Synthesis of a Photo cleavable Initiator from 3-Hydroxybenzaldhyde

Michael DeGirolamo, Deepthi Bhogadhi
Department of Chemistry, University of New Hampshire, Durham, NH
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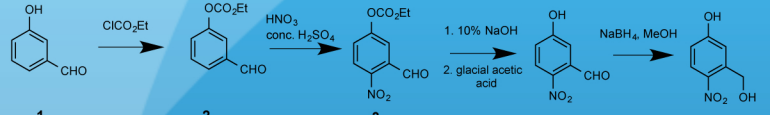
Introduction

The synthesis of 5-hydroxy-2-nitrobenzyl alcohol (**5**) was initially investigated to some degree by Cava and Skiles in 1978 during their synthesis of a subsessiline. Their work was further examined by Kang and Moon in 2009 as a part of forming photocleavable initiator. The goal of this experiment is to synthesize **5** starting from 3-hydroxybenzylaldehyde (**1**) which can be used to synthesize a photocleavable intiator in star-polymer synthesis. The first step in the synthesis is to protect the alcohol 1 on 3-hydroxybenzaldehyde with ethyl chloroformate. The protected alcohol was then treated with nitric and concentrated sulfuric acid to afford product **3.** The protecting group was removed using 10% NaOH to prodcue 5-hydroxy-2-nitrobenzylaldehyde (**4**). Kang and Moon took a product **4** from the subsessiline synthesis of Cava and reduced it using $NaBH_4$ to give **5** which can be used as a starting reagent to form a photo cleavable initiator in star-polymer synthesis.



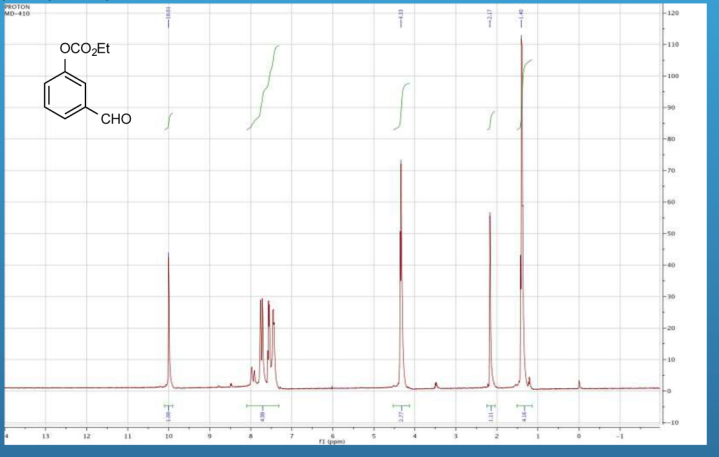
1 **2** 69% **3** 29% **4** **5**

Scheme 1: Synthesis of 5-hydoroxy-5-nitro-benzylalcohol starting from 3-hydroxybenzylaldehyde

Results and Discussion:

- The product from the first reaction gave a 69% yield and an NMR was taken and shown on the right
- The shift at 1.40 corresponds to the CH_3 group at the end of the -OCOOEt functional group, the shift at 4.33 corresponds to the CH_2 hydrogens on the -OCOOEt functional group these show that the protecting group was successfully added
- The shift at 7.3-8.1 correspond to the phenyl hydrogens
- The shift at 10.01 corresponds to the aldehyde hydrogen showing that the group was intact
- The melting point of the nitrated product **2** was 58-60 °C which is close to the literature value of 60-61 °C. the difference could be due to moisture in the product since it was broader and slightly lower
- The third step in the reaction scheme producing product **4** was unsuccessfully recrystallized from crude in ethanol:water leading to an incorrect NMR

Reagents	Results
3-hydroxybenzaldehyde **1**, $ClCO_2Et$ in pyridine	5.21 g, 69%yield, correct product shown by NMR
Ethyl-3-Formylphenyl Carbonate, HNO_3 in conc. H_2SO_4	1.52 g, 29% yield MP 58-60 °C
Ethyl 3-Formyl-4-nitrophenyl Carbonate **2**, 10%NaOH, glacial acetic acid	Product unsuccessfully recrystallized form crude in ethanol:water



Conclusions: The first few steps of the reaction where successful and proven by NMR and melting point comparisons to literature. The third step was unsuccessfully recrystallized in ethanol:water. A column could be run to purify the sample further and receive the desired compound.

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References:

1. Cava, Michael P, Skiles. Jerry W; Subsessiline Structure Revision and Synthesis; *Journal of Organic Chemistry*, **1979,** 44(3), pp409-411
2. Kang, Minhyuck, Moon Bongjin; Synthesis of Photocleavable Poly(styrene-*block*-ethylene oxide) and Its Self-Assembly into Nanoporous Thin Films; *Macromolecules*, **2009,** 42 (1), pp 455-458