

Effect of Phenyl Substituents on the Photosolvolytic of 9-phenyl-9-Fluorene

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ABSTRACT: The goal of this research is to photosolvolyze 9-phenyl-9-fluorene derivatives **2a-f**. The synthesis of these compounds will start with 9-fluorenone and will be made through lithiation or a Grignard reagent. We have created a synthesis for compounds **2d** and **2c**, and are still working on synthesizing **2a**, **2b**, **2e**, and **2f**. After we find a synthesis process that works for all six derivatives, we will photosolvolyze each of them to try to find a structure reactivity relationship between various electron donating and electron withdrawing groups.

Introduction The design of chromophores that undergo photosolvolytic has been a recent highlight in the research produced by the Winter laboratory. Their and many other groups' use of the boron-dipyrrromethane (BODIPY) scaffold has allowed for the utilization of photosolvolytic reactions initiated with visible radiation to perform the decaging of molecules¹⁻⁴ and for imaging techniques⁵ with spatio-temporal control. An earlier study conducted by Wan and Krogh investigated the photosolvolytic of 9-fluorene and select derivatives.⁶ Their study is an important example in the difference in reactivity that occurs between thermal and photochemical solvolysis reactions. Those derivatives that were able to generate a carbocation intermediate that was stabilized by Hückel's Rule of aromaticity facilitated solvolysis thermally, but not photochemically. However, if a carbocation intermediate instead breaks Hückel's Rule and is antiaromatic, that system underwent photosolvolytic, such as 9-fluorene exhibits (**Figure 1**).

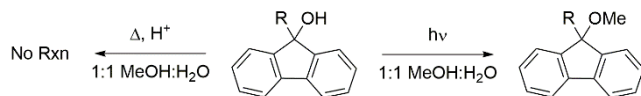
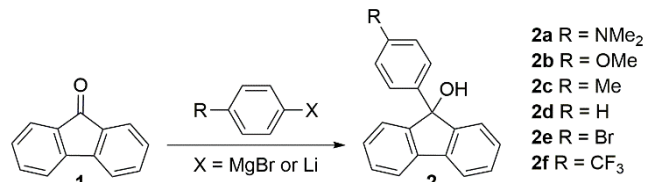


Figure 1: Solvolysis of 9-fluorene occurs under irradiation in a 1:1 methanol:water mixture, but not when heated in the presence of acid in a 1:1 methanol:water mixture.

This striking difference in thermal versus radiative pathways lead us to wonder what other ideas of stabilization via thermal reactions would be flipped when undergoing a radiative pathway? Specifically, we desire to investigate how electronic effects will affect the carbocation intermediate in a photosolvolytic reaction? To accomplish this, derivatives of 9-phenyl-9-fluorene will be synthesized and their rate of photosolvolytic will be determined. This work is still in progress, so this paper will discuss what has been accomplished to date.

Results and Discussion The desired compounds to be tested will be synthesized, starting with 9-fluorenone (**1**), via 1,2-addition to the carbonyl carbon with either phenyl Grignard reagents or phenyl-lithium compounds (**Scheme 1**). The desired substituents to replace the hydrogen at the para-position of the phenyl group to provide evidence for the electronic effects on the rate of photosolvolytic of 9-phenyl-9-fluorene will be: dimethylamino, methoxy, methyl, bromo, and trifluoromethyl.



Scheme 1: Proposed synthesis of compound **2a-2f**.

Successful synthesis of compounds **2c** and **2d** have been completed to date. The synthesis of **2d** is made simpler with the commercial availability of phenylmagnesium bromide. To 9-fluorenone dissolved in ether, the purchased phenylmagnesium bromide is added in excess. After washing the reaction mix with ammonium chloride, **2d** is isolated. The synthesis of the remaining analogues has proven to be considerably more troublesome. Contrary to our efforts, simple mixing of the corresponding phenyl bromide with magnesium turnings in dry diethyl ether or tetrahydrofuran yielded little to no Grignard formation. Attempts expose fresh magnesium metal via physical means, chiefly, breaking the turnings into smaller pieces or grinding with a mortar and pestle, did little to aid in the formation of the Grignard. Following the work from Zhang, et. al.⁷, magnesium powder was utilized, but with no success in Grignard formation.

