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Structure and Potential Scheme Reaction of a New Benzo[h]quinoline Derivative

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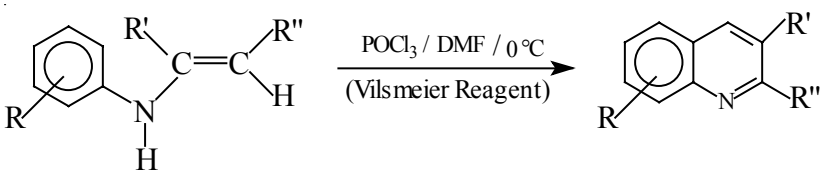
A new product namely, 2-methyl-3-ethyl methanoate benzo[h]quinoline was synthetized from an arylenamine using Vilsmeier reagent. The product was identified by classical and usual spectroscopic techniques as well as X-ray structure determination and a detailed potential scheme reaction way was proposed.

Key Words: Benzoquinoline, Spectroscopic analysis, Vilsmeier reagent, Heterocycle, X-ray.

INTRODUCTION

The synthesis, chemical and pharmacological properties of quinoline and benzoquinoline derivatives constitute an important domain of investigation[1-10].

Complex of vilsmeier is very used in synthesis strategy of this class of coumpounds[10]. It's particulary used to formylate aryl coupounds for extend with a carbon atom an aryl structure[11] or to formylate and cyclized amides to quinolinic derivatives[1,3]. From enamines, as a starting material, quinoline derivatives was obtained with a good yield[12,13]:



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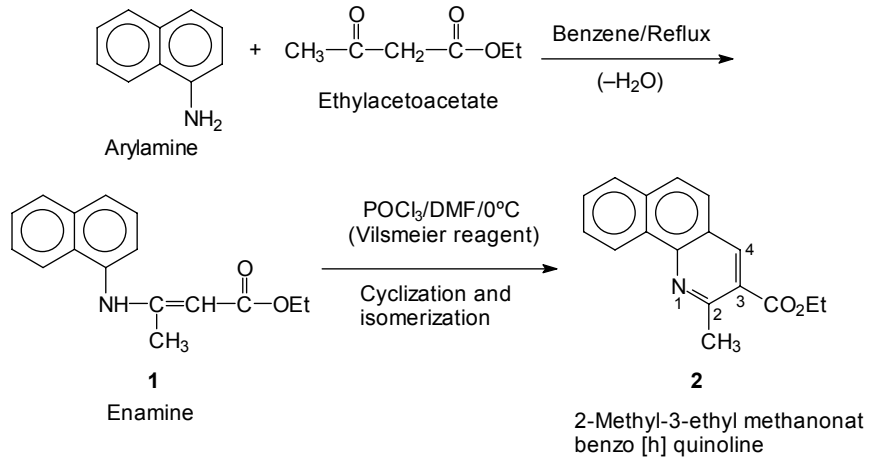
The potentialities of Vilsmeier-Haack reaction[10,14], allowed us to synthesize a new stable benzoquinoline compound under crystalline state namely: 2-methyl-3-ethyl méthanoate benzo[h]quinoline (**2**) as indicated in the following scheme:



EXPERIMENTAL

Preparation of Vilsmeir reagent: To 0.015 mol of freshly distilled and anhydrous dimethyl formamide, 0.015 mol of phosphorus oxychloride was added drop wise at 0-5°C with continuis stirring. At the end of the addition the agitation is carried on during 0.5 h at room temperature before use[14].

Synthesis of enamine 1: To equimolecular mixture of naphthylamine and acetylacetoacetate dissolved in dry benzene is added 5 drops of anhydrous acetic acid as catalyst. The reaction mixture is heated under reflux for 4 h. The water formed is removed using Dean Stark system and the benzene solvent is eliminated by rotavapor. The residue is dried in a dessicator under high vacuum to give enamine **1** as a purple oily product. Yied: 86 %.

