7. Preparation of a Positive Photoresist

Topic: photochemistry, photolithography  
Level: undergraduate organic chemistry  
Time: 6 hours  
Equipment: microscope slides, heavy-walled suction filtering flask, buchner funnel, filter paper, opaque stencil/mask  
Chemicals: 2-diazo-1-naphthol-5-sulfonic acid sodium salt monohydrate, chlorosulfonic acid, 4-methoxyphenol, triethylamine, Novolac resin, petroleum ether, acetone, tetrahydrofuran

Abstract

This experiment involves the preparation of a solution inhibitor, 1-diazo-1,2-naphthoquinone-5-(4-methoxyphenyl) sulfonate and subsequent use of this molecule as part of a simple positive photoresist.

Introduction

This experiment involves the preparation of 1-diazo-1,2-naphthoquinone-5-(4-methoxyphenyl) sulfonate and subsequent use of this molecule as part of a simple positive photoresist. The procedure is adapted from one originally developed by Bramwell et al.\textsuperscript{1} Diazonaphthoquinones are used as solution inhibitors because of their insolubility in the aqueous base solutions typically used to develop positive photoresists. Upon photoexcitation, the diazonaphthoquinones undergo a Wolff rearrangement to form an indenecarboxylic acid which is soluble in aqueous base, thereby allowing dissolution of the photoresist.

\begin{center}
\begin{tikzpicture}
\node (start) at (0,0) {1-diazo-1,2-naphthoquinone-5-sulfonate};
\node (end) at (3,0) {indenecarboxylic acid};
\node (inhibitor) at (1.5,0) {solution inhibitor};
\node (soluble) at (3,0) {aqueous base soluble};
\node (insoluble) at (0,0) {aqueous base insoluble};
\node (rearrangement) at (1.5,0) {Wolff rearrangement};

\draw[->] (start) -- node[above]{$\text{hv}$} (inhibitor);
\draw[->] (inhibitor) -- node[above]{$\text{N}_2$} (soluble);
\draw[->] (soluble) -- node[above]{$\text{H}_2\text{O}$} (end);
\end{tikzpicture}
\end{center}

Figure 1. Photoinduced Wolff rearrangement of a 1-diazo-1,2-naphthoquinone-5-sulfonate to yield an indenecarboxylic acid.

Background and Theory

Lithography is a technique used by the microelectronics industry in the fabrication of integrated circuits. In this context, the lithographic process involves using an exposure technique to transfer a pattern from a mask to a polymer film.
and finally to a semiconducting substrate. A variety of modes of exposure can be employed for this purpose including UV or X-ray radiation and electron- or ion-beams. The photolithographic process\textsuperscript{2,3} whose main features appear in Figure 1-1, employs UV radiation and is the primary technique currently used in industrial applications. Briefly, a thin film (0.5 -10 \(\mu\)m) of a photosensitive polymer, termed a resist, which has been spin-coated onto a semiconducting substrate is exposed to light through a mask. The mask is composed of a pattern which prevents light from reaching certain regions of the resist and allows it in other regions. Interaction of light with the resist induces a chemical change, creating a latent image of the pattern from the mask, in the resist. This photoinduced chemical change causes a difference in the dissolution rate between exposed and unexposed regions. Development of the resist with an appropriate solvent selectively dissolves the exposed or unexposed regions, producing positive or negative tone images, respectively. After the development step, regions of the substrate are left exposed, allowing them to be etched, thereby transferring the pattern to the substrate. Finally, the remaining resist is washed away to leave the bare, patterned substrate. Repetition of these steps with different masks and resists allows for the construction of detailed 3-dimensional circuit patterns.

![Figure 2. Schematic representation of the photolithographic process.](image-url)
The first positive resists were composed of a diazonaphthoquinone sensitizer and a copolymer of variously substituted phenols with aldehydes, termed Novolacs, as the polymer resin. In these positive resists, the exposed regions of the film become more soluble to an aqueous base developer than the unexposed regions. The solubility difference is derived from the fact that while Novolacs are soluble in aqueous base, diazonaphthoquinones are not, and their presence in sufficient amounts inhibits solubilization of the resist prior to exposure. As shown in Figure 1, the main photoproduct of the diazonaphthoquinone is base soluble, thereby allowing solubilization of the resist after exposure to light. Upon absorption of a photon, the diazonaphthoquinone loses nitrogen to form a carbene which undergoes Wolff rearrangement to a ketene. The ketene is attacked by water to form an indenecarboxylic acid.

