ISSN: 0974 - 7516 Volume 10 Issue 5

Organic CHEMISTRY
An Indian Journal
Microreview

OCAIJ, 10(5), 2014 [176-178]

An overview on synthetic methods of terpinyl acetate

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ABSTRACT

Several synthetic methods of terpinyl acetate using different catalysts such as solid superacids (SO^{2-}_4 / MxOy, SO^{2-}_4 /SnO_2 - CeO_2, SO^{2-}_4 / SnO_2 - TiO_2, SO^{2-}_4 / SnO_2 - TiO_2, SO^{2-}_4 / ZrO_2 and SO^{2-}_4 / ZrO_2- SnO_2 -Nd_2O_3), activated carbon heteropolyacids, phosphoric acid / ionic liquid composite system, acidic functional polyether ionic liquid, $SnCl_4 \cdot 5\ H_2O$, acidic ionic liquid and acetic anhydride phosphate acid have been reviewed in the present paper. Yields of terpinyl acetate are improved by the addition of the above mentioned catalysts. Due to low investment costs and simple process these methods are having the advantages on other processes.

KEYWORDS

Overview;
Synthetic methods;
Terpinyl acetate;
Catalyst.

INTRODUCTION

Terpinyl acetate is one type of perfumes and the colorless liquids. It is widely used as a synthetic flavouring agent[1]. There are two steps to synthesize terpinyl acetate. The first step is that terpilenol is gotten by using turpentine as a feedstock. The second step is that terpineol and acetic anhydridel react to produce terpinyl acetate. Concentrated sulphuric acid is one of the main catalysts, but apart from several advantages, such as more secondary reaction taking place, low yield and purity of terpinyl acetate, it has a lot of disadvantages also. Lot of waste water is discharged during the process causing severe environmental pollution problem and at the same time equipments are corroded[2].

In the present paper, synthetic methods of terpinyl acetate using different catalysts such as solid superacids (SO^{2-}_4 / MxOy, SO^{2-}_4 /SnO_2 - CeO_2, SO^{2-}_4 / SnO_2 - TiO_2, SO^{2-}_4 / SnO_2 - TiO_2, SO^{2-}_4 / ZrO_2 and SO^{2-}_4 / ZrO_2- SnO_2 -Nd_2O_3), activated carbon heteropolyacids, phosphoric acid / ionic liquid composite system, acidic functional polyether ionic liquid, $SnCl_4 \cdot 5\ H_2O$, acidic ionic liquid and acetic anhydride phosphate acid with the microwave heating method have also been introduced.

RESULTSAND DISCUSSION

Solid superacids as catalysts to generate terpinyl acetate

Yu Shitao[3] experimented several kinds of SO^{2-}_4 / MxOy solid super acid, such as SO^{2-}_4 / TiO_2, SO^{2-}_4 / ZrO_2, SO^{2-}_4 / SnO_2 and SO^{2-}_4 / Fe_2O_3, as catalysts to synthesize terpinyl acetate. Among of them, the catalyst, SO^{2-}_4 / TiO_2 has the highest catalytic activity. The effect of the reaction conditions, such as the reaction time, the molar ratio of terpineol to acetic anhydridel, the reaction temperature and the amount of SO^{2-}_4 / TiO_2 had been studied. The best conditions were that the reaction time, the molar ratio of terpineol to acetic anhydridel, the reaction temperature and the amount of

SO^{2-}_4 / TiO_2 were 7 hours, 1.0 : 1.7, 60 °C and 2.0 g, respectively. The highest yield of terpinyl acetate was 84.5 %.

Guo Haifu[4] used SO^{2-}_4 /SnO_2 - CeO_2 as a catalyst to generate terpinyl acetate. The effect of reaction conditions such as the reaction time, the molar ratio of terpineol to acetic anhydridel, the reaction temperature and the amount of SO^{2-}_4 /SnO_2 - CeO_2 had been discussed. The best conditions were that the reaction time, the molar ratio of terpineol to acetic anhydride, the reaction temperature and the amount of SO^{2-}_4 /SnO_2 - CeO_2 were 3.5 hours, 1.0 : 1.2, 50 °C and 3 % (of terpineol mass), respectively. The highest yield and selectivity of terpinyl acetate were 98.3 % and 82.4% separately.

Zhao Qianrong[5] prepared SO^{2-}_4 / SnO_2 - TiO_2 composite solid super acid by sol-gel method. SO^{2-}_4 / SnO_2 - TiO_2 was used as a catalyst and terpineol and acetic anhydride as feedstocks to produce terpinyl acetate. The best conditions were that the reaction time, the molar ratio of terpineol to acetic anhydridel, the reaction temperature and the amount of SO^{2-}_4 / SnO_2 - TiO_2 were 5 hours, 1.0 : 1.8, 40 °C and 1.8 % (of terpineol mass), respectively. The highest yield and selectivity of terpinyl acetate were 98.7 % and 88.9% separately. Therefore, SO^{2-}_4 / SnO_2 - TiO_2 has higher catalytic activity and selectivity.

Wu Chunhua[6] studied to use nanometer solid superacids SO^{2-}_4 / ZrO_2 as a catalyst to synthesize terpinyl acetate. The best conditions were that the reaction time, the molar ratio of terpineol to acetic anhydride, the reaction temperature and the amount of SO^{2-}_4 / ZrO_2 were 5 hours, 1.0 : 1.3, 50 °C and 3 % (of terpineol mass), separately. The highest yield of terpinyl acetate was 100 %.