Synthesis of benzoquinoline derivative 2: To a freshly prepared Vilsmeier reagent, is added under inert atmosphere, 0.05 mol of the enamine **1** dissolved in 25 mL of purified chloroform. The resultant mixture is stirred at 0°C for 2 h and then allowed to stand at room temperature before transferred it in a saturated $NaHCO_3$ aqueous solution.

The organic layer was separated and the aqueous phase was extracted with chloroform. The combinated organic phases was dried with anhydrous magnesium sulfate.

After the evaporation of $CHCl_3$ *in vacuo* the yellow solid residue is left overnight to crystallized completely giving crude 2-methyl-3-(methanoate ethyl)benzo[h]quinoline (**2**).

Purification is achieved by recrystallization from a mixture of Et_2O/hexane (1:4) giving yellow crystal tablets. Yield: 85 %; m.p. = 78.5°C.

Mass spectrum: m/z 165.1; $[M]^+$ 100 %.

Purification of the solvents: All solvents have been dried, distilled and freshly used without any conservation[15].

X-ray structure analysis: Data for X-ray structure analysis were collected at room temperature on a Nonius Kappa CCD diffractometer with MoKα radiation (l = 0.71073 Å) and graphite monochromator. Structure was solved by direct method and refined against F^2 with the full-matrix, least-squares methods using SHELXS-97 and SHELXL-97, respectively.

Crystallographic data (excluding structure factors) for this structure have been deposited with the cambridge crystallographic data center as supplementary publication CCDC-229947.

The strutures of all isolated products were also characterized by m.p., IR, MS, ^1H and ^{13}C NMR and TLC[11,16].

RESULTS AND DISCUSSION

Single crystals of the title compound were obtained by slow evaporation of a Et_2O/hexane (1:4) solution. The ORTEP drawing of the molecular structure and selected bond lengths are given in Fig. 1. These data are in agreement with the structure deduced from the classical spectroscopic techniques.

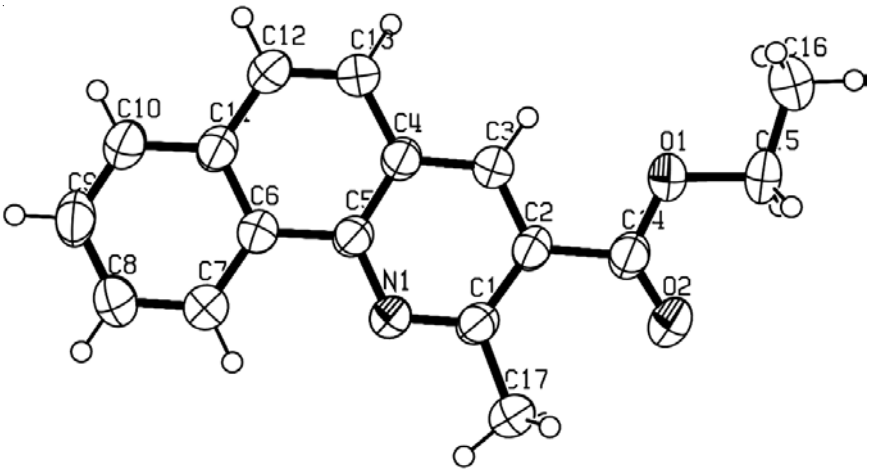
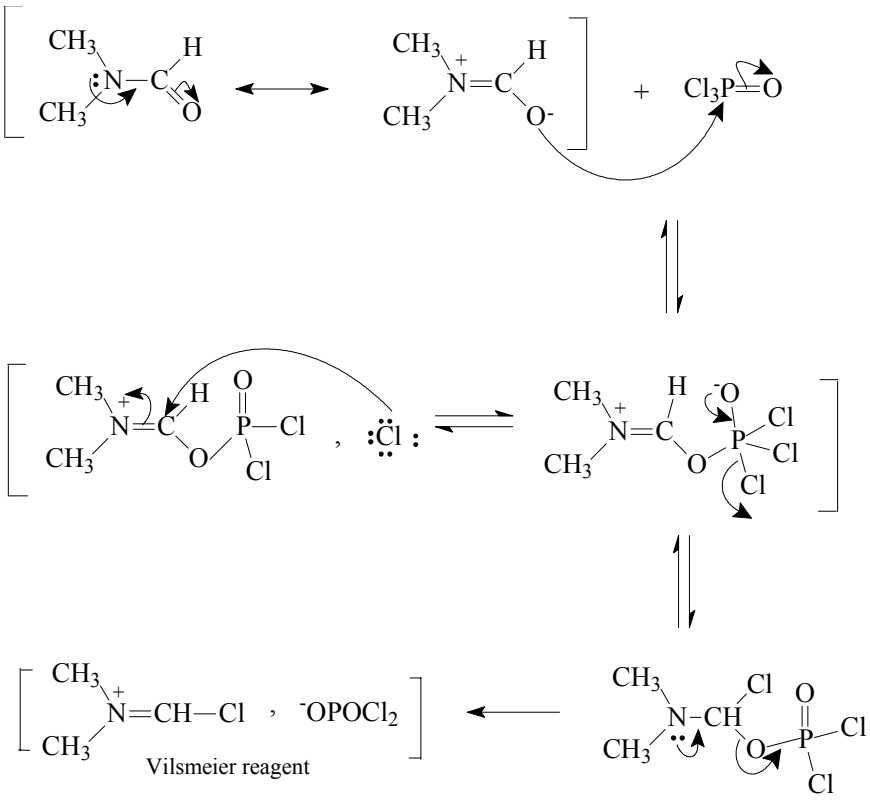