**Equipment and Chemicals**

- microscope slides, heavy-walled suction filtering flask, buchner funnel, filter paper, opaque stencil/mask, 2-diazo-1-naphthol-5-sulfonic acid sodium salt monohydrate, chlorosulfonic acid, 4-methoxyphenol, triethylamine, Novolac resin, petroleum ether, acetone, tetrahydrofuran

**Procedure**

Note: The entire procedure must be performed in subdued light to avoid premature initiation of the Wolff-rearrangement. Whenever possible, manipulations should be performed in foil covered flasks.

Preparation of 1-diazo-1,2-naphthoquinone-5-(4-methoxyphenyl) sulfonate
1. Carefully add chlorosulfonic acid (7 mL) to a foil covered flask containing sodium 1-diazo-1,2-naphthoquinone-5-sulfonate (1.5 g) so as to maintain the reaction temperature below 60 °C. (Caution: Chlorosulfonic acid is toxic, corrosive and reacts violently with water.)
2. Heat the reaction mixture with stirring for 15 min at 65 - 70 °C. The temperature should not be allowed to go above 75 °C in order to avoid thermal activation of the Wolff rearrangement.
3. Cool the flask in an ice bath and add cold water (50 mL) dropwise such that the reaction temperature does not exceed 75 °C. (Caution: The addition of water will liberate large quantities of gaseous HCl and H₂SO₄.)
4. Collect the yellow precipitate of 1-diazo-1,2-naphthoquinone-5-sulfonyl chloride with vacuum filtration and dispose of the filtrate carefully.
5. Dissolve the 1-diazo-1,2-naphthoquinone-5-sulfonyl chloride in a minimum amount of tetrahydrofuran (~ 6 mL) and add 4-methoxyphenol (0.61 g).
6. To the solution add triethylamine (1 mL) dropwise with stirring and allow to stir for 30 minutes.
7. Add cold water (50 mL) to the reaction mixture and chill in an ice bath to precipitate out the product as a yellow solid.
8. Collect the solid using vacuum filtration, wash it with cold water until the washings are colourless (~25 mL), air dry and wash with petroleum ether (25 mL).
9. Dissolve a small amount of the product in deuterated chloroform and obtain an $^1$H NMR to identify it as the desired product and to determine purity.

Preparation of the Photoresist
1. Dissolve the Novolac resin (0.5 g) and 1-diazo-1,2-naphthoquinone-5-(4-methoxyphenyl) sulfonate (0.2 g) in acetone (10 mL) with stirring.
2. Being careful to protect the photoresist solution from light, place a few drops on a microscope slide so that the slide is completely covered with a reasonably uniform film of the photoresist.
3. Carefully place the microscope slide in an oven at 60 °C for 10 minutes so as to remove residual solvent.
4. Place a mask (such as a key, coin, or acetate sheet with opaque lettering) over the photoresist and place both in the Luzchem photoreactor equipped with 10 lamps and irradiate for a length of time sufficient to noticeably darken the colour of the photoresist film.
5. Prepare 100 mL of a solution of NaOH in water with a pH of 12 - 13 to use as a developer solution.
6. After the irradiation, dip the exposed microscope slide in the developer solution and gently swirl until dissolution of the exposed areas is complete.
7. Dip the microscope slide in water to remove excess developer and stop the development of the image.
8. Repeat the exposure and development steps with other photoresist films, varying both exposure time and development time to improve image resolution.

Questions
1. Many modern photoresists contain compounds such as diphenylsulfonyl diazomethane, (shown below) which photogenerate sulfonic acids. Draw the likely mechanism for photoinduced acid generation by this molecule.

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2. How would you change the photolithographic procedure employed here in order to improve the resolution/reproducibility of the developed image?
References