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双(3,5-二甲基苯基)膦的合成

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摘要:为了推动在国内尚无商业化产品的双(3,5-二甲基苯基)膦在不对称催化合成精异丙甲草胺中应用,对双(3,5-二甲基苯基)膦的合成工艺进行了研究.以双(3,5-二甲基苯基)氧膦为原料,通过二异丁基氢化铝还原得到双(3,5-二甲基苯基)膦,最佳条件为:双(3,5-二甲基苯基)氧膦与二异丁基氢化铝摩尔比为1:3,溶剂为四氢呋喃,反应温度65℃,反应时间1h,产率为89%.实验结果表明:该方法操作简单,副反应少且容易控制.

关键词:膦配体;二异丁基氢化铝;还原

中图分类号:TQ457.2

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0 引言

精异丙甲草胺是一种高效、低毒、低残留的选择性芽前除草剂^[1].精异丙甲草胺是异丙甲草胺的S构型体,在相同使用量的情况下,它的活性是异丙甲草胺的1.4~1.6倍^[2].使用异丙甲草胺作为除草剂,意味着有50%无除草活性的R-构型异丙甲草胺释放到农田中,既浪费了资源,也造成了环境污染,世界各国已相继限制了异丙甲草胺的使用.未来在我国也必然将限制或取消异丙甲草胺的使用,因此,研究开发精异丙甲草胺的不对称合成工艺势在必行.但在合成工艺中,作为催化剂的双膦配体Xyliphos的制备是研究的关键.在双膦配体制备中,双(3,5-二甲基苯基)膦在国内尚无商业化产品,也难以从国外购买.因此,开发其有效的合成工艺将推动精异丙甲草胺的不对称合成工艺的发展.

文献报道的双(3,5-二甲基苯基)膦制备方法有以下几种^[3-7]:**a.**采用硼烷还原二取代氧膦,该方法中会产生不需要的副产品,且难以控制硼烷;**b.**采用四氢铝锂还原二烷基氯化膦,该方法中原料是极易吸湿的,反应难以控制;**c.**采用二苯基硅还原二取代氧膦,该方法需要高温反应;**d.**采用三氯硅氢和三乙胺还原二取代氧膦,该方法中三氯硅氢腐蚀性强,且沸点低,难以用于工业化生产;**e.**采用二异丁基氢化铝还原双(3,5-二甲基苯基)氧膦得到,该方法与以上方法相比副反应少,容易控制.本

研究就方法e的反应条件进行了研究.

1 实验部分

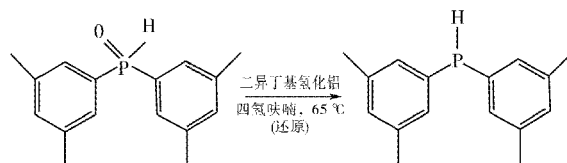
1.1 试剂及仪器

双(3,5-二甲基苯基)氧膦为工业级,其他药品及试剂均为市售分析纯.

GF254层析硅胶板;Bruker ARX-400核磁共振仪(¹H NMR以TMS为内标,³¹P NMR以85% H₃PO₄为外标);北京泰克有限公司X-4型数字显示熔点仪.

1.2 合成原理

反应方程式如下:



1.3 实验方法

a.氮气保护下,将1 mol/L二异丁基氢化铝/四氢呋喃(6 mL,6.0 mmol)加入100 mL三口瓶中,然后加热至65℃,开始滴加双(3,5-二甲基苯基)氧膦(476 mg,2.0 mmol)的四氢呋喃溶液4 mL,15 min滴完.滴加完毕,继续65℃下回流1 h.

b.点板跟踪反应,待反应完全后,缓慢滴加10 mL质量分数5%的氢氧化钠溶液,搅拌10 min,再加甲基叔丁基醚:正己烷=1:110的溶液10 mL,继续搅拌10 min,萃取,有机层在氮气保护下加硫酸镁干燥,并在氮气保护下浓缩,得无色

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油状液体双(3,5-二甲基苯基)膦(400 mg, 1.78 mmol). ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = -41.39, \text{d}, 1\text{JPH} = 220 \text{ Hz}$.

2 结果与讨论

2.1 反应时间的选择

固定反应温度 65°C , 双(3,5-二甲基苯基)氧膦与二异丁基氢化铝摩尔比为 1:3, 溶剂为四氢呋喃, 产物产率随反应时间的变化趋势如图 1 所示, 随着反应时间的延长, 收率逐渐提高, 当反应时间达到 1 h 时, 产物产率较高, 此时再延长反应时间, 产率变化不大.

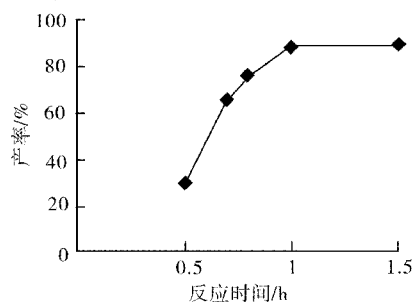


图 1 反应时间对产率的影响

Fig. 1 Influence of reaction time on yield

2.2 反应温度的选择

固定反应时间 1 h, 双(3,5-二甲基苯基)氧膦与二异丁基氢化铝摩尔比为 1:3, 溶剂为四氢呋喃, 反应温度对产物产率的影响如图 2 所示, 室温下不易还原, 随着温度的升高, 收率明显提高. 但当温度达到回流温度时, 继续升温, 对收率的影响不大, 所以最佳反应温度为 65°C .

