

# 芳烃[5,5]-重排反应的研究进展

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收稿日期: 2021年10月11日; 录用日期: 2021年11月23日; 发布日期: 2021年11月30日

## 摘要

1,4-二取代芳烃结构广泛存在于许多天然产物及药物分子中。因此, 如何快速有效地实现芳烃分子的对位选择性C-H官能团化是化学研究人员关注的热点问题之一。芳烃对位直接引入所需官能团是合成1,4-二取代芳烃最为直接的途径, 但目前芳烃选择性对位C-H键官能团化依旧充满挑战。而芳烃[5,5]-重排为芳烃对位C-H键官能团化提供了独特的解决方案。本文主要针对Claisen型、联苯胺型及苯醌亚胺衍生物与苯酚的[5,5]-重排进行总结、归纳和分析, 并对该重排的发展做出展望。

## 关键词

[5,5]-重排, C-H键官能团化, 芳烃, 区域选择性

# The Progress of [5,5]-Rearrangement Reaction

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Received: Oct. 11<sup>th</sup>, 2021; accepted: Nov. 23<sup>rd</sup>, 2021; published: Nov. 30<sup>th</sup>, 2021

## Abstract

The ubiquity of 1,4-disubstituted arenes in natural products and drugs ensures a constant demand for their efficient and selective synthesis. Introduction of functionalities onto *para*-position of arenes is the most straightforward strategy for the synthesis of 1,4-disubstituted arenes. However, reports with respect to such transformation are rare, and developing an efficient method realizing remote *para*-selective C-H functionalization of arenes still remains a challenge. Aromatics [5,5]-rearrangement provides a unique solution for the functionalization of

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aromatic C-H bonds at the *para*-position. In this review, we will summarize and analyze Claisen-type, benzidine-type and reaction of phenol with iminobenzoquinone via [5,5]-rearrangement of aromatics, and make an outlook for the future development of this field.

## Keywords

[5,5]-Rearrangement, C-H Bond Functionalization, Aromatics, Regional Selectivity

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## 1. 引言

$\sigma$  重排反应是符合 Woodward-Hoffmann 规则的一种周环反应[1]。通过  $\pi$  电子及  $\sigma$  键的协同迁移重组构成新的分子结构。这类反应是有机化学中的一类重要反应, 具有独特的区域选择性和立体选择性, 并且可以实现分子结构重组及 C-C 键的形成。在各类  $\sigma$  重排反应中, 以 Claisen 重排为代表的[3,3]-重排, 由于化学、区域、立体选择性高, 而广受化学家们的关注[2]-[18]。在过去一百年间, 化学家对该类反应的关注度从未减少, 至今已有多钟类型的[3,3]-重排反应被发展出来, 包括 Claisen 重排[19] [20]、Cope 重排[21] [22] [23]、Overman 重排[24] [25] [26] [27]等多个人名反应。与此形成鲜明对比, [5,5]-重排反应研究较少。尽管利用前线轨道理论(FMO)对所涉及轨道对称性的分析表明, 最高占据轨道 HOMO 中两个 P 轨道的对称性是匹配的, [5,5]-重排在热学上是允许的, 反应是经过一个十元环的中间过渡态。但同时 [3,3]-重排在热学上也是允许的, 且是经过一个六元环椅式的中间过渡态, 所以一般很难避免[3,3]-重排反应的竞争[28]。基于此, 本文主要讨论芳烃[5,5]-重排反应, 包括 Claisen 型重排、联苯胺类的重排及苯醌亚胺衍生物与苯酚的重排。

## 2. Claisen 型芳基二烯基醚重排

早在 1968 年, Frater 和 Schmid 等人[28]发现 *N,N*-二乙基苯胺与芳基二烯基醚在 186°C 下反应 5 小时, 不仅能得到[3,3]-重排产物图 1 (3) (24%), 同时也意外得到了[5,5]-重排产物图 1 (2) (37%)。

