

Fluorescent Symmetric Phenazines from the Reactions of β -Lapachone and Nor- β -lapachone with Ammoniating Agents

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The reactions of β -lapachone **1** and nor- β -lapachone **4** with several ammoniating agents give rise to symmetric phenazines which exhibit high, solvent dependent, fluorescence quantum yields.

In an earlier paper⁴ on the reactions of 1,2-naphthoquinones from *Tabebuia* sp., β -lapachone **1** and nor- β -lapachone **4** with glycine, we isolated and identified three symmetric, highly fluorescent, phenazines, the isomeric pair **2** (*transoid*)/**3** (*cisoid*) and the *cisoid* form **6**, albeit as subproducts in trace amounts (Scheme 1).

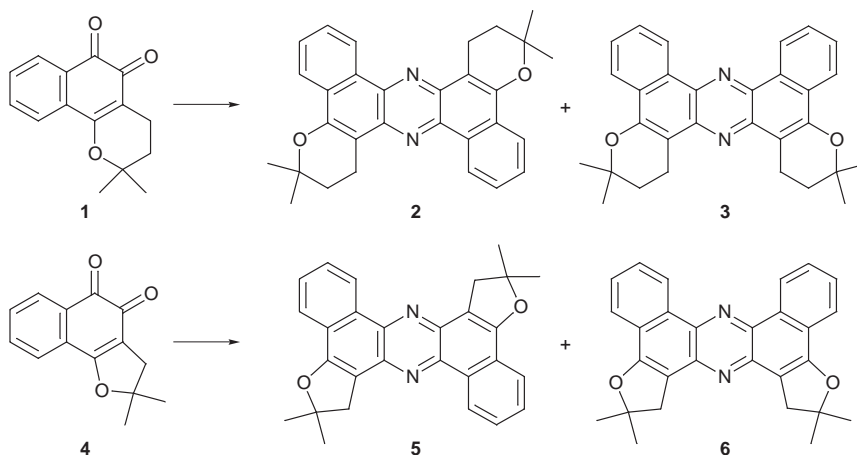
The present work concerns efforts to prepare these phenazines in better yields by reacting **1** and **4** with ammoniating agents [AcONH₄, HCO₂NH₄ or (NH₄)₂CO], in several solvents and under various reaction conditions (Tables 1 and 2, see full text). We report an extension of the scope of this new type of reaction, yielding highly fluorescent compounds which are potential use in photophysics studies.

Under the conditions used here, it was possible to isolate and identify the phenazine **2**, a *transoid* form, described here for the first time, which is an isomer of the previously reported *cisoid* **3** form. The total yields for the isomeric mixtures **2/3** and **5/6** are in the range of 4–48% and 5–31%, respectively. Not only the total yields, but also the isomeric pair ratio in each reaction, are dependent on the solvent and reaction conditions. Although these yields are not good from a synthetic point of view, these results are a major improvement compared to the trace amounts reported⁴ for the reactions of **2** and **4** with glycine. The phenazines are easily isolated from the highly complex mixture of more polar products on a silica gel chromatography column,

using a mixture of hexane–ethyl acetate and gradually increasing the polarity of the solvent mixture. Under these conditions the isomeric phenazines **5** and **6** emerge from the column as a mixture of isomers and complete separation of them from each other is only possible by careful selection of the chromatographically rich fractions containing the phenazines, in each case followed by several chromatographic cycles. It is important to observe that the *transoid* forms in both reactions emerge first from the column under the chromatographic conditions used.

All four phenazines exhibit high, solvent dependent, fluorescent quantum yields (Table 3, see full text), making them of potential use in laser studies. The influence of the solvent on the UV–VIS absorption and fluorescence spectra (Table 3) was used as a guideline for diastereoisomeric structural assignment, corroborated by ¹H–¹H nuclear Overhauser enhancement (NOE) studies. Physical and spectra data of **3**, **5** and **6** are given in ref. 4.

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Scheme 1

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Techniques used: ^1H , ^{13}C NMR, IR, and UV-VIS stationary and time resolved fluorescence emission spectroscopy.

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References: 10

Table 1: β -Lapachone **1** amination reactions

Table 2: Nor- β -lapachone **4** amination reactions

Table 3: Phenazine absorption and fluorescence spectroscopic data

References cited in this synopsis

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