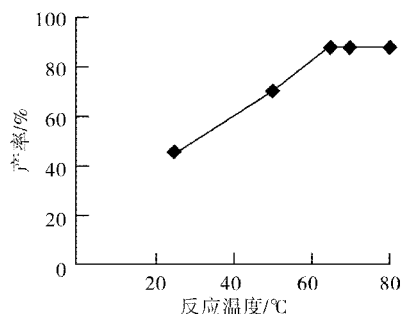


图 2 反应温度对产率的影响

Fig. 2 Influence of reaction temperatures on yield

2.3 二异丁基氢化铝用量的选择

固定反应时间 1 h, 反应温度为 65°C , 溶剂为四氢呋喃, 考察二异丁基氢化铝用量对产物产率的影响, 结果如表 1 所示.

由表 1 可知, 随着二异丁基氢化铝的增加, 还原收率逐渐提高, 这符合化学反应的一般规律. 但二异丁基氢化铝的增加到一定程度, 双(3,5-二甲基苯基)膦的收率提高并不明显. 综合考虑各种因

素, 双(3,5-二甲基苯基)氧膦与二异丁基氢化铝摩尔比为 1:3 为宜.

表 1 二异丁基氢化铝对产率的影响

Table 1 Influence of quality of molar ratio of oxide and di-iso-butyl aluminum hydride on yield

氧膦与二异丁基氢化铝摩尔比	产率/%
1:1	25.4
1:2.5	78.5
1:3	89
1:4	91.3
1:4.5	92.2

2.4 反应溶剂的选择

固定反应时间 1 h, 反应温度为 65°C , 双(3,5-二甲基苯基)氧膦与二异丁基氢化铝摩尔比为 1:3, 考察不同溶剂对收率的影响, 结果如表 2 所示.

表 2 溶剂对收率的影响

Table 2 Influence of solvent on yield

溶剂种类	产率/%
乙醚	69.3
四氢呋喃	89.0
二甲基甲酰胺	88.2
甲基叔丁基醚	72.1
正己烷	60.4

由表 2 可知, 四氢呋喃为最佳反应溶剂, 二甲基甲酰胺虽然也行, 但后处理十分困难.

3 结 语

通过对不同反应条件的研究, 发现采用二异丁基氢化铝还原双(3,5-二甲基苯基)氧膦制备双(3,5-二甲基苯基)膦的最佳反应时间为 1 h, 反应温度为 65°C , 双(3,5-二甲基苯基)氧膦与二异丁基氢化铝摩尔比为 1:3, 溶剂为四氢呋喃. 该方法操作简单, 副反应少且容易控制, 后处理简单, 是双(3,5-二甲苯基)膦的一种有效制备工艺.

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Preparation of bis (3,5-dimethylphenyl) phosphine

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Abstract: Bis(3,5-dimethyl phenyl)phosphine is an effective ligand for asymmetric synthesis of S-metolachlor and there is no commercial product in domestic at present. In order to promote the development of asymmetric synthesis process of S-metolachlor, the synthetic process was studied in this paper. With bis(3,5-dimethyl phenyl)phosphine oxide as raw material, bis(3,5-dimethyl phenyl)phosphine was synthesized by deoxidization through diisobutyl aluminium hydride, and the optimal conditions were the ration of bis(3,5-dimethyl phenyl) phosphine oxide to diisobutyl aluminum hydride mole of 1:3, reaction temperature of 65 °C, reaction time of 1 h, and the production rate of 89%. The results show that this method is simple, and easy to control with less side reactions.

Key words: phosphorus ligands; DIBAL; deoxidized

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Synthesis and aggregation-induced emission of 1,1-dimethyl-3,4-diphenyl-2,5-bis(2'-thienyl) silole

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Abstract: The incorporation of siloles in small molecules or polymers is of interest and importance in chemistry and functionalities due to its excellent electronic and optoelectronic properties. A novel compound 1,1-dimethyl-3,4-diphenyl-2,5-bis(2'-thienyl) silole (TST) was synthesized by palladium-catalyzed cross-coupling reaction. The photophysical properties of TST were characterized by ultraviolet (UV) spectra and photoluminescence (PL) spectra. Interestingly, TST was practically nonemissive in solutions, but its aggregates were highly luminescent ("aggregation-induced emission" or AIE). When the isolated molecules in solutions were cooled to extremely low temperature, they emitted intense light comparable to that in the aggregated state. These results show that deactivation of nonradiative decay by suppression of intramolecular vibrational and torsional motions leads to the increased PL efficiency of TST. The present study suggests that TST is the potential material for fabrication in organic light-emitting devices (OLED).

Key words: silole; photoluminescence; aggregation-induced emission

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