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Synthesis de alkoxy and aryloxyphthalonitriles key precursors for the synthesis of substituted phthalocyanines

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Introduction

Owing to their properties, phthalocyanines have been the aim of intensive studies on their application in photodynamic therapy, thus design of new derivatives being of special interest (Mody and Pandey, 2001).

A factor to be taken into account when designing these colourants is the property of forming aggregates that decrease their photodynamic effect, since only monomers are good generators of singlet oxygen, which is the cytotoxic species responsible for tumor death (Henderson and Dougherty, 1992).

Phthalocyanines substituted with bulky groups on the periphery can produce a decrease in the formation of aggregates, and consequently, an improvement in the photodynamic effect of the photosensitizer (Fernández *et al.*, 1996).

A synthetic route that involves the nucleophilic aromatic substitution of 3-nitro phthalonitrile (**1**) and 4-nitrophthalonitrile (**2**) (Snow and Jarvis, 1984) with an adequate oxygenated nucleophile was explored to obtain intermediates, whose post-tetramerization will lead to zinc (II) phthalocyaninates.

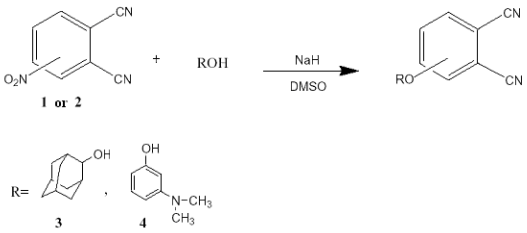
Methodology

3-(2-Adamantoxy)phthalonitrile, 4-(2-adamantoxy) phthalonitrile, 4-(3-dimethylamino-phenoxy)phthalonitrile and 3-(3-dimethylaminophenoxy) phthalonitrile were prepared.

These compounds were purified by medium pressure chromatography, recrystallized, and characterized by spectroscopic methods, ^{1}H-NMR, mass spectrometry and infrared spectroscopy.

Results

Adamantol (**3**) was reacted with phthalonitrile (**1**) and (**2**) in alkaline medium using DMSO as solvent in order to obtain 3-(2-adamantoxy) phthalonitrile and 4-(2-adamantoxy) phthalo-nitrile, respectively. Under similar conditions, when **1** or **2** were reacted with 3-dimethylaminophenol (**4**) compounds 4-(3-dimethylaminophenoxy)phthalonitrile and 3-(3-dimethylaminophenoxy)-phthalonitrile were obtained.



Conclusions

The synthesized compounds were obtained in 30% yield, and excellent purity quality.

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