

芳烃萃取剂 N-甲酰吗啉的合成*

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摘 要:研究了以吗啉为原料, 用甲酸或甲酸甲酯等做酰化剂, 在催化剂存在下, 并且在一定的反应温度、反应时间和常压下合成 N-甲酰吗啉。实验结果表明: 吗啉的转化率可达 95 % 以上, 经精馏后 N-甲酰吗啉的纯度可达 98 % 以上。

关键词: N-甲酰吗啉; 吗啉; 酰化; 合成

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1 前言

N-甲酰吗啉(NMF)主要用作从混合芳烃制精苯工艺的萃取剂, 也是甲乙酮的生产原料。目前, 用于分离精制芳烃的主要溶剂有环丁砜、N-甲基吡咯烷酮、四甘醇、二甲基甲酰胺等。国外研究结果报道, 制取精苯的最佳溶剂是 N-甲酰吗啉。它具有化学性质稳定、无毒、无腐蚀性等特点, 且由于其结构的特殊性, 溶解芳烃后可大大降低芳烃的相对挥发性, 有利于把非芳烃分离出去, 既可使芳烃的纯度提高又能增加芳烃的收率, 还能大大降低生产能耗。同时 N-甲酰吗啉与环丁砜等其他几种抽提溶剂相比较还具有污染小, 环保效果好的特点。

合成 N-甲酰吗啉的主要原料吗啉国内产量大约 5000 t/a。吗啉除大部分用于医药中间体外, 其它用途开发几乎没有进行, 这又为 N-甲酰吗啉产品的开发提供了充足的原料。因此, 该项研究为吗啉产品的进一步应用提供了一条有意义的途径。

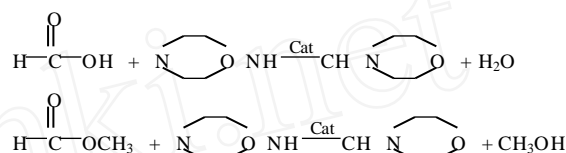
2 N-甲酰吗啉合成

2.1 酰化反应机理和反应过程

氨类化合物的酰化是发生在氨基氮原子上的亲电取代反应。酰化剂中酰基的碳原子上带有部分正电荷, 能与氨基氮原子上的未共用电子对相互作用, 形成过度态络合物, 然后转化成酰胺。N-酰化反应的难易, 与氨类化合物和酰化剂的反应活性, 以及空间效应都有密切关系, 氨基氮原子上的电子云密度愈大, 空间阻碍愈小, 则反应活性愈强。

以吗啉为原料合成甲酰胺的方法为: 吗啉用

甲酸直接酰化; 甲酸甲酯和吗啉反应; 吗啉与一氧化碳的羰化也可合成甲酰胺。和 法的反应方程式如下:



笔者对 法进行了研究。

2.2 实验装置

吗啉与甲酸甲酯在一定反应条件下, 在催化剂作用下, 合成 N-甲酰吗啉。反应液加入精馏塔中进行精馏, 并用色谱分析反应液和精馏各馏分的含量。由此确定吗啉的转化率和 N-甲酰吗啉纯度。以确定优惠反应条件。

3 实验结果与讨论

3.1 甲酸甲酯与吗啉合成 NMF

将甲酸甲酯与吗啉按一定比例混合, 在催化剂 ZD-1 存在下, 连续搅拌足够时间, 合成 N-甲酰吗啉。表 1 和表 2 分别给出不同反应时间和温度下合成反应物的实验结果。

表 1 反应时间对产物的影响实验结果

| 序号 | 配比 | 温度() | 催化剂 | 时间(h) | 转化率(%) |
|----|-------|---------|------|-------|---------|
| 1 | 1.2 1 | 85 ~ 90 | ZD-1 | 3 | 98.5 |
| 2 | 1.2 1 | 85 ~ 90 | ZD-1 | 2 | 98.3 |
| 3 | 1.2 1 | 85 ~ 90 | ZD-1 | 1 | 93.5 |
| 4 | 1.2 1 | 85 ~ 90 | ZD-1 | 0.5 | 78.7 |
| 5 | 1.2 1 | 85 ~ 90 | ZD-1 | 0.3 | 58.4 |

注: 配比指甲酸甲酯与吗啉的摩尔比; 转化率指吗啉的转化率。

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表 2 反应温度的影响

| 序号 | 配比 | 温度() | 催化剂 | 时间(h) | 转化率(%) |
|----|-------|-------|------|-------|---------|
| 1 | 1.2 1 | 90 | ZD-1 | 2 | 98.3 |
| 2 | 1.2 1 | 85 | ZD-1 | 2 | 98.5 |
| 3 | 1.2 1 | 75 | ZD-1 | 2 | 97.9 |
| 4 | 1.2 1 | 65 | ZD-1 | 2 | 90.5 |
| 5 | 1.2 1 | 50 | ZD-1 | 2 | 74.9 |

