



Model Studies of the Doebner Modified Knoevenagel Condensation

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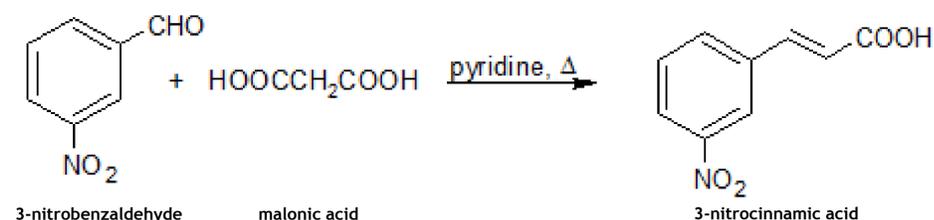
Abstract

Previous work¹⁻⁶ on an initial model system for the synthesis of polyaromatic dyes for potential use in solar energy collection used the Doebner modified Knoevenagel condensation. This project is continuing the work on this approach to establish its viability.

Introduction

Previous work on the Doebner modified Knoevenagel condensation under investigation¹ (Fig. 1) resulted in poor material recovery (34.8%) and an impure product. The first step in the current project is to reinvestigate the reaction conditions, work-up protocol and purification techniques of the original protocol to optimize product formation and simplify the procedure where possible.

Figure 1



Experimental

Trial 1: 20 mL of pyridine, 0.500g of 3-nitrobenzaldehyde, and 0.344g of malonic acid were added to a 50-ml round-bottomed flask (RBF) with a magnetic stir bar. The solution was allowed to reflux for two hours. The reaction solution was acidified using 6M HCl, which caused precipitation of a white solid. The mixture was stored in the freezer overnight to accommodate further precipitate formation. The mixture was filtered *via* vacuum filtration resulting in collection of an off-white solid and a clear and colorless filtrate. The dried solid weighed 0.198g. and thin layer chromatography (TLC) analysis using 5% ethyl acetate in methylene chloride indicated two substances were present, indicating the need to further purify the material. The recovered solid was then purified using silica gel column chromatography using a 5% ethyl acetate in methylene chloride. The recovered white solid was then characterized using H-NMR.

Trial 2: 5mL of pyridine, 0.5001g of 3-nitrobenzaldehyde, and 0.348g of malonic acid were used. This reaction was allowed to reflux for 24 hours. The work-up conditions and separation techniques remained identical to trial one. The collected solid weighed 0.539g.

Trial 3: 5 mL of pyridine, 0.5001g of 3-nitrobenzaldehyde, and 0.345g of malonic acid were allowed to reflux for two hours. The work-up conditions and separation techniques remained identical to trial one. The recovered solid weighed 0.674g.

Purification of the solids obtained from trials two and three will be completed using silica gel column chromatography using 5% ethyl acetate in methylene chloride.

Table 1

Trial #	Volume of Pyridine (mL)	Mass of 3-nitrobenzaldehyde (g)	Mass of malonic acid (g)	Reflux Time (hours)	Material recovered (g)
1	20	0.5	0.344	2	0.198
2	5	0.501	0.348	24	0.539
3	5	0.501	0.345	2	0.674

Results and Discussion

The original procedure utilized a second nitrogenous base in addition to the pyridine solvent. It was decided that pyridine alone could function as both solvent and base. Because H₂SO₄ can act as an oxidizing agent, HCl was chosen as the work-up acid due to its non-oxidizing nature.

Because this reaction is second order, concentration of reactants is crucial to reaction rate and product formation. The original researchers use of heat to remove the pyridine solvent by evaporation was now postulated to be a critical part of product formation. Upon reducing pyridine volume to 5mL, the amount of material collected in trials 2 and 3 rose significantly. (Table 2)

Table 2

Trial #	Material Recovered (%)
Original	34.8
1	23.5
2	63.5
3	79.7

The next step is to purify the solid materials recovered and determine percent yield of any 3-nitrocinnamic acid produced. Based on these results, it will be possible to further determine whether an extended reaction time is necessary.

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References

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