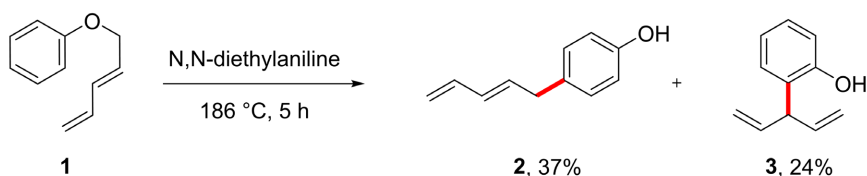
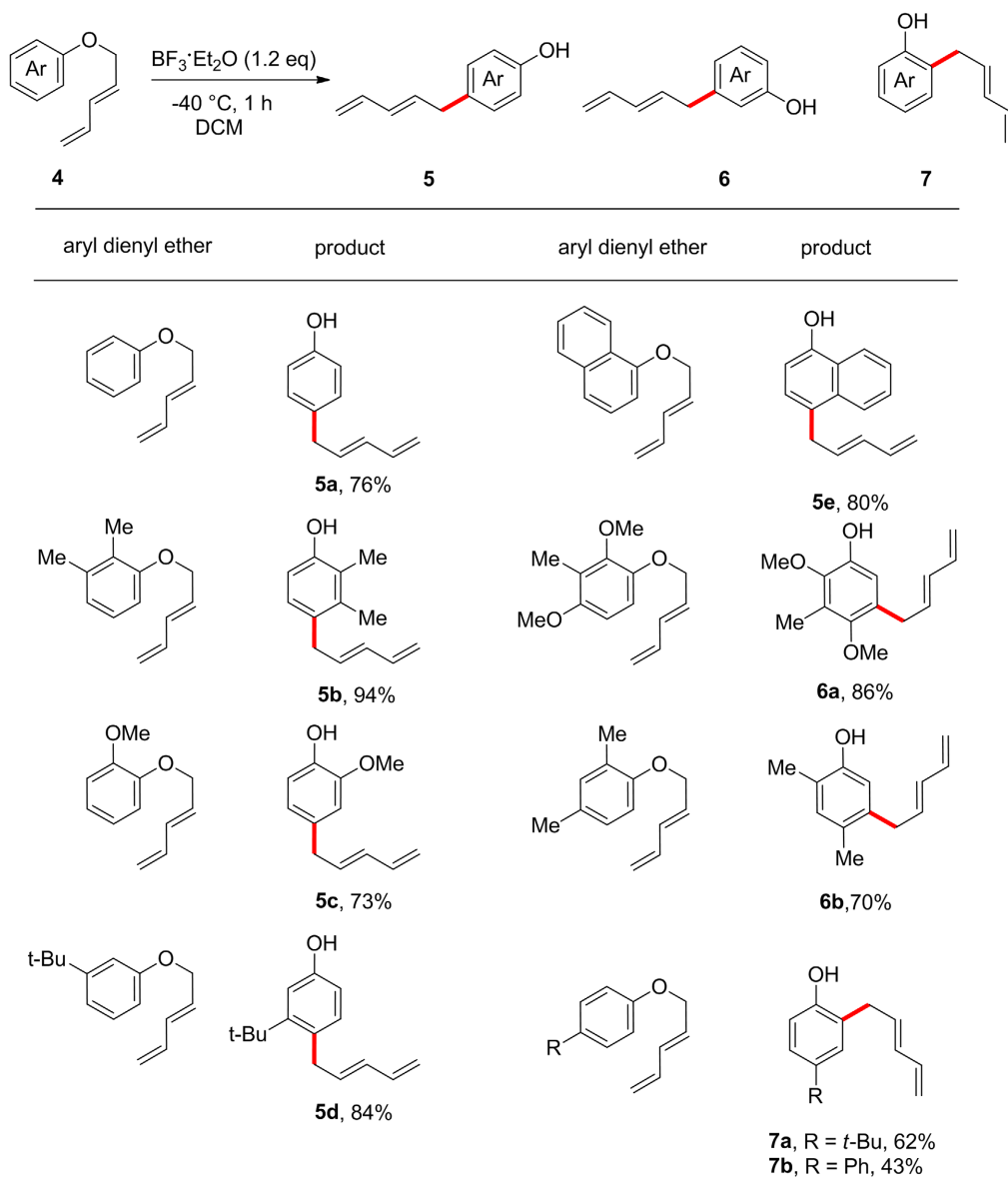


