

羟基(对甲苯磺酰氧基)碘苯的制备与应用

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收稿日期: 2022年2月25日; 录用日期: 2022年3月25日; 发布日期: 2022年4月6日

摘要

羟基(对甲苯磺酰氧基)碘苯作为一种安全、有效、污染小的高价碘化合物, 近年广泛应用于有机化学与药物化学的研究中。本课题组一直从事高价碘氧化剂的制备与应用研究, 其中对高价碘化合物中的亚碘酰苯、二酰氧碘苯、羟基(对甲苯磺酰氧基)碘苯做了大量的研究工作。本文结合自己课题组的研究成果综述了羟基(对甲苯磺酰氧基)碘苯以及衍生物的制备方法与实际应用。

关键词

羟基(对甲苯磺酰氧基)碘苯, 高价碘化合物, 制备与应用, 综述

Preparation and Application of Hydroxy(sulfonyloxy)iodoarenes

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Received: Feb. 25th, 2022; accepted: Mar. 25th, 2022; published: Apr. 6th, 2022

Abstract

Hydroxy(sulfonyloxy)iodoarenes, as a safe, effective and low-polluting hypervalent iodine compounds, have been widely used in the research of organic chemistry and medicinal chemistry in

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文章引用: 周德军, 盛遵田, 李广乾, 马文龙, 王寒露, 李子怡, 周景春. 羟基(对甲苯磺酰氧基)碘苯的制备与应用[J]. 化学工程与技术, 2022, 12(3): 133-141. DOI: 10.12677/hjct.2022.123019

recent years. Our research group has been engaged in the preparation and application of hypervalent iodine compounds. In particular, we have done a lot of research on iodosylbenzene, bisacyloxyiodobenzenes and hydroxy(sulfonyloxy)iodoarenes in hypervalent iodine compounds. In this paper, the preparation methods and practical applications of hydroxy (*p*-toluenesulfonyloxy) iodobenzene and derivatives are reviewed based on the research results of our group.

Keywords

Hydroxy(sulfonyloxy)iodoarenes, Hypervalent Iodine Compounds, Preparation and Application, Review

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1. 引言

羟基(对甲苯磺酰氧)碘苯 $\text{PhI}(\text{OH})\text{OTs}$, Hydroxy(tosyl)iodobenzene (HTIB) 是一类重要高价碘(III)化合物之一, 最早是由 Neiland 和 Karele 在 1970 制得(Neiland O Y, Karele B Y. Zhurnal Organicheskoi Khimii, 1970, 6(4): 885)。在 1976 年化学家 Koser 确定了该化合物的结构, 并对其进行了系统研究, 此试剂被命名为 Koser 试剂[1]。关于 Koser 试剂以及衍生物的合成和应用已有多篇文献报道过[2]-[29], 但目前只有 HTIB 在市场上销售。经详查文献, 在此总结了已报道过的代表性羟基磺酰氧碘化合物(1~11)。该类化合物通常使用对应的碘苯在有机磺酸存在下被过氧化物氧化或者使用适当的对甲苯磺酸和二乙酰氧碘苯进行配体交换反应而制得[30]-[44] (图 1)。本文详细介绍了羟基(对甲苯磺酰氧)碘苯衍生物的种类、制备方法、合成应用以及对此类化合物的展望, 希望能够为有机化学和药物化学工作者提供帮助。

