

Synthesis and spectroscopic characterization of halogen- and cyano- substituted pyridinevinylene model compounds for fluorescent properties

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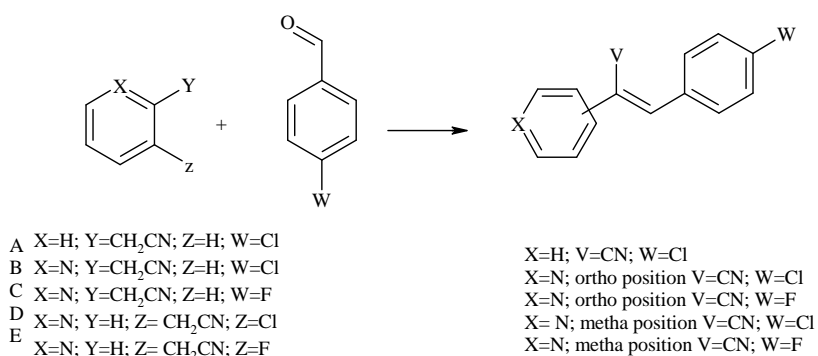
1. Abstract

The present work reports the reactions conditions to obtain model structures of novel pyridinevinylene compounds with terminal Cl or F, as well as compounds with a –CN group on the C=C linkage to evaluate their spectroscopy properties. 2,6-Lutidine, 2,4-lutidine, 2-pyridylacetonitrile, 3-pyridylacetonitrile, 4-pyridylacetonitrile and phenylacetonitrile were reacted at a molar relation adequate with to corresponding *p*-fluorobenzaldehyde, *p*-chlorobenzaldehyde to estimate the reactivity of –CH₂CN or CH₃ group. The compounds were characterized by IR, ¹H-NMR, and Mass spectrometry.

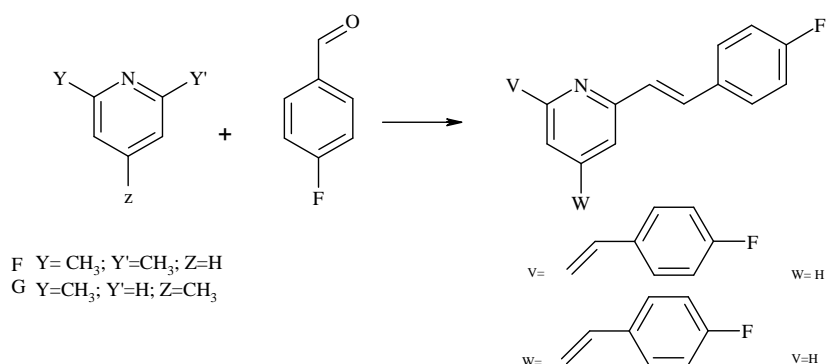
2. Introduction

Considerable attention has been given in recent years to developing reactions under solvent-free conditions[1]. The Knoevenagel condensation reaction was originally reported in 1896. Since then, systematic studies in the literature have been reported[2-4]. For example, a series of alkylidene cyanoacetic esters were prepared by condensing ketones with methyl cyanoacetate using secondary amines such as piperidine and diethylamine as catalysts. Other authors have shown that the Knoevenagel condensation is a complex reaction that depends not only on the relative reactivity of the reactants, but also on the strength of the employed bases, the nature of the solvents and their dissociating powers, as well as the present of side reactions. The difficulty of controlling all experimental conditions likely explains why the Knoevenagel condensation has been not widely employed or studied since the 1960s.

“Green chemistry” syntheses without catalyst or solvent have previously been applied to obtain several styrylpyridines and interesting intermediates[5,7]. In this work, the same solvent-free, catalyst-free conditions were used for the syntheses of ten conjugated molecules. Pyridinevinylene compounds with terminal Cl or F, as well as molecules with a –CN group on the C=C linkage, were synthesized in order to obtained compounds with fluorescent properties. Only temperature was used to control the reactions; the products were precipitated using a 2N NaOH solution. Each compound (schemes 1 and 2) was characterized by IR, ¹H-NMR and Mass spectrometry.



Scheme 1



Scheme 2

3. Experimental part

3.1. Materials and instruments

2,6-Lutidine, 2,4-lutidine, phenylacetonitrile, 2-pyridylacetonitrile, 3-pyridylacetonitrile, *p*-fluorobenzaldehyde, *p*-chlorobenzaldehyde, were acquired from Aldrich Chemical Co. and were distilled before used. IR spectra of the products were recorded on a Vertex model 70 Bruker 750 FT-IR spectrophotometer by ATR. ¹H-NMR spectra were obtained on a Varian 300-MHz NMR spectrometer in CDCl₃. Melting points were measured using an SEV (0–300 °C) apparatus and are uncorrected

3.1 Syntheses of compounds

The condensation reaction was made according to scheme 1. The compounds A to E were obtained from the corresponding acetonitrile with the corresponding aldehyde at a molar ratio of 1:1. The mixtures were reacted at a temperature between 120 °C and 140 °C

with a reaction time between 20-40 h. The condensation reaction for compounds scheme 2. The compounds were obtained from the lutidine with the corresponding aldehyde. The molar ratio of the lutidine to the other reactant was 2:1. The mixtures were reacted at temperatures between 120 and 140 °C using reaction times of 20-24 h, for the compounds on Scheme I.

All reactions were carried out at reflux in absence of any condensing agent or solvent. At all times during the reaction, the mixtures appear oily with a brown to red color. The mixtures were treated with a solution of NaOH 2N to precipitate the products as powders. These products were purified by recrystallization with hexane or cyclohexane and characterized by IR ^1H -NMR and Mass spectrometry

4. Results and discussion

Schemes I and II show the reactions used to produce the compounds with and without cyano groups in their structures. To obtain the target compounds, the reaction temperature, time and the presence of substituents -F, -Cl and -CN play important roles in the products formation. The condition reactions were better than other reactions reported previously under the same conditions[6-10].

4.1 FTIR, NMR and Mass characterization

The FTIR spectra of all compounds showed characteristic bands assigned to the double bond $\nu(\text{-C=C-})$ of alkenes conjugated with an aromatic ring[11-13] as well as bands characteristic of a -C-H out of plane bending vibration for a double bond in the *trans* configuration(scheme 2). Also the bands for C-F and C-Cl were detected. The observed IR peaks are consistent with the expected structures. From ^1H -NMR, the principal evidence[13]for the formation of compounds were the doublets due to protons in the *trans* position of a double bond. The IR characterization of compounds showed bands assigned to stretching $\nu(\text{C=C})$ of a double bond shifted to a higher wavelength than is typical, suggesting that the -CN group has been attached to the double bond. The reaction conditions of compounds allowed to obtain these compounds with a good yield, with shorter reaction times than the other compounds, and without the problem of separation

after reaction. These attributes may be explained by the high reactivity of $\text{-CH}_2\text{CN}$ through the nitrogen atom in the structure.

5. Conclusion

A series of highly soluble pyridinevinylene derivatives containing either two or three rings (pyridine or benzene) were prepared from a halogen-substituted benzaldehyde with acetonitrile. They were prepared via the Knoevenagel route using green chemistry conditions (without solvent or catalyst).

6. References

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Acknowledgements

The authors acknowledge VIEP, CONACYT for financial support (Projects: 00094, 44237 and 46360).