Fig. 1. ORTEP drawing of the title compound

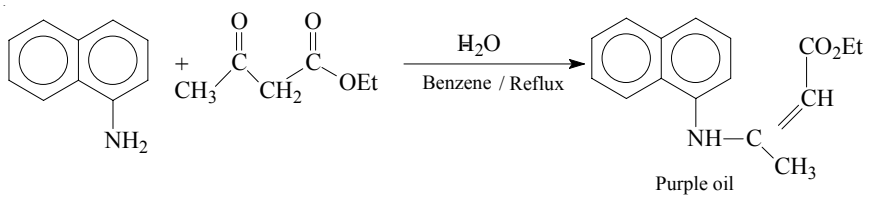
Crystal data: $C_{17}H_{15}NO_2$, m.w. = 265.30, triclinic, space group P-1, a = 7.2488(4), b = 7.4137(3), c = 12.8750(8) Å, α = 104.587(2), β = 90.061(2), γ = 92.418(2)°, V = 668.96(6) $Å^3$, Z = 2, Dc = 1.317 g cm^{-3}, R1 = 0.0661, wR2 = 0.1530 for 2312 observed reflections with I > 2σ(I).

Selected bond lengths: N1-C1 : 1.329(3), N1-C5 : 1.352(3), O1-C14: 1.344(3), O1-C15 : 1.452(3), O2-C14 : 1.201(3), C1-C2 : 1.424(3), C2-C3: 1.373(3), C2-C14 : 1.486(3) Å.

