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Synthesis of Functionalized Pararosaniline over Mild Conditions †

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Abstract: Dyes and pigments have many applications, and their growing development is driven by their increased use. As a contribution to this topic, in this work, the synthesis of functionalized pararosaniline was evaluated with the aim to obtain an amphiphilic dye. Pararosaniline is a dye highly soluble in water and polar solvents, presenting three amino groups in its structure. We realized that the functionalization of pararosaniline by direct coupling of amino groups with halogenated fatty acids leads to amides derived from fatty acid. In the synthesis, fatty acid chloride from sunflower oil and basic catalysts were used. Over a single step one-pot procedure carried out at room temperature in moderate reaction time, a new functionalized pararosaniline was synthesized. The results showed that after derivatization with chloride of fatty acids, the dye exhibits solubility both in water and in non-polar systems with different color intensities.

Keywords: amphiphilic dye; derivatization; mild conditions

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1. Introduction

Dyes and pigments are the most important colorants used to add color or to change the color of different materials. They are widely used in the textile, pharmaceutical, food, cosmetics, plastics, paint, ink, photographic and paper industries. A Dye is a coloured compound due to the presence of chromophore and its fixed property to the acid or basic groups such as OH, SO3H, NH2, NR2, etc. [1]. The polar auxochrome makes the dye water-soluble and binds the dye to materials by interaction with the oppositely charged groups present on their surface [2].

Solubility of a colorant constitutes a fundamental property for dye industry. In this direction, the development of amphiphilic compounds represents a key element for applications of dyes in materials science.

As a contribution to this topic, in this work, the synthesis of functionalized pararosaniline was evaluated with the aim to obtain an amphiphilic dye.

Pararosaniline is a widely spread dye that presents amine groups in their molecular structure. It is used in textile and paper industries, as well as in microbiological analysis. Despite being broadly applied, this pure hydrophilic dye is only limited to polar systems. Taking into account that the amide functionality exists in numerous biological, pharmaceutical, and agrochemical molecules [3], we considering this strategy for functionalization of pararosaniline using chlorides of fatty acids as reactants. This synthesis method over mild conditions, is not only easy and most economical, but it would also allow us to obtain a dye with amphiphilic properties.

2. Material and Methods

2.1. Fatty Acids Preparation

Fatty acids were prepared via acid neutralization of vegetal soap from sunflower oil. A mixture of sunflower oil and water (50:50; 240 g) was reacted with 60 g of 30 wt. % sodium hydroxide aqueous solution at 60 °C for 12 h to generate vegetal soap. Then the soap was acidified with sulfuric acid 18 M to pH less than 2. The lower aqueous layer was discarded and the upper fatty acids layer was washed using cold water and then dried using anhydrous sodium sulfate. Finally, fatty acids were recrystallized with acetone at -20 °C.

2.2. Synthesis of Fatty Acid Chlorides

For the fatty acid chlorides preparation [4], 10 g of fatty acids were dissolved in 100 ml of n-hexane, and 5.0 g of phosphorus pentachloride were added to the solution. The mixture was refluxed for 3 h. Then, the solution was cooled to room temperature and washed twice with cold water. The organic phase was dried with anhydrous sodium sulphate, and the solvent was removed under vacuum. The obtained product was an oily yellow liquid.

2.3. Derivatization Procedure of Pararosaniline

The functionalized pararosaniline was synthetized by direct coupling of amino groups of pararosaniline with fatty acid chlorides catalyzed with bases, according to Figure 1. $Ca_3(PO_4)_2$, KOH and NaOH were evaluated as catalysts. Typically, pararosaniline (1 mmol) and catalyst (2 mmol) were added to 30 mL of tetrahydrofuran (THF). Then, a fatty acid chlorides solution (2 mmol) in THF (70 mL) was added. The reaction mixture was stirred at room temperature for 6–12 h. After this time, the reaction was neutralized with a solution of hydrochloric acid 1 M. Previous filtration, the solvent was evaporated and the resulting solid was dried in oven under reduced pressure and stored at 4 °C.