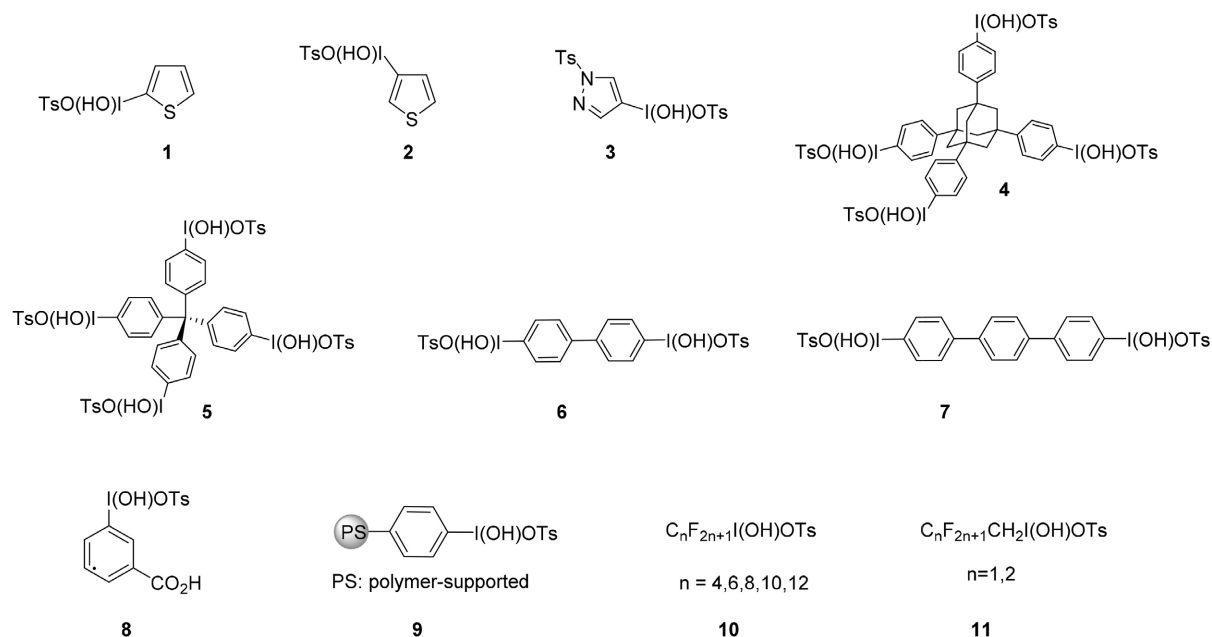


Figure 1. Representative hydroxy(*p*-toluenesulfonyloxy)iodine aromatic compounds

图 1. 代表性羟基(对甲苯磺酰氧)碘芳香化合物

2. 羟基(对甲苯磺酰氧基)碘苯衍生物的制备方法

Togo 课题组报道了一种便利的一锅法制备羟基磺酰氧碘芳香化合物的方法。在有机碘酸存在的室温条件下,碘苯及其衍生物和 *m*CPBA 反应可以制得各种羟基磺酰氧碘芳香化合物(Yamamoto, Y., & Togo, H. Synlett, 2005(16), 2486-2488)。此外 Olofsson 课题组也报道了从芳烃 **12** 直接制备羟基磺酰氧碘芳香化合物 **13** 的改进法。这种便利的一锅法方案涉及到芳烃 **12** 的碘化 - 氧化 - 配体交换[45] (图 2)。

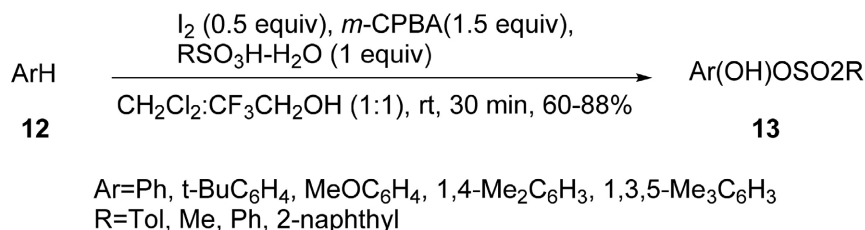


Figure 2. Preparation of Hydroxysulfonyloxyiodoaromatic compounds from aromatic hydrocarbons

图 2. 由芳烃直接制备羟基磺酰氧碘芳香化合物

另外, Koser 课题组还通过 HTIB 中的配体交换制备了几种烷氧基(甲苯磺酰氧)碘苯衍生物[46] [47] [48]例如, HTIB **14** 和三甲基原甲酸酯反应得到了甲氧基(对甲苯磺酰氧)碘苯 **15**。同样, 甲氧基(对甲苯磺酰氧基)碘苯 **15** 和薄荷醇进行配体交换反应以 95% 的收率得到手性甘草碱化合物 **16** (图 3)。