实验结果表明:当反应温度大于 75 时吗啉的转化率基本保持不变,而小于 75 时吗啉的转化率有所下降。随着反应时间的延长,吗啉的转化率逐渐增加,但是超过 2 h 后,反应的转化率增加不明显。较适宜反应温度为 75 ,反应时间为 2 h。

表 3 为反应原料配比对收率的影响实验结果。

表 3 反应原料配比的影响

| 序号 | 配比 | 温度() | 催化剂 | 时间(h) | 转化率(%) |
|----|--------|-------|------|-------|---------|
| 1 | 1.2 1 | 85~90 | ZD-1 | 2 | 98.3 |
| 2 | 1.1 1 | 85~90 | ZD-1 | 2 | 97.9 |
| 3 | 1.05 1 | 85~90 | ZD-1 | 2 | 94.4 |
| 4 | 0.92 1 | 85~90 | ZD-1 | 2 | 87.2 |

考虑到吗啉的价格比甲酸甲酯的价格要高许多,反应时应使吗啉尽量转化,以达到好的经济效益。所以在反应过程中应使甲酸甲酯过量,但过量太多则会增加后续回收过程的负担。从实验结果可以看出,当甲酸甲酯与吗啉的摩尔比在 1.05~1.2 1 时吗啉的转化率已达到了要求,但以其摩尔比 1.2 1 为宜。

3.2 反应物料的精制和分离

甲酸甲酯与吗啉在催化剂作用下进行反应,反应釜液中除生成 N-甲酰吗啉外,同时还生成副产物甲醇,此外,还含有未转化的甲酸甲酯和吗啉以及原料中带入的甲基吗啉和水等,为获得高纯度的 N-甲酰吗啉,必须将反应釜液进行分离。考虑到 N-甲酰吗啉的沸点较高,采用减压精馏的方法进行精馏,实

验结果见表 4。

表 4 反应釜液的精馏结果

| 序号 | 釜液组成(%) | | | 精制后组分含量(%) | | |
|----|----------|-------|--------|-------------|-------|-------|
| | 甲醇 | 吗啉 | NMF | NMF | 吗啉 | 其它 |
| 1 | 35.54 | 0.182 | 63.787 | 98.676 | 0.356 | 0.968 |
| 2 | 34.45 | 0.767 | 64.513 | 99.287 | 0.167 | 0.546 |
| 3 | 29.68 | 0.119 | 59.734 | 98.943 | 0.235 | 0.822 |
| 4 | 31.24 | 0.347 | 61.476 | 99.078 | 0.311 | 0.611 |

实验结果表明:采用精馏方法能够将反应釜液中 N-甲酰吗啉与其它组分分离,使 N-甲酰吗啉纯度 98.6 % ,能够满足实际生产的要求。

4 结论

实验研究结果表明: 甲酸甲酯与吗啉在催化剂 ZD-1 作用下能够生成 N-甲酰吗啉,吗啉的转化率大于 95 % ; N-甲酰吗啉合成反应控制工艺条件为:反应温度 85~90 ,原料配比 1.2 1 (mol),反应压力常压,反应时间 2 h; 采用精馏的方法可以得到含量 98.6 % 的 N-甲酰吗啉产品。

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triacetate reaches 96 %. The catalyst have many advantages, such as easy to be recovered, feasible to be used repeatedly, and less pollution to the environment.

Key words: Solid superacid catalyst; Glycerol triacetate; Catalytic esterification

The Synthesis of 3, 4 - Difluorochlorobenzene from p - Dichlorobenzene. ZHANG Cu-e, *etc* (Xi 'an Modern Chemistry Research Institute, Xi 'an 710065, China) J.fine chem. intermediates, 2003, 33(4) :22 ~ 23

The synthesis method of 3, 4 - difluorochlorobenzene was reported by one-step direct fluorination of p - dichlorobenzene. 2, 5-dichloronitrobenzene was synthesized by nitrating p - dichlorobenzene with nitric acid and sulfuric acid. In the process of direct fluorination, tetraphenyl phosphonium bromide, potassium fluoride and sulfolane was used as catalyst, fluorating agent, and high boiling point agent respectively. The terminal product was gotten by distillation in water vapor, fractionation, and purification. The yields for nitration and rectification to fluorating product are over 95 % and 49.8 % respectively. The purity is over 98 %.

