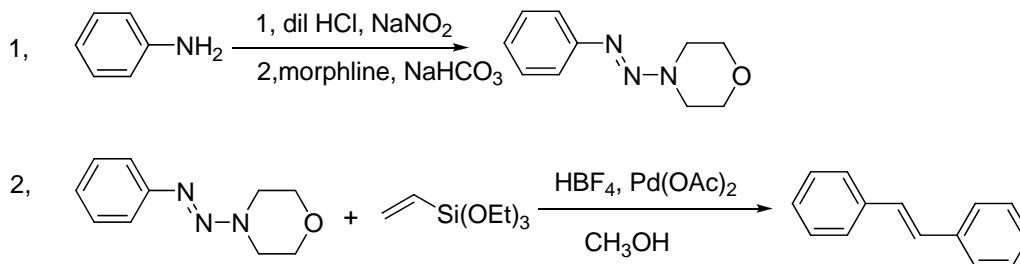


## 用乙烯基三乙氧基硅烷合成反式二苯乙烯



### 1、操作流程

#### A. 苯基偶氮吗啉

50 mL 锥形烧瓶中配一个搅拌磁子，加入 1.0 mL 苯胺(1.02g, 11.2 mmol)和 4.7 mL 6 N 盐酸(HCl) (27.3 mmol)，混合物在水浴上加热制成清澈的溶液。冷却到 0°C，产生大量沉淀。将 0.82 g 亚硝酸钠(11.9 mmol)溶于 1ml 水配成的溶液在 10 分钟内滴加到苯胺盐酸盐溶液中，0°C 下继续搅拌 20 分钟(Note 1)，在 10 分钟内将 1.2 mL 吗啉(1.1 g, 12.6 mmol)逐滴加入到上述溶液中。接着加入 12ml 水，再逐滴加入 17ml 10% NaHCO<sub>3</sub> 溶液(Note 2)。溶液继续搅拌 1 小时，将沉淀出的固体抽滤出来，用冷水洗涤，抽干。将固体溶于 10 mL 热石油醚(60-90°C)中，加 0.1g 活性炭处理。混合物趁热过滤，浓缩至 5 mL。冷却到 -25 °C，析出的固体尽快抽滤，空气中干燥后称重(Note 3)。

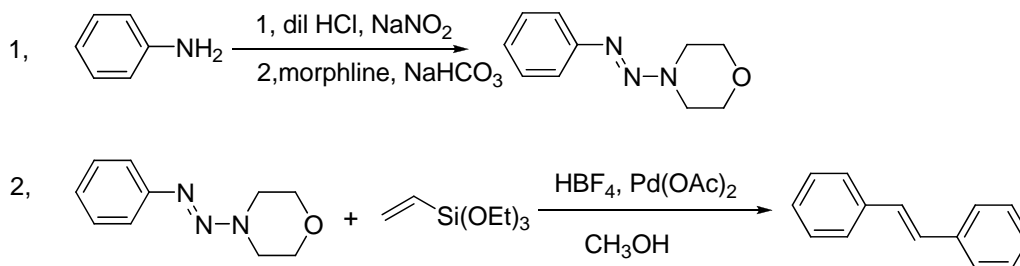
#### B. 反式二苯乙烯

50ml 圆底烧瓶中配一个搅拌磁子，加入 0.5g 上步制备的三氮化合物(2.6 mmol)和 6 ml 甲醇。溶液冷却到 0°C，在 10 分钟内将 1.2 mL 40% HBF<sub>4</sub>(5.5 mmol)逐滴加入。滴加完成后，移去冰浴，反应体系逐渐升温到室温。再搅拌 10 分钟(Note 4)，加入 6 mg Pd(OAc)<sub>2</sub>(0.026 mmol)，接着滴加三乙氧基乙烯基硅烷溶液(0.25 g, 0.28 mL, 1.3 mmol 溶于 0.5 mL 甲醇)。再加入第二批 Pd(OAc)<sub>2</sub> (0.006 g, 0.026 mmol)，并在室温下继续搅拌 30 分钟(Note 5)。混合物加热到 40°C 保持 20 分钟，最后加热到回流，保持 15 分钟(Note 6)。将溶液减压浓缩至一半体积，加 7-8 ml 水。将沉淀出的固体抽滤出来，水洗，空气中干燥。用乙醇重结晶纯化。