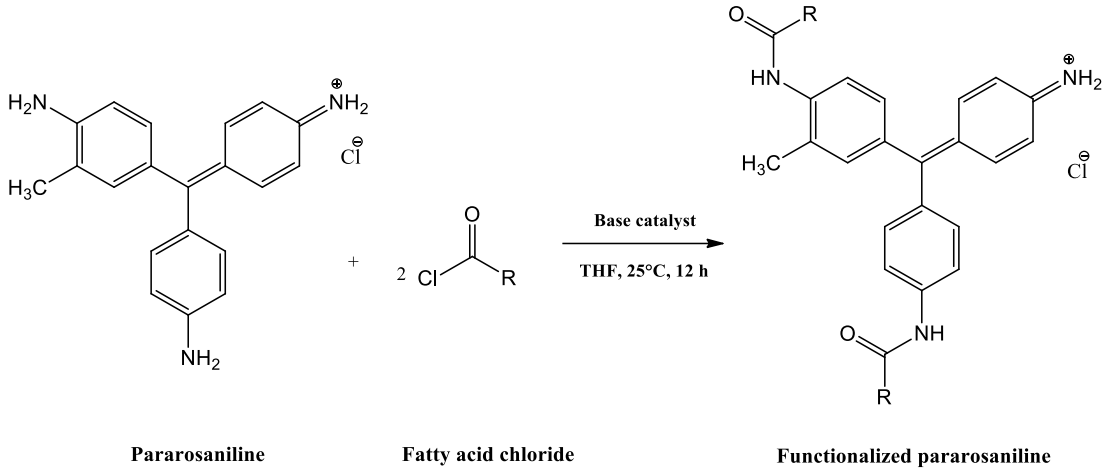

Figure 1. Scheme of direct coupling reaction of amino groups of pararosaniline with fatty acid chlorides catalyzed with bases over mild conditions.

3. Results and Discussion

3.1. Evaluation of Pararosaniline Derivatization

We began our investigation with the coupling of amine groups of pararosaniline with fatty acid chlorides using different inorganic bases, monitoring the reaction progress by TLC. The coupling led to functionalized pararosaniline as a product only when NaOH and KOH were used. With $Ca_3(PO4)_2$ the product was not evidenced. The reaction with NaOH was comparatively slower than with KOH, requiring 12 h to obtain the same results. Based on this, we can conclude that over the mild experimental conditions evaluated

and using KOH as a base, it is possible to synthesize functionalized paroroaniline in only 6 h of reaction time.

3.2. Characterization of Functionalized Pararosaniline

Functionalized pararosaniline was chemically characterized by FTIR and by solubility tests in water-oil systems, comparing their properties with non-functionalized pararosaniline.

Functional groups present in the structure of these dyes were identified from the FTIR spectra. Compared with pararosaniline, the FTIR spectrum of funcionalized pararosaniline showed distinctive absorption bands at around 1660, 1550, 1280 cm^{-1}, assigned to stretching vibrations of amide C=O bonds, bending mode of amide N-H bonds, and to symmetric stretching vibrations of C–N bonds respectively [5,6]. The presence of these bands indicated the C-NH-C=O bond formation on derivatized dye.

On one hand, the solubility of these materials was evaluated in a water-oil system. As can be seen in Figure 2, pararosaniline was only soluble in the aqueous phase. On the other hand, functionalized pararosaniline was soluble both in the aqueous and oily phases, showing different color intensities. Similar results were observed with other polar-non polar system.

Figure 2. Picture of pararosaniline and functionalized pararosaniline dissolved in a water-oil system at different concentrations.

4. Conclusions

Over a single step one-pot procedure carried out at room temperature in moderate reaction time, a new functionalized pararosaniline was synthesized. The fuctionalization involved the addition of hydrocarbon chains to the polar pararosaniline structure resulting in an additional hydrophobic contribution. The results showed that after derivatization with chloride of fatty acids, the dye exhibited solubility both in water and in oil with different color intensities, depending of the dye concentration present in the system.

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References

1. Bouzidi, A.; Baaka, N.; Salem, N.; Mhenni, M.F.; Mighri, Z. Limoniastrum monopetalum stems as a new source of natural colorant for dyeing wool fabrics. *Fibers Polym.* **2016**, *17*, 1256–1261. doi:10.1007/s12221-016-5664-z.
2. Chattopadhyay, S.N.; Pan, N.C.; Roy, A.K.; Saxena, S.; Khan, A. Development of natural dyed jute fabric with improved colour yield and UV protection characteristics. *J. Text. Inst.* **2013**, *104*, 808–818. doi:10.1080/ 00405000.2012.758352.
3. Yusuf, M.; Shabbir, M.; Mohammad, F. Natural colorants: historical, processing and sustainable prospects. *Nat. Prod. Bioprospect.* **2017**, *7*, 123–145. doi:10.1007/ s13659-017-0119-9.
4. Youngs, C.G.; Epp, A.; Craig, B.M.; Sallans, H.R. Preparation of long-chain fatty acid chlorides. *J. Am. Oil Chem. Soc.* **1957**, *34*, 107–108. https://doi.org/10.1007/BF02640442.
5. Silverstein, R.; Bassler, G.C.; Morrill, T.C. *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley & Sons, Inc.: Chichester, UK, 1991; ISBN 0-471-63404-2.
6. Richard, L. Heinemann Comparative Spectroscopy of Basic Fuchsin, Schiff Reagent, and a Formalin-Schiff Derivative in Relation to Dye Structure and Staining. *Stain Technol.* **1970**, *45*, 165–172. doi:10.3109/10520297009067473.