A review of Grignard formation by Garst and Soriaga⁸ has yielded some promising results in the synthesis of **2c**. 4-bromotoluene was added to magnesium turnings in tetrahydrofuran, which was subsequently sonicated for 60 minutes. This facilitated the formation of the desired Grignard reagents, to which 9-fluorenone was added. After washing the reaction mix with ammonium chloride, compound **2c** was able to be isolated. It was also found that addition of 1,2-dibromoethane in a catalytic amount, with or without sonication, also showed consumption of the magnesium, with addition reducing the time required during sonication to 30 minutes.

With the limited success in the synthesis of compounds **2** via Grignard reagents, we attempted using lithium-halogen exchange to produce the desired compounds. To synthesize compound **2b**, a procedure was adapted from Zeng, et. al.⁹ with promising, but not confirmed, results. 4-bromoanisole was dissolved in dry tetrahydrofuran under an inert atmosphere and cooled to -78°C . To this solution was added *n*-butyl lithium dropwise and allowed to stir at -78°C for 60 minutes, which was followed by dropwise addition of 9-fluorenone dissolved in dry tetrahydrofuran. The reaction was allowed to warm to room-temperature overnight and washed with ammonium chloride. Development of thin-layer chromatography plates indications consumption of the starting 9-fluorenone and the appearance of a new, more polar compound, but isolation of this spot has not been achieved as of yet.

Conclusion Progress has been made in the synthesis of compounds **2a-f**. In this work, compounds **2c** and **2d** were synthesized and isolated. Efforts will continue to troubleshoot the synthesis of the remaining compounds. After successful synthesis and isolation of the remaining compounds of interest, testing of the photosolvolytic rate in a 50% methanol/water mixture will commence. This study should result in the discernment of the electronic effects on the rate of photosolvolytic, and lead to ideas of how photogenerated

carbocations can be further stabilized, facilitating further enhancement of other photochemical reactions.

Experimental Section

9-phenyl-9-flourenol (2c): A 2-neck round-bottom flask was dried in a 110°C oven overnight. The flask was removed from the oven, was charged with a magnetic stir bar, connected to a condenser on one port and a septa added to the other port. The system was then evacuated and allowed to cool to room temperature under vacuum. After cooling, the system was filled with nitrogen gas. 9-flourenone (**1**) (0.2 g, 1.11 mmol) was dissolved in 2 mL diethyl ether and the mixture syringed into the 2-neck flask. To the system was then added phenylmagnesium bromide (3 M in diethyl ether, 0.75 mL, 2.22 mmol) dropwise. The reaction was allowed to stir at room temperature for one hour. The reaction was quenched with saturated ammonium chloride and extracted with dichloromethane. The organic layer was dried over sodium sulfate and the solvent removed under vacuum. The residue was purified by column chromatography (silica gel, 1:10 ethyl acetate:hexanes) to afford 9-phenyl-9-flourenol (**2c**) as a white solid.

9-(p-tolyl)-9-flourenol (2d): To a 3-neck round-bottom flask was added magnesium turnings (0.2914 g, 12 mmol), THF (4 mL), and 4-bromotoluene (2.0514 g, 12 mmol). Two ports were sealed with septa and one was connected to a condenser. The system was then sonicated for 5 minutes. A glass stir rod was then used to crushed the Mg turnings, 2-3 drops of 1,2-dibromoethane added, and the system sonicated again for an additional 30 minutes. After 30 minutes of sonication, the solution had turned a gray-brown color. A solution of 9-flourenone (**1**) (0.1036 g, 0.6 mmol) in THF (2 mL) was then added slowly to the flask via a syringe. The vial containing the 9-flourenone solution was rinsed with 1 mL THF and added. After stirring overnight at room temperature, the reaction was quenched with ammonium chloride and extracted with diethyl ether. The organic layer was dried over sodium sulfate and the solvent removed under vacuum. The residue was purified by column chromatography (silica gel, 1:10 ethyl acetate:hexanes) to afford 9-(p-toyl)-9-flourenol as a white solid.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest.

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