### 2. 注意事项

- 1、这时可得到清澈溶液
- 2、小心！有剧烈的 CO<sub>2</sub> 放出。产物开始沉淀。
- 3、小心！所有 1-芳基三氮化物都有毒，不要用手直接接触。
- 4、这一阶段溶液变清澈
- 5、一些产物生成后就沉淀出来
- 6、不经过 40°C 保持 20 分钟而直接加热到回流会降低产率。

## (E)- Stilbene using Silane, ethenyltriethoxy



### 1. Procedure

A. *Phenylazomorpholine*. In a 50-mL Erlenmeyer flask equipped with a magnetic stirring bar are placed *aniline* (1.02 g, 1.0 ml, 11.2 mmol) and 6 N *hydrochloric acid* (HCl), ( 4.7 mL, 27.3 mmol ) and the mixture is warmed on a water bath to make a clear solution. It is cooled to 0°C to produce a heavy precipitate. A solution of *sodium nitrite* (0.82 g, 11.9 mmol) in water (1 mL) is added dropwise over 10 min. Stirring is continued at 0°C for 20 min ([Note 1](#)), and *morpholine* (1.1 g, 1.2 mL, 12.6 mmol) is added dropwise to the above solution over 10 min. Water (12 mL) is added followed by the dropwise addition of 10% aqueous *sodium bicarbonate* solution (17 mL) ([Note 2](#)). After the solution is stirred for a further hour, the precipitated solid is filtered, washed with water and dried in air. The solid is dissolved in hot light petroleum (60-80°C) (10 mL) and treated with activated charcoal (0.1 g). The mixture is filtered while hot and the filtrate concentrated to ca. 5 mL. Upon cooling to -25°C, the precipitated solid is filtered, dried in air and weighed ([Notes 3](#)).

B *trans-stilbene*. A 50-mL round-bottomed flask equipped with a magnetic stirring bar is charged with the above triazene (0.5 g, 2.6 mmol) and *methanol* (6 mL). The stirred solution is cooled to 0°C and 40% *tetrafluoroboric acid* (HBF<sub>4</sub>, 1.2 mL, 5.5 mmol) is added dropwise over 10 min. After the addition is complete, the ice bath is removed and the reaction brought to room temperature. It is stirred for an additional 10 min ([Note 4](#)) and *palladium acetate* [Pd(OAc)<sub>2</sub>, 0.006 g, 0.026 mmol] is added followed by the dropwise addition of a solution of *vinyltriethoxysilane* (0.25 g, 0.28 mL, 1.3 mmol) in *methanol*(0.5 mL). A second lot of Pd(OAc)<sub>2</sub> (0.006 g, 0.026 mmol) is added and stirring continued for a further 30 min at room temperature ([Note 5](#)). The mixture is warmed to 40°C for 20 min and finally heated under reflux for 15 min ([Note 6](#)). The solution is concentrated under reduced pressure to half its volume and water (7-8 mL) is added. The precipitated solid is

filtered, washed with water and dried in air. It is then purified by recrystallization from ethanol.

## 2. Notes

1. At this point a clear solution is obtained.
2. *Caution: Vigorous evolution of carbon dioxide occurs.* The product began to precipitate.
3. *Caution: All 1-aryl triazenes are toxic and direct hand contact should be avoided.*
4. The solution became clear at this stage.
5. Some of the product, as it formed, precipitated.
6. Inferior yields were obtained when the reaction is heated directly under reflux without being held at 40°C for ca. 20 min.