Figure 1. Rearrangement of aryl dienyl ether

图 1. 芳基二烯基醚的重排

在 1985 年, Maruyama 等[29]采用不同的路易斯酸对 Frater 和 Schmid 的反应条件进行优化, 发现在  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  的作用下芳基二烯基醚能高选择性地生成对位重排产物图 2 (5a-5e), 并发现苯环的邻位或对位取代基会对该重排反应的选择性产生较大的影响。当对位有烷基或是其它供电子基团时, 重排反应优先发生在间位图 2 (6a, 6b)。另外, 当对位含有较大体积的官能团, 如叔丁基和苯基时, 重排反应优先发生在邻位图 2 (7a, 7b)。



**Figure 2.** Claisen-type rearrangement of 2,4-pentadienyl phenyl ethers with different substituents  
**图 2.** 不同取代基的 2,4-戊二烯基苯基醚的克莱森型重排

为了进一步探究该反应的机理, Maruyama [29]进行了同位素标记实验, 首先制备了三类不同结构的氘代 2,4-戊二烯芳基醚, 在  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  的作用下发生重排。结果显示, 对位无取代基或带有较小取代基(如,  $-\text{OMe}$ ,  $-\text{Me}$ )时, 反应都会经历[5,5]-重排过程, 并生成相应的重排产物(见图 3 式 1, 式 2), 而当对位的取代基变为位阻较大的基团(如,  $-\text{t-Bu}$ )时, 会抑制[5,5]-重排反应(见图 3 式 3)。

对位无取代基或连有较小取代基的底物都需经历[5,5]-重排生成对应的重排产物。对位无取代基 2,4-戊二烯芳基醚会经历中间体 **I**, 生成相应的[5,5]-重排产物, 对位带有较小取代基的底物也会经历[5,5]-重排的过程生成中间体 **II**, 再通过[1,2]迁移生成相应的重排产物。Maruyama 为了探究对位为较大位阻取代基时, 进行了交叉实验, 向反应中加入苯酚(见图 3 式 4), 发现苯酚在反应完后只剩 58%, 推测该反应可能不仅会发生分子内的反应, 也会发生分子间的反应。