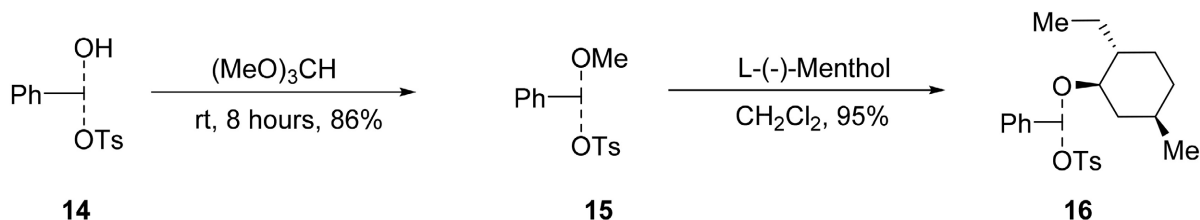


Figure 3. Ligand exchange of HTIB to obtain alkoxy sulfonyloxyiodobenzene

图 3. HTIB 经配体交换得到烷氧磺酰氧碘苯

3. 羟基(对甲苯磺酰氧基)碘芳香化合物的实际应用

Koser 课题组首次报道了羟基(对甲苯磺酰氧基)碘苯 PhI(OH)OTs 的 X 射线晶体结构。通过对 HTIB 晶体结构分析,发现了碘原子周围的 T 字形几何构型以及 2.47Å(I-OTs)和 1.94Å(I-OH)两个不同的 I-O 共价键。通过几种羟基(对甲苯磺酰氧基)碘芳香化合物的 X 射线晶体结构分析,得出在 HTIB 的苯环中引入取代基对高价碘中心的几何形状没有太大影响[49] [50] [51] [52] [53]。Richter 课题组报道了 HTIB 衍生物的晶体结构,得出与 Koser 课题组相类似的研究结果,另外还扩展到了氧桥酸酐化合物。羟基(甲磺酰氧基)碘苯的分子几何形状与 HTIB **14** 的相似,由于分子内 I \cdots O 二次键合,羟基甲磺酰氧碘苯和另一分子羟基(甲磺酰氧基)碘苯形成固态二聚体。Richter 课题组还分析羟基(甲磺酰氧基)碘苯和 HTIB 在水溶液中的状态,在水溶液中羟基(甲磺酰氧基)碘苯和羟基(对甲苯磺酰氧基)碘苯均完全电离,得到 PhI^+OH 和相应的磺酸根阴离子,但它们彼此不形成离子对[54]。

羟基(有机磺酰氧基)碘芳香化合物 **18** 最典型的反应是在羰基化合物 **17** 的 α -碳上导入磺酰氧基得到产物 **19** (Koser G F. Aldrichimica Acta, 2001, 34(3): 89-102) (图 4)。

Muniz 课题组发现改良后的 HTIB 试剂可以促进烯烃分子内胺化反应得到相应的吡啶,尤其是由 PhIO 和 2,4,5-三异丙基苯磺酸制备的 HTIB 衍生物,在温和条件下促进 2-氨基苯乙烯 **20** 高收率转化为吡啶 **21**

[55] (图 5)。

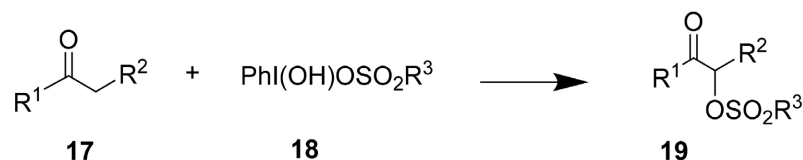

 $R_1, R_2 = \text{alkyl, aryl}; R_3 = \text{Me, 4-MeC}_6\text{H}_4, \text{ etc.}$

Figure 4. Introduction of sulfonyloxy group to the α -carbon of the carbonyl group

