New methodology of naphthoquinones esterification with long-chain fat acids

Gilles, V.; Vieira, A. M.; Lacerda Jr. V.; de Castro, E. V. R. and Greco, S. J.*

1 LSO&M – Laboratório de Síntese Orgânica e Medicinal. Universidade Federal do Espírito Santo. Vitória, Brazil.
2 NCQP – Núcleo de Competências em Química de Petróleo. Universidade Federal do Espírito Santo. Vitória, Brazil.

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INTRODUCTION

Among the eldest reactions known, esterification is the simplest method to obtain esters of carboxylic acids. Since the first methodology developed by Fischer in 1895, a considerable number of new procedures have been developed like the use of anhydrides, acyl chlorides and condensation agents.

However, the only report of juglone esterification comes from Maruo et al. where they used acyl chlorides in pyridine as shown in Scheme 1.


In this work, we describe our studies about a new methodology to prepare naphthoquinone esters of long-chain acids.

RESULTS AND DISCUSSION

Palmitic acid was chosen as model to esterification reaction with juglone. We first investigated Fischer classical method using PTSA, ultrasound and disecant (Scheme 2, Condition a) with no success.

Scheme 2. General methodology study of esterification of juglone with palmitic acid.

On our second attempt, acid catalysis using boric acid was applied (Scheme 2, Condition b). The crude product contained many subproducts making it impossible to purify. This unsuccessful attempt might be related to juglone instability under high temperature, leading to severe degradation.

The use of TsCl as activating agent failed as well (Scheme 2, Condition c). Then, we started new attempts with condensation agents, where CDI was the first choice (Scheme 2, Condition d). This method proved unsuccessful probably by the release of imidazole, which basicity may degrade the substrate. We then change to DCC that does not generate basic residue (Scheme 2, Condition e). CeCl₃ was also add to increase the electrophilicity of the anhydride generate in situ enabling ester synthesis.

Table 1 shows the reactional time and yield.

Table 1. Results concerning esterification of juglone with DCC.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Reaction Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric</td>
<td>24</td>
<td>7</td>
</tr>
<tr>
<td>Palmitic</td>
<td>72</td>
<td>18</td>
</tr>
<tr>
<td>Stearic</td>
<td>72</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Yields are close to other described in literature with avoidance of inert atmosphere, anhydrous solvent and dangerous reactants.

CONCLUSION

In conclusion, we present a new attempt of esterification of naphthoquinones with success for three fatty acids using a less dangerous and easier methodology.

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REFERENCES


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