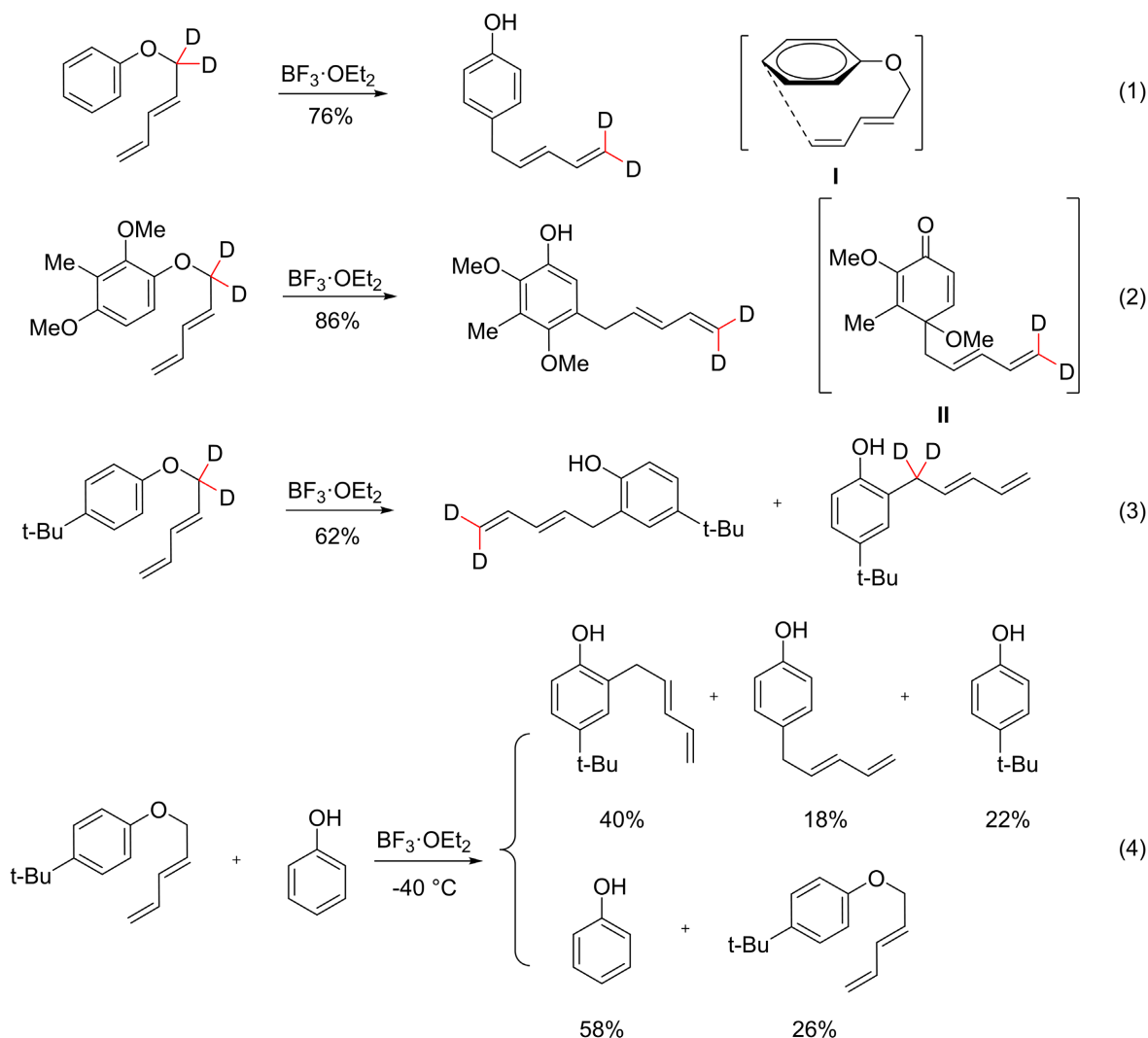


Figure 3. Deuterium rearrangement experiments of different 2,4-pentadiene aryl ethers