图 4. 羰基 α -碳上导入磺酰氧基

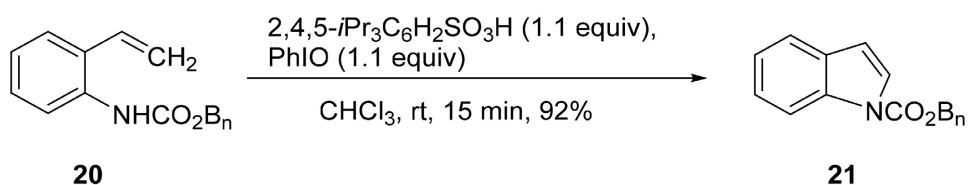


Figure 5. Coupling to prepare indole

图 5. 偶联制备吲哚

Rao 课题组多次报道了通过使用 HTIB 从脞 **22** 中得到 3,6-二取代-1,2,4,5-四二氢嗪 **23** (图 6)。相应的 3,6-二取代-1,2,4,5-四二氢嗪 **23** 可以在对甲苯磺酰基(Ts)去保护后, 经四丁基氟化铵(TBAF)处理很容易芳构化得到四嗪[56] [57] [58] [59]。

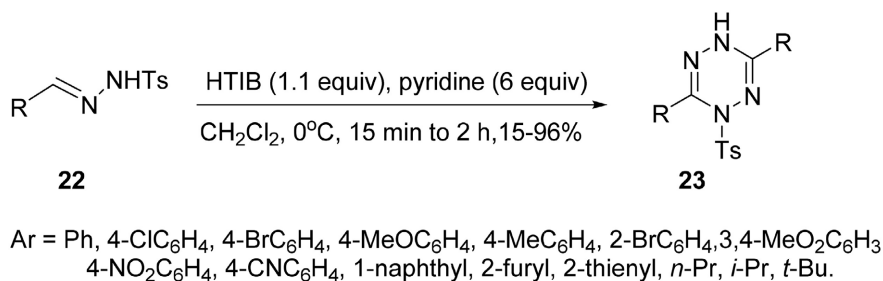


Figure 6. Oxidation of hydrazone to tetrazine

图 6. 氧化脞得到四嗪

Justik 和 Koser 报道烯烃经 HTIB 处理可进行氧化重排。芳族烯烃 **24** 与 HTIB 在甲醇水溶液中氧化重排, 以良好产率得到 α -芳基酮 **25** (图 7)。这种区域选择性氧化重排反应在环状烯烃中可用于环收缩反应 [60]。

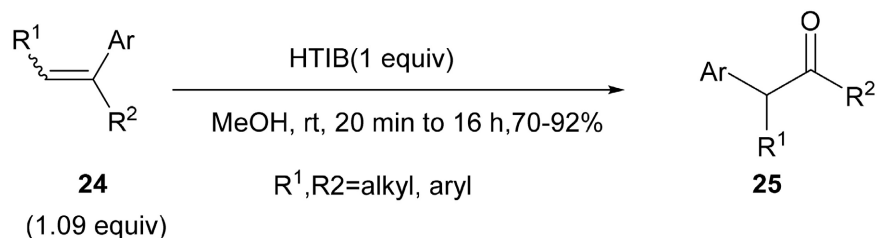


Figure 7. Oxidative rearrangement

图 7. 氧化重排反应

TIB 在温和条件下可用作环扩张诱导剂。Silva 课题组报道了 HTIB 诱导化合物 **26** 扩环得到主要产物苯并环庚基酮衍生物 **27** [61] (图 8)。

