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>1770</td>
<td>1700</td>
<td>67.40</td>
<td>7.83</td>
</tr>
<tr>
<td>1760</td>
<td>1700</td>
<td>70.50</td>
<td>5.37</td>
</tr>
<tr>
<td>1755</td>
<td>1700</td>
<td>81.10</td>
<td>5.70</td>
</tr>
<tr>
<td>1710</td>
<td>1660</td>
<td>76.50</td>
<td>5.50</td>
</tr>
<tr>
<td>1770</td>
<td>1710</td>
<td>69.31</td>
<td>8.30</td>
</tr>
<tr>
<td>Ester</td>
<td>V $\text{c=0cm}^{-1}$ Ester</td>
<td>V $\text{c=0cm}^{-1}$ Amide</td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td></td>
</tr>
<tr>
<td><img src="image1" alt="Ester 1" /></td>
<td>1760</td>
<td>1705</td>
<td></td>
</tr>
<tr>
<td><img src="image2" alt="Ester 2" /></td>
<td>1760</td>
<td>1690</td>
<td></td>
</tr>
<tr>
<td><img src="image3" alt="Ester 3" /></td>
<td>1766</td>
<td>1710</td>
<td></td>
</tr>
<tr>
<td><img src="image4" alt="Ester 4" /></td>
<td>1720</td>
<td>1660</td>
<td></td>
</tr>
<tr>
<td><img src="image5" alt="Ester 5" /></td>
<td>1760</td>
<td>1705</td>
<td></td>
</tr>
<tr>
<td><img src="image6" alt="Ester 6" /></td>
<td>1760</td>
<td>1700</td>
<td></td>
</tr>
<tr>
<td><img src="image7" alt="Ester 7" /></td>
<td>1770</td>
<td>1705</td>
<td></td>
</tr>
</tbody>
</table>
Application of five of the prepared esters as plasticizers for PVC and polystyrene showed them fairly efficient and could be used instead of (Dioctyl phthalamate)(Dop). Figures 1 and 2 show the results of such experiments. Up to 30% of the esters were used and mixed with (PVC) and polystyrene as plasticizers.

<table>
<thead>
<tr>
<th>Ester</th>
<th>V c=0cm⁻¹ Ester</th>
<th>V c=0cm⁻¹ Amide</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="" alt="ester1" /></td>
<td>1710</td>
<td>1655</td>
</tr>
<tr>
<td><img src="" alt="ester2" /></td>
<td>1765</td>
<td>1700</td>
</tr>
<tr>
<td><img src="" alt="ester3" /></td>
<td>1760</td>
<td>1715</td>
</tr>
<tr>
<td><img src="" alt="ester4" /></td>
<td>1715</td>
<td>1635</td>
</tr>
</tbody>
</table>
Fig. (1): The effect of the plasticizers to the softening point of P.V.C

Dioctyl Phthalate  DOP:

Ethyl N,N-diethyl phthalamate  IV:

Methyl N,N-dibenzy1 phthalamate  V:

β-naphthyl N,N-dibenzy1 phthalamate  VI:

Ethyl N,N-diphenyl phthalamate  VII:

Iso-butyl N,N-diethyl phthalamate  VIII:
References

2. T.M. Priadi, J. org. chem. 37, 4184 (1972)
8. T.M. Pyradi and A. Jawod , Iraqi J. chem accepted for publication.