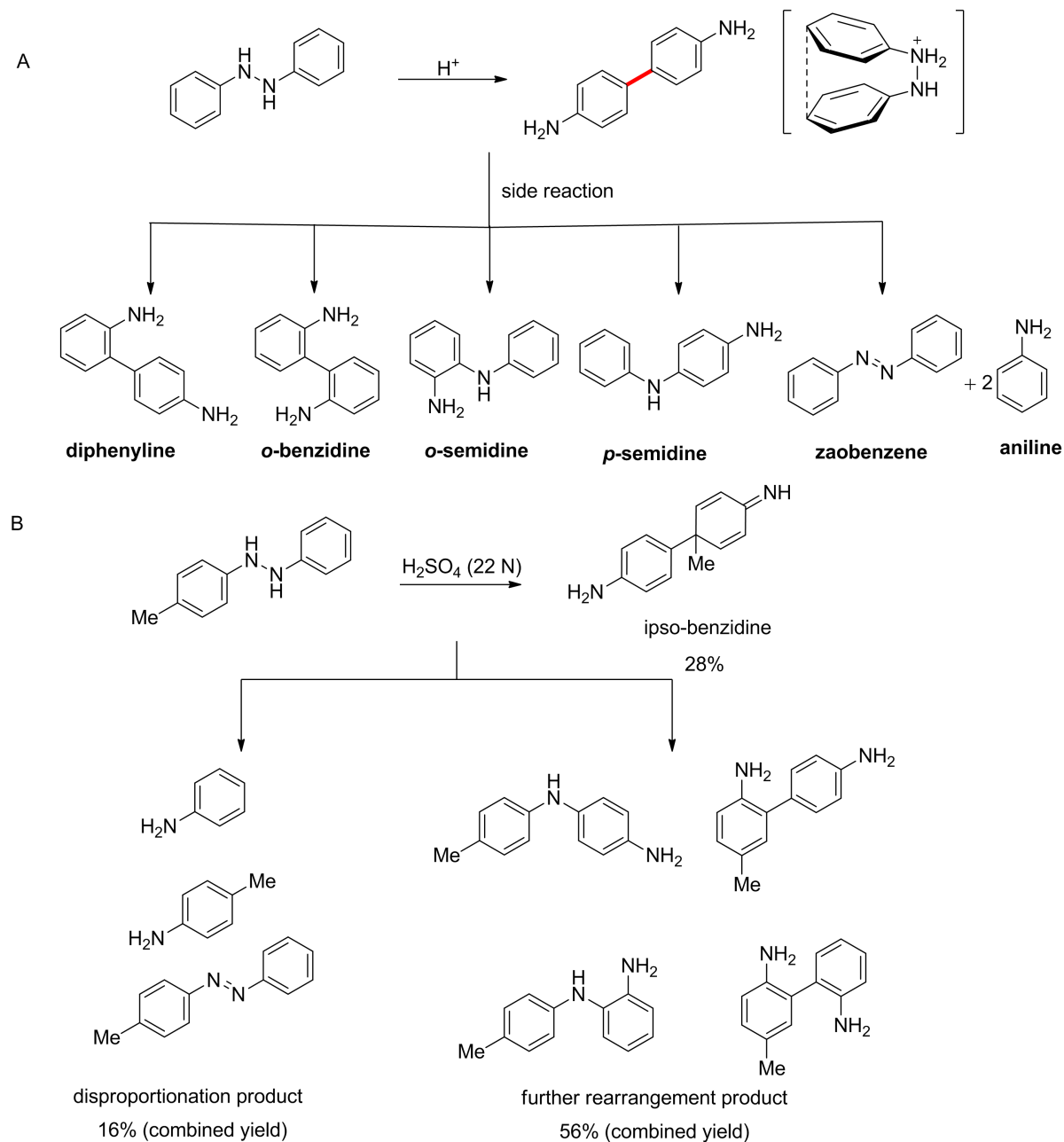
图 3. 不同 2,4-戊二烯芳基醚的氘代重排实验

Naruta 等人通过一系列的条件优化大大提高了该重排反应的对位选择性, 但遗憾的是它所报道的底物适用范围较窄, 并没有展现出良好的官能团兼容性, 因此该结果未获得更多的关注。