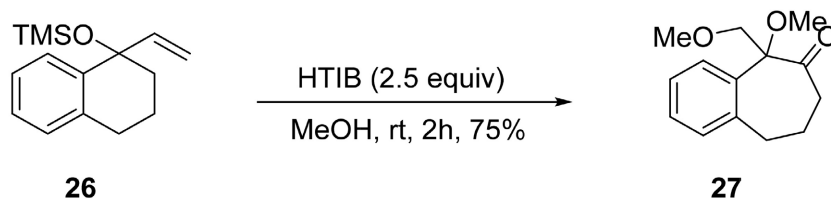


Figure 8. Induce ring expansion reaction
图 8. 诱导扩环反应

HTIB 可以用作分子间 C-C 键交叉偶联反应的有效氧化剂。Kita 课题组报道了 HTIB 诱导杂环化合物交叉偶联得到多种有用的混合联芳。例如，在三甲基溴硅烷存在下，在六氟异丙醇溶液中，取代噻吩 **28** 和 1-甲氧基萘 **29** 使用 HTIB 交叉偶联得到产物 **30** [62] (图 9)。

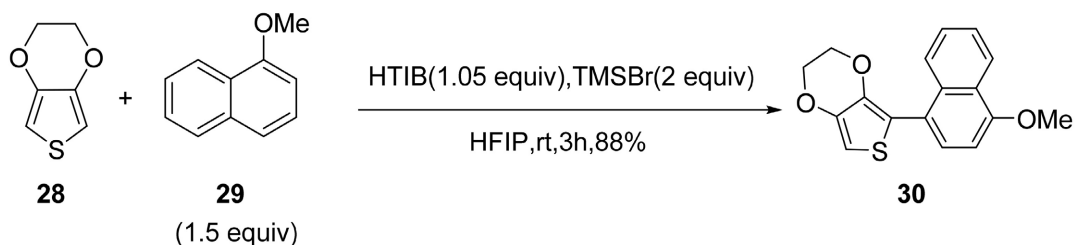


Figure 9. Aromatic heterocyclic coupling reaction
图 9. 芳香杂环偶联反应

Zhu 课题组报道用 HTIB 处理硫脲 **31** 可得到脱硫化氢产物碳二酰亚胺 **32**，此方法是一种有效制备碳二酰亚胺的方法[60] [63] (图 10)。

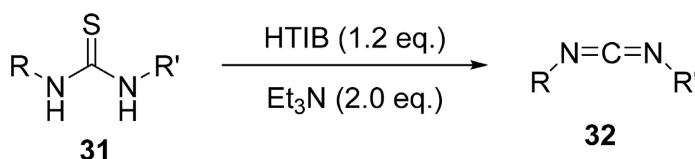


Figure 10. Preparation of imide by reaction with thiourea
图 10. 与硫脲反应制备二酰亚胺

课题组报道 4-羟基香豆素 **33** 用 HTIB 处理可以在 3 位引入磺酰氧基得到化合物 **34**，此方法拓展了香豆素衍生物的合成范围[64] (图 11)。

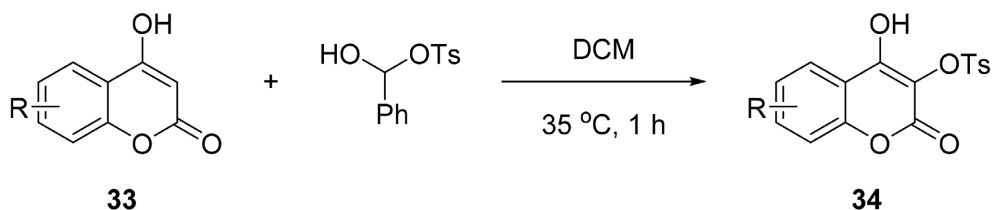


Figure 11. Introduction of oxygen at the 3-position of coumarin
图 11. 在香豆素 3 位导入氧

4. 羟基磺酰碘芳香化合物的合成与应用展望

羟基磺酰碘芳香化合物的合成已经取得了诸多成就。此类化合物不仅合成简便,而且作为一种安全、有效、污染小的试剂,已经在有机合成和药物化学中广泛应用。羟基磺酰碘芳香化合物作为一种反应试剂虽然扮演着重要角色,但仍需要我们不断探索与研究新功效新用途。乙酰碘苯已经表明可以和缺电子酚反应,可以将芳香环部分导入酚的结构里得到相应的芳香醚化合物,羟基磺酰碘苯衍生物目前还没有相关报道。

基金项目

北京本草方源药业科研合作项目(H20-523)。

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