Microscale Preparation of Difluorenylidene and trans-2,3-Dibenzoylspiro[cyclopropane-1-9'-fluorene]

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Of the experiments involving fluorene derivatives (1–15), the oxidation of fluorene to fluorenone (1–5) and the reduction of fluorenone to fluoreneol (6–8) are the most common. This synthetic sequence can be extended by converting fluoreneol to 9-chlorofluorene, the latter serving as a precursor to the title compounds.

The formation of 1 appears to be complete within 2 min, as indicated by TLC. A most likely mechanism, involving fundamental organic paths, is deprotonation at C-9 with S$_2$2 displacement of chloride ion by the anion of 9-chlorofluorene to give an intermediate that undergoes E2 elimination, generating 1 as shown below (16). In these reactions, F1 represents fluorene and B is the base.
Compound 1 is prepared by adding a sulfolane/methanol solution of potassium hydroxide to a sulfolane solution of 9-chlorofluorenone, letting it stand for several minutes, adding water to precipitate 1, centrifuging, washing with water, and recrystallizing from dichloromethane/ethanol. Student yields range from 5 to 25 mg (12–81%) and average 30%. Manipulation of such small quantities is made practical by the vivid orange-red color and low density of this conjugated hydrocarbon.

When the reaction is done in methanolic potassium hydroxide solution, the mixture appears yellow after several days at 25 °C and 9-methoxyfluorenone can be isolated, demonstrating the ability of sulfolane to enhance base strength and promote the first mechanistic step leading to 1 (17).

The product that emerges on heating a sulfolane solution of equimolar quantities of 9-chlorofluorenone, base, and trans-dibenzoylethylene is not 1, but the spirocyclopropane 2 (18). The reaction is an example of tandem cycloaddition, an established method of cyclopropanation (19).

Students were given the puzzle of deducing the structure of the product from the IR, $^{13}$C, and $^1$H NMR spectra. The formation of 2 rather than 1 may be interpreted to mean that nucleophilic addition of the anion of 9-chlorofluorenone to dibenzoylethylene is faster than the $S_{N}2$ displacement of chloride ion from 9-chlorofluorenone. Yet the time required for 2 to emerge is longer than for 1. An apparent anomaly may be rationalized if it is assumed that the deep magenta color that immediately develops on the addition of base, and also in the absence of 9-chlorofluorenone, is due to a charge transfer or addition complex of base with dibenzoylethylene. The color fades as the reaction proceeds, and the rate-determining step may be the release of base from this complex.

Student yields are meager, averaging 34%, but the emphasis is on product identification. High yields of 2 are obtained by the action of 9-diazoxyfluorenone on trans-dibenzoylethylene (18, 20).

### Experimental Procedure

#### 9-Chlorofluorenone

To the crude fluorenol that was prepared from 400 mg of fluorenol in a 25 mL Erlenmeyer flask without isolation (7), add 5 mL of conc. HCl. Invert a 100-mL beaker over the flask and continue heating the mixture for 15 min. After this time, remove the flask and cool to room temperature. The product appears as a "glob" at the bottom of the flask.

Add the contents of the reaction vessel to 30 mL of ice-cold water in a 50-mL Erlenmeyer flask. Collect the solid on a small Büchner funnel at reduced pressure. Wash with small portions of deionized water until the filtrate allows blue litmus to remain nearly blue.

#### Recrystallization

Add 3–4 mL of ethanol to the product in a 25-mL Erlenmeyer flask and heat on a steam bath. If the solid does not dissolve, add ethanol in 1-mL increments with heat until solution occurs. Allow the mixture to cool to room temperature and then in an ice bath to maximize precipitation. Filter the solid on a Hirsch funnel at reduced pressure; wash dropwise with 1–2 mL of cold ethanol. Lit. mp 93–94 °C (21).

#### Difluorenylidene 1

Weigh ca. 50 mg (0.25 mmol) of 9-chlorofluorenone into a centrifuge tube. Add 0.4 mL (400 μL) of sulfolane. bp = 285 °C, from an automatic delivery pipet. Gently heat the tube and heat it on a steam bath or with a hair dryer to dissolve the solid. To this solution add 0.6 mL (600 μL) of 1M KOH in sulfolane/methanol (4:1). Mix the contents on a vortex mixer and note the changes that occur. While the mixture stands for 10 min or longer, compare the appearance with that of the same reaction done in methanol or ethanol (which has been prepared earlier by the instructor).

#### Isolation and Purification

Add ca. 5 mL of deionized water to the tube to precipitate the product from solution. Use of a vortex mixer maximizes contact between the organic solution and the water.

**CAUTION:** Difluorenylidene can stain the skin. Wear gloves.

Centrifuge the tube. Remove the supernatant liquid with a Pasteur pipet. Wash the solid twice with deionized water, using the centrifuge as before. Add dichloromethane dropwise to the wet solid at the bottom of the tube until the product just dissolves. Then add ca. 5 mL of ethanol. On standing for several minutes, the purified difluorenylidene will emerge. Chill in an ice-water bath to maximize precipitation. Collect the solid at reduced pressure on a Hirsch funnel; wash the solid with a few drops of cold ethanol. Lit. mp 190 °C (22). TLC (silica gel, pet ether) $R_f$ = 0.16; $R_f$ 9-chlorofluorenone = 0.33.

#### trans-2,3-Dibenzoylethylene (cyclopropane-1,9-fluorene) 2

Weigh exactly 80 mg (0.080 g, 0.400 mmol) of dry 9-chlorofluorenone, prepared previously into an 11-mL glass vial. To this solid, add from a graduated pipet 1.5 mL of a 0.266 M solution of trans-dibenzoylethylene (0.400 mmol) in sulfolane. Cap the vial and dissolve the 9-chlorofluorenone by swirling or with the aid of a vortex mixer.

Using an automatic delivery pipet, add to the mixture 0.40 mL of 1 M potassium hydroxide in sulfolane/methanol (4:1). Note the changes that occur. Place the capped vial in a 100-mL beaker partly filled with water and heat on a steam bath for about 5 min. There will be a pronounced color change. Alternatively, the vial may be suspended within the steam bath for ca. 20 min. After heating, remove the vial from the beaker and add 5 mL of 95% ethanol with swirling to homogenize the mixture. A tiny crystal of the product may be added. Store the labeled vial in a refrigerator until the next period, at which time the product will emerge. At the next period, use a Pasteur pipette to remove the supernatant liquid. Add 1 mL of cold ethanol to wash the crystals and remove the wash liquid with a pipette. Wash with another 1 mL of cold ethanol and finally with 1 mL of a 1:1 ethanol/water mixture to leave a nearly colorless product.

#### Purification

The mp of this crude material is <180 °C. Recrystallize the product by dissolving it in ca. 1 mL of acetone and adding 4–5 mL of ethanol. Precipitate the product by chilling in an ice-water bath. Collect it on a Hirsch funnel at reduced pressure and wash with a few drops of cold ethanol. Lit. mp 203 °C (20). Examine ca. 1 mg of the product for the presence of a carbon–carbon double bond.
bond by the use of dilute aqueous potassium permanganate with tert-butyl alcohol as the solvent.

IR (CHCl₃) ν 3010, 1610, 1450, 1341, 1300, 1210 cm⁻¹

¹H NMR (CDCl₃) δ 7.2–7.8, aromatic multiplet 18 H; 4.60 s 2H

¹³C NMR (CDCl₃) ppm 193, 141, 140, 137, 133, 128.6, 128.3, 127.8, 127.5, 122, 120, 45, 40

Literature Cited