### 3. 联苯胺型的[5,5]重排

#### 3.1. N-N 联苯胺型的[5,5]重排

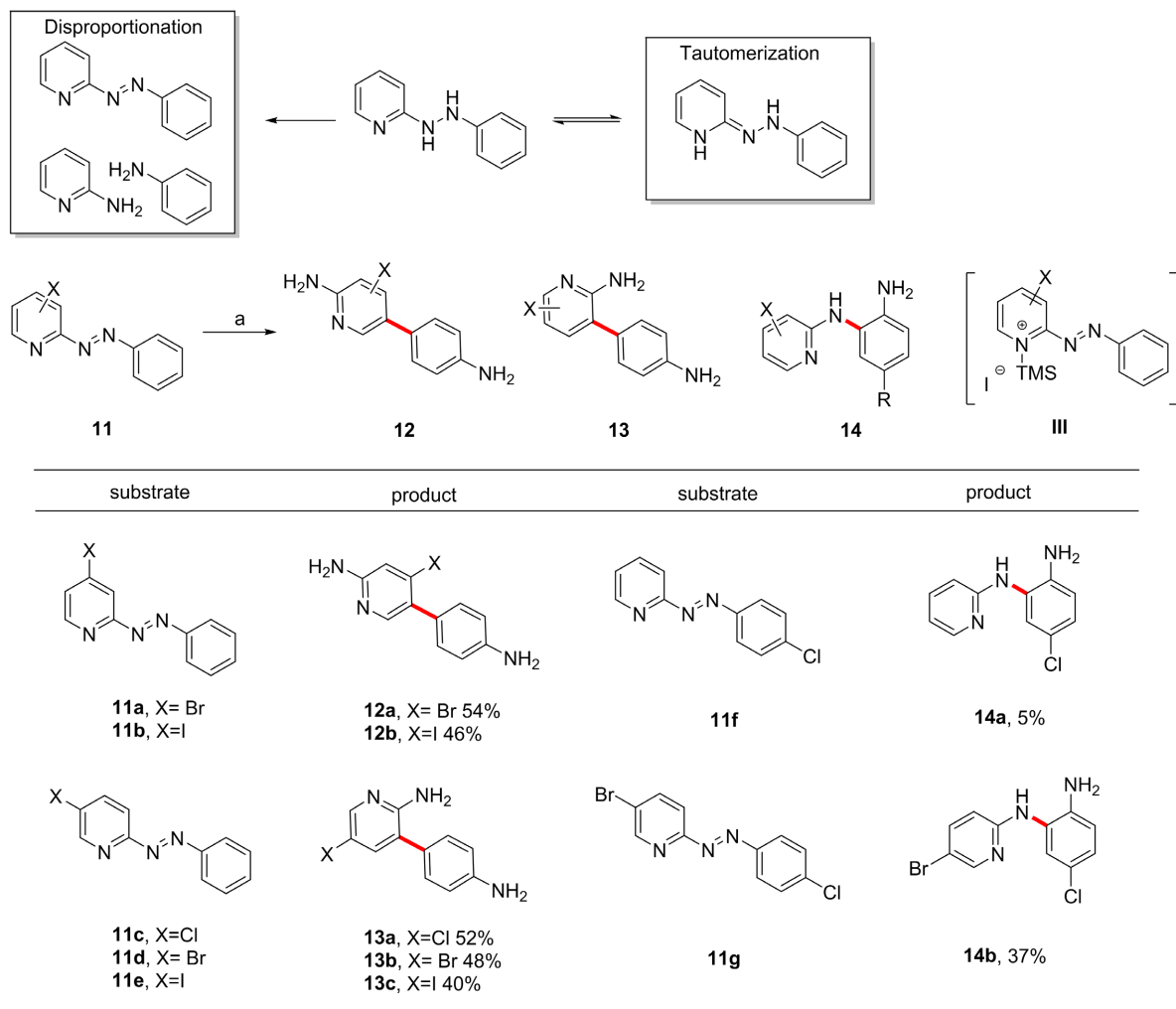
1863 年, Hofmann 在研究偶氮苯的氢化反应时得到了对联苯胺, 发现了著名的联苯胺重排[30]。但是该反应的选择性不好, 除了生成对联苯胺, 还会生成 2,4'-联苯胺, 邻联苯胺, 邻半联苯胺和对半联苯胺, 此外反应中还有少量的歧化产物偶氮苯和苯胺产生(见图 4(A))。该结果在当时并未受到科学家的广泛关注。直到 1963 年, Badger 等[31]在合成苯并[c]喹啉时, 成功分离得到了 35%联苯胺, 但当时他们并没有意识到这是一种新型的[5,5]-重排反应, 而把他们的实验结果归因于不确定的光化学反应。在 2016 年, Bouillon 等[32]在 Badger 的反应基础上, 采用对位有取代基的 *N,N*-二芳基肼进行反应, 拿到了 28%的[5,5]-重排的产物, 除此之外还拿到了 16%的歧化产物和 56%进一步重排的产物(见图 4(B))。