Li Shumin[7] introduced rare earth solid super acid SO^{2-}_4 / ZrO_2- SnO_2 -Nd_2O_3 as a catalyst to synthesize terpinyl acetate. The effect of the reaction conditions, such as the reaction time, the molar ratio of terpineol to acetic anhydridel, the reaction temperature and the amount of SO^{2-}_4 / ZrO_2- SnO_2 -Nd_2O_3, had been discussed. The best conditions were that the reaction time, the molar ratio of terpineol to acetic anhydridel, the reaction temperature and the amount of SO^{2-}_4 / ZrO_2- SnO_2 -Nd_2O_3 were 5 hours, 1.0 : 1.5, 50 °C and 2 % (of terpineol mass), respectively. The highest yield of terpinyl acetate was 92.9 %.

Activated carbon heteropolyacids as a catalyst

Xie Hui[8] explained how to use activated carbon heteropolyacids to synthesize terpinyl acetate. The best conditions were that the reaction time, the molar ratio of terpineol to acetic anhydride, the reaction temperature and the amount of activated carbon heteropoly acids were 5.5 hours, 1.0 : 1.3, 70 °C and 4.8 % (of terpineol mass), separately. The highest yield of terpinyl acetate was 85.2 %. After activated carbon heteropolyacids was used 10 times, the yield of terpinyl acetate still arrived at 80.3%.

Phosphoric acid / ionic liquid composite system as a catalyst

Liu Shiwei[9] introduced three kinds of H_3PO_4 / [R mim]BF_4 composite as catalysts to produce terpinyl acetate. Among of them, H_3PO_4 / [C_4 mim]BF_4 and H_3PO_4ÿ[C_8 mim]BF_4, both have high catalytic activity. H_3PO_4 / [C_4 mim]BF_4 was the sample. The best conditions were that the reaction time, the molar ratio of terpineol to acetic anhydride, the reaction temperature and the amount of H_3PO_4 / [C_4 mim]BF_4 were 10 hours, 1.0 : 1.5, 40 °C and 3 % (of terpineol mass), separately. The highest yield of terpinyl acetate was 86.5 %.

Acidic functional polyether ionic liquid as a catalyst

Liu Shiwei[10] introduced acidic functional polyether ionic liquid, 1-(3-sulfonic group)propyl – 3 - polyoxyethyleneimi - dazole dihydrogen phosphate ([HSO_3 - $(CH_2)_3$ - im - $(CH_2CH_2O)_n$ H] H_2PO_4), as a catalyst to synthesize terpinyl acetate. Effects of the reaction conditions, such as the reaction time, the molar ratio of terpineol to acetic anhydridel, the reaction temperature and the amount of acidic functional polyether ionic liquid had been discussed. The best conditions were that the reaction time, the molar ratio of terpineol to acetic anhydridel, the reaction temperature and the amount of acidic functional polyether ionic liquid were 8 hours, 1.0 : 1.5, 40 °C and 1.5 g, respectively. The highest yield and selectivity of terpinyl acetate were 99.5 % and 87.8 %, separately. After acidic functional polyether ionic liquid was reused 6 times, the yield and selectivity of terpinyl acetate were 99.4 % and 88.3 %.

$SnCl_4 \cdot 5\ H_2O$ as a catalyst

Zhao Qianrong[11] described the synthetic method of terpinyl acetate by using $SnCl_4 \cdot 5\ H_2O$ as a catalyst. The best conditions were that the reaction time, the molar ratio of terpineol to acetic anhydride, the reaction temperature and the amount of $SnCl_4 \cdot 5\ H_2O$ were 5 hours, 1.0 : 1.4, 30 °C and 2.5 g, respectively. The highest yield and selectivity of terpinyl acetate were 94.1 % and 93.3 % separately.

Acidic ionic liquid as a catalyst

Ji Kaihui[2] used acidic ionic liquid, $[HSO_3$-pmim$]H_2PO_4$, to synthesize terpinyl acetate. The best conditions were that the reaction time, the molar ratio of n(a-pinene) : n($[HSO_3$-pmim$]HPO_4$) : n(chloroactic acid) : n(acetic acid), the reaction temperature and the amount of $[HSO_3$-pmim$]HPO_4$ were 10 hours, ÿ5 : 0.9 : 5 : 1 4, 40 °C and 1.5 g, respectively. The highest yield of terpinyl acetate was 85.6 %. After acidic ionic liquid was reused 5 times, the yield of terpinyl acetate still reached 83.5 %.

Acetic anhydride phosphate acid as a catalyst with microwave heating method

Wu Chunhua[12] explained how to use acetic anhydride phosphate acid as a catalyst with intermittent microwave heating method to synthesize terpinyl acetate. The best conditions were that the reaction time, the molar ratio of terpineol to acetic anhydride, the reaction temperature (microwave power) and the amount of acetic anhydride phosphate acid were 2 hours, 1.0 : 1.25, 100 W and 4 % (of terpineol mass), separately. The highest yield of terpinyl acetate was 86.53 %.

CONCLUSION

Based on the above discussion and review, nanometer solid superacids SO^{2-}_4 / ZrO_2 is one of the best catalysts for the highest yield of terpinyl acetate (almost 100 %). On the other hand, activated carbon heteropolyacids is the worst of the catalysts since the maximum yield of terpinyl acetate was only 85.2 %.

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