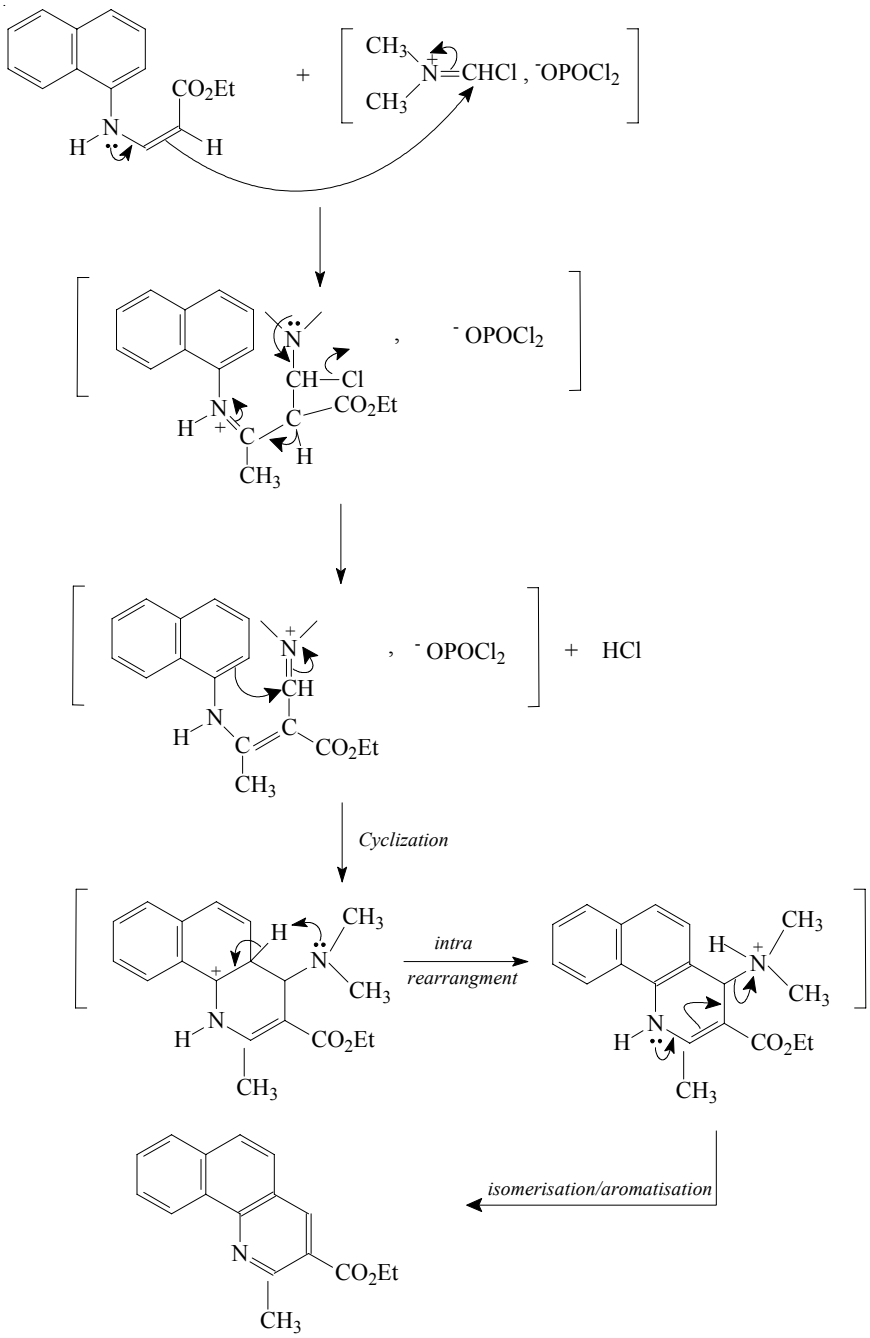
The extension and the aromatic character of the conjugated system confer to the product an important stability.



Step-I. Vilsmeier complex formation



Step-II. Arylenamine synthesis



Step-III. Cyclization and isomerization

Scheme-I. Potential mechanism scheme reaction

Conclusion

A facile and efficient synthesis of a new benzoquinoline derivative from an enamine using Vilsmeier reagent is reported. In regard to biological and potential antimalaria activities of benzoquinoline derivatives, hemisynthesis reactions work and offer a practical access to the metal complex derivatives of the title compound, which are under investigation in our group.

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