**Figure 4.** [5,5]-rearrangement of benzidine

**图 4.** 联苯胺[5,5]-重排

在 1957 年, Wildgrube 等<sup>[33]</sup>发现了第一例吡啶-芳基联苯胺的重排, 由于该反应存在互变异构和一系列歧化产物(见图 5 式 1), 导致反应产率不高。2016 年, Leung 等<sup>[34]</sup>研究该反应时发现, 在反应中加入三甲基碘硅烷有利于提高反应产率, 这可能得益于吡啶环上的 N 效应。反应在三甲基碘硅烷的作用下, 生成吡啶鎓盐(III), 再在氯化锡的作用下生成杂联二芳基化合物(见图 5 式 2)。研究发现: 无取代的 1,4-氨基吡啶图 5 (11a,11b), 能以中等产率拿到产物图 5 (12a,12b)。当吡啶环图 5 (11c-11e)或是芳环图 5 (11f) 的反应位点被取代时, [5,5]-重排的过程被阻断, 不能生成相应[5,5]-重排的产物。当进行[5,5]-重排的两个位点都被取代时图 5 (11g), [5,5]-重排的过程也没有发生, 只有 37%的图 5 (14b)生成。



Conditions: (1) diazo compound (1 equiv), TMSI (1.1 equiv), rt, 8 h; (2) SnCl<sub>2</sub>, EtOH-HCl, 110 °C.

**Figure 5.** Rearrangement of pyridine-aryl benzidine

**图 5.** 吡啶-芳基联苯胺的重排

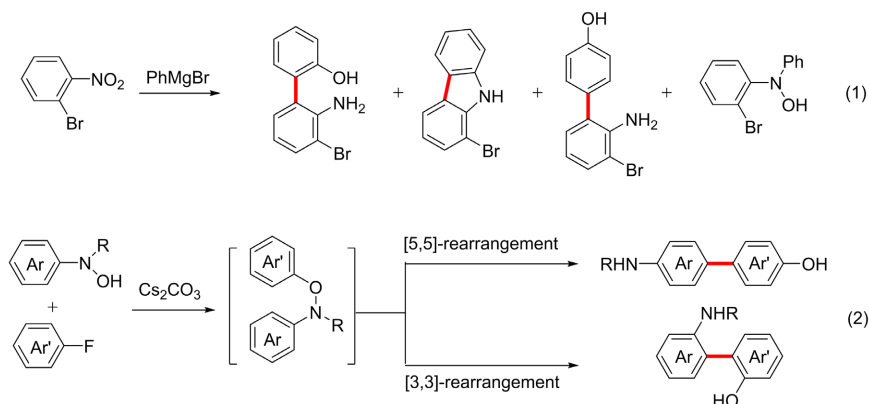
### 3.2. N-杂原子的联苯胺型的[5,5]重排

2013年, Kürti等[35]在研究硝基苯和芳基格式试剂的反应时,也发现了有少量[5,5]-重排的产物(见图6式1)。另外,最近王梅祥课题组[36]在一锅法制备多取代联芳烃的过程中,也发现N-O连接的二芳基羟胺在碱性条件下会发生[5,5]-重排,但同时也会伴随着[3,3]-重排反应(见图6式2)。

联苯胺类型的[5,5]-重排为合成多官能团联芳烃提供了新的思路,但该反应通常面临选择性差的问题,同时还伴随着一些副反应,除了会生成[3,3]-重排产物,还有歧化产物生成,如对联苯胺,对半联胺,邻半联胺,邻联苯胺和邻对联苯胺。此外,它的反应机理曾长期困扰着化学家们,直到20世纪80年代,Shine等通过同位素标记动力学实验才证实了对联苯胺的形成是通过[5,5]-迁移实现的。