Key words: p-dichlorobenzene; 2, 5-dichloronitrobenzene; 3, 4-difluorochlorobenzene; preparation

The Synthesis of 4-tert-Butylbenzyl Chlorid. WANG Da - wei, *ect.* (School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China) J.fine chem. intermediates, 2003, 33(4) :24 ~ 25

4-tert-Butylbenzyl Chloride was prepared from tert-butylbenzene with paraformaldehyde and hydrochloric acid. Optimum reaction conditions are as follow: n (tert-butylbenzene): n (formaldehyde): n (hydrochloride) is 1:3:3, the reaction temperature 80 ~ 85 °C, the reaction time 15h, and phosphoric acid as catalyst.

Key words: tert-Butylbenzene; 4-tert-Butylbenzyl Chloride; Chloromethylation; Synthesis

The Synthesis of N- formylmorpholine. ZOU Dong-lei¹, SUI Zhen-ying². (1. College of Environment and Sources; 2. College of applied technology, Jilin University, Changchun, 130026, China) J.fine chem. intermediates, 2003, 33(4) :26 ~ 27

The synthesis of N-formylmorpholine was studied. Morpholine is the main raw material, and formic acid or methyl methanoate is aclyting agent. In the presence of catalyst, morpholine was reacted under thermory and pressure. The result of experiment show that at the presence of catalyst the conversion of morpholine reaches 95 %, and purity of distilled N-formylmorpholine reaches 99 %.

Key words: N-formylmorpholine; morpholine; aclytion; synthesis

The Synthesis of Two Diazoic Dyes Containing Triazole. LI De-jiang¹, SUN Bi-hai², LI Bin². (1. Department of Chemistry, Yunyang Teachers College, Danjiangkou 442700, China; 2.

Department of Engineering, Wuhan Institute of Chemical Technology, Wuhan 430073, china) J.fine chem. intermediates, 2003, 33(4) :28 ~ 30

Two diazoic dyes were synthesized by the diazo-reaction and coupled reaction of 5-amino-1H-1, 2, 4-triazole-3-carboxylic acid with 1-amino-8-naphthol-3, 6-disulfonic acid, m-phenylenediamine, m-nitrophenylamine, and beta-naphthol. Their properties were especially discussed; and their structures were confirmed by elemental analysis, IR, UV, and ¹H NMR.

Key words: diazoic dyes; synthesis; characterization; properties

Studies on the Synthesis of m-Chlorobenzaldehyde from Benzaldehyde by Direct Chlorination. TONG Gang-sheng, *etc.* (The Chemical Engineering Department of Xiangtan University, Xiangtan Hunan, 411105, China) J.fine chem. intermediates, 2003, 33(4) :31 ~ 33

The synthesis method of m-chlorobenzaldehyde from benzaldehyde by direct chlorination was studied. Anhydrous aluminium was picked out as the best catalyst from many kinds of catalysts. By parameters and orthogonal test, the effects of the concentration of raw material, the catalyst, reaction temperature, and reaction time was investigated. The optimized conditions for reaction were obtained as follows: benzaldehyde 1.33 mol L⁻¹, anhydrous aluminium 1.70 mol L⁻¹, reaction time 30min, reaction temperature 50 °C. Under the optimized conditions, the conversion of benzaldehyde is over 90 %. The overall yield of m-chlorobenzaldehyde is 79 % with 88 % selectivity, and there almost is no structural isomer as by-products.

Key words: benzaldehyde; m-chlorobenzaldehyde; catalyzed chlorination

Preparation of Cyclohexane from Benzene and Hydrogen with Non-stable Method. WEI De-liang¹, PENG Hong-jian¹, GONG Jian². (1. The Department of Organic Chemistry, The South University Xiangya Medical Institute Changsha, 410078, China; 2. the Department of Chemistry and Chemical Engineering, Hunan Normal University Changsha 410081, China) J.fine chem. intermediates, 2003, 33(4) :34 ~ 35

Low-Ni improvement oxide aluminum catalyst and non-stable method were adopted to prepare cyclohexane from benzene and hydrogen. The method has such advantages as saving equipment, simplifying technology process, enhancing yield rate and selectivity, and controlling reaction factors easily. It is good to be widely used in industry.

Keywords: low-Ni improvement oxide Aluminum catalyst; non-stable method; cyclohexane

The Summary of 300t/a Ethylamine process. ZHOU Qi-jie. (Zhuzhou Chemical Industry Group Co. Ltd, Zhuzhou Hunan, 410064, China) J.fine chem. intermediates, 2003, 33(4) :36 ~ 37

Adding purification and modifying process conditions, ethylamine was produced in the original 1000 t/a installation, which only produced diethylamine before. In the same time, diethyl-