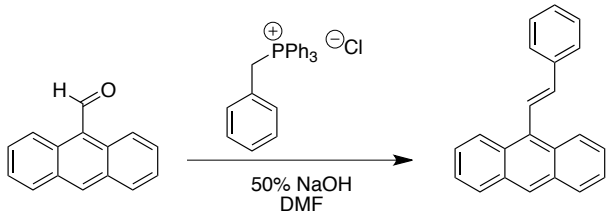
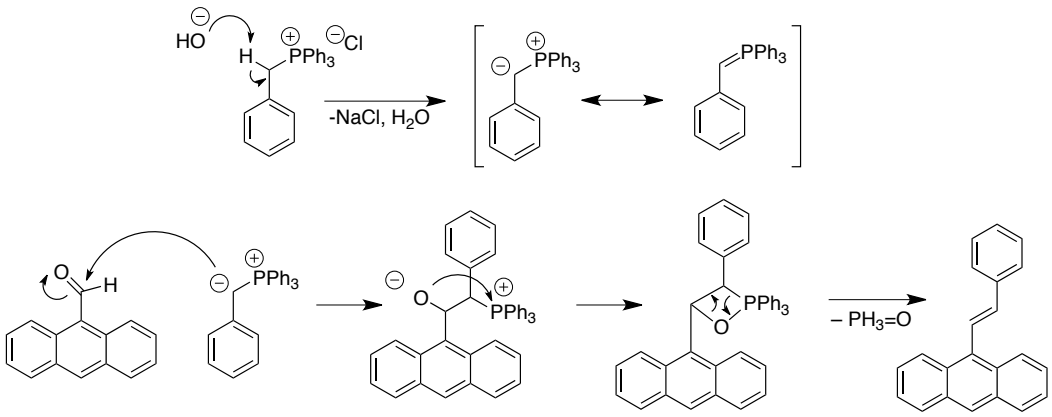
The WITTIG REACTION With CHEMILUMINESCENCE!

In the Wittig reaction, an aldehyde or ketone is treated with a phosphorous ylide (also called a phosphorane) to give an olefin. Phosphorus ylides are usually prepared bytreatment of a phosphonium salt with a base, and phosphonium salts are usually prepared from the phosphine and an alkyl halide.



The key step of the mechanism is the formation of the oxaphosphetane, the cyclic intermediate. Wittig reactions can give either the E or Z isomer of the alkene depending on the nature of the phosphonium reagent. In this reaction, we expect primarily the E isomer.

Mechanism:



PART I. Synthesis of trans-9-(2-Phenylethenyl)anthracene

In a 25-mL Erlenmeyer flask place a small stir bar, 0.50g of 9-anthraldehyde, 0.87g of benzyltriphenylphosphonium chloride. Dissolve the mixture in 6 mL of DMF. Vigorously stir the mixture for at least 5 minutes. Carefully added 0.200 uL (10 drops) of 50% sodium hydroxide (50% NaOH w/w) solution to the rapidly stirred reaction mixture. Use the DMF in the flask to wash any solid off the walls of the Erlenmeyer flask. Note: The reaction changes color during this period, starting out dark yellowish and ending reddish-orange after 30 minutes.

After stirring vigorously for 30 minutes, added 4 mL of a 1:1 of 1-propanol/distilled water to precipitate the product (yellow solid). Collect the crude product by vacuum filtration.

Recrystallize the crude product with as little 1-propanol as possible (ca. 4 mL). After recrystallization, a yellowish crystalline solid is obtained.

DCM = Dichloromethane
DMF = N,N'-Dimethylformamide
NaOH = Sodium Hydroxide

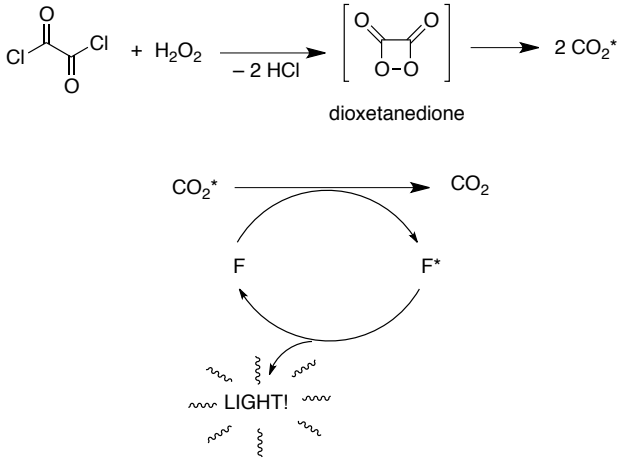
Note: Use a Pasteur pipette with bulb to measure out the 0.200 uL (10 drops) of 50% NaOH. The pipette must be held exactly vertically straight for the desired amount.

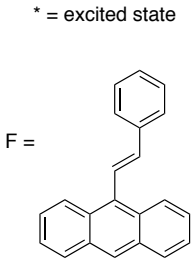
Part II. Procedure for Chemiluminescence

In a 13-100mm test tube, placed 2 mL of 10% oxalyl chloride/dichloromethane solution, 2 mL of

DCM, 1 mg of the fluororescer, and 2 mL of 30% hydrogen peroxide.
In a darkened hood, mix the solution thoroughly with a Pasteur pipette and bulb. Record observations. Color: Light-blue color lasts for 10 seconds and turns purple color for an additional 15 to 30 seconds.

Mechanism for Chemiluminescence





SAFETY NOTE:

Caution should be use when handling the following reagents due to their corrosive properties: dichloromethane, sodium hydroxide, oxalyl chloride, and hydrogen peroxide. Assume all reagents and products are toxic. Wear gloves at all times.

Note for Lab Services:
The 10% oxalyl chloride in dichloromethane should be prepared fresh. In addition, each lab section should have its own bottle. If the bottle is left uncapped, results will differ from section to section therefore it is best for each lab section to have their own.

Prelab Questions:

1) Please describe how one would make the phosphonium salt used in this reaction. Please draw the reaction and show the mechanism.
2) In lecture, we described that strong bases such as BuLi are often required to deprotonate phosphonium salts, yet in this reaction we can use NaOH hydroxide. What is the pka' (that is the pka of the conjugate acid) for both of these bases? Why, in this reaction, can we use such a relatively weak base as NaOH? Please illustrate with using molecular orbital drawings and resonance structures.
3) In this reaction, E and Z alkene isomers could potentially form, yet only the E isomer is observed. Please speculate as to why.

Postlab Questions:

1) Why is the product from this reaction colored? Please include a discussion of the appropriate orbitals in your answer.
2) Why does the product precipitate from the reaction mixture when IPA/water is added to the DMF solution?
3) What is the fate of the $Ph_3P{=}O$ by product in this reaction?
4) Write a mechanism for the formation of dioxetanedione from the chemiluminescence step.