### 4. 苯酚与苯醌亚胺衍生物的重排

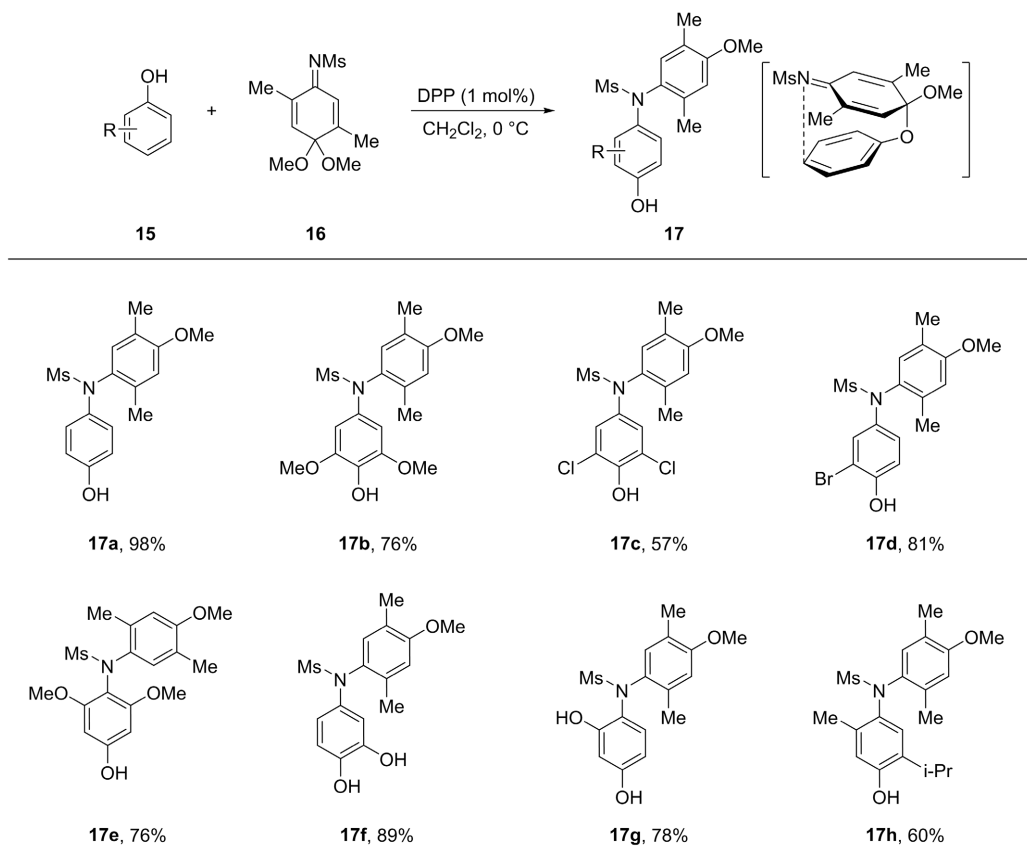
2017年,许庆龙[37][38][39][40]课题组发现苯醌亚胺衍生物与苯酚组装形成重排中间体,在DPP(磷酸二苯酯)催化下,发生[5,5]-重排反应,生成苯酚对位C-H官能团化产物。



**Figure 6.** N-O benzidine type [5,5] rearrangement

**图 6.** N-O 联苯胺型的[5,5]重排

该反应对不同取代基的底物具有良好的耐受性。值得注意的是,具有一定空间位阻的 3,5-二甲氧基苯酚参与的反应,仍然能拿到相应的对位 C-H 胺化产物图 7 (17e),产率为 76%。该反应还耐受带有二羟基基团的底物,如邻苯二酚能得到 89%直接对位 C-H 胺化产物。通过该反应可以实现苯酚对位 C-N 键的构建,为唑啉衍生物的合成提供了思路。该反应具有原料易得、反应条件温和、酸催化剂简单、催化剂负载低等特点,但该反应同样受限于结构特殊的底物。



**Figure 7.** Rearrangement of benzoquinone imine derivatives and phenol

**图 7.** 苯醌亚胺衍生物跟苯酚的重排

## 5. 结论

在过去的一个多世纪里, 科学家们从未停止对芳烃[5,5]-重排反应的研究, 并取得了一些显著的研究成果, 为 1,4-二取代芳烃的合成提供了借鉴。但是我们深入分析可以发现以上所报道的几类[5,5]-重排反应大都具有一定的反应局限性: 1) 由于重排反应研究对象通常为相对稳定的重排前体, 致使许多稳定且结构多样的重排前体较难制备, 从而限制了该重排反应的广泛应用; 2) 反应的选择性不好, 常常伴随[3,3]-重排或分子间歧化等反应。因此, 发展高效的[5,5]-重排反应仍然是合成化学的重要任务之一。

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