VERSITA

Chemical Papers 67 (6) 586–593 (2013)
DOI: 10.2478/s11696-013-0359-z

ORIGINAL PAPER

KI-catalysed synthesis of 4-methylcatechol dimethylacetate and fragrant compound Calone 1951®

[a]Ya-Zheng Zhang, [a]Qian Yang, [a,b]Shao-Jian Huang, [a]Zi-Ping Luo, [a,c]Wen-Ping Li, [a]Li-Chun Dong*

[a]*School of Chemistry and Chemical Engineering, Chongqing University, Chongqing, 400044, China*

[b]*Zhanjiang Testing Center for Environmental Protection, Zhanjiang, Guangdong, 524022, China*

[c]*Shandong Shangyu Chemical Co. Ltd., Shandong, 274300, China*

Received 4 June 2012; Revised 28 November 2012; Accepted 1 December 2012

Synthesis of the fragrant compound Calone 1951® from 4-methyl catechol and methyl bromoacetate entails three successive reactions: the Williamson reaction, Dieckmann condensation, and hydrolysis–decarboxylation reaction. In this paper, the synthesis of 4-methylcatechol dimethylacetate (MCDA) via the Williamson reaction by adding KI as catalyst was investigated. It was found that the addition of an appropriate amount of KI can significantly increase the product yield due to generation of methyl iodoacetate via the reaction between KI and methyl bromoacetate. The synthesised MCDA as well as Calone 1951® were first characterised by melting points, HPLC, IR, and NMR analyses. Next, the effect of the key operating factors on MCDA synthesis by the Williamson reaction was investigated and the optimum operating conditions were obtained via a group of orthogonal experiments. The verification experiments demonstrated that, under the optimum operating conditions, the MCDA yield could be increased from 78.5 % to 95.4 % by the addition of an appropriate amount of KI; the corresponding yield of Calone 1951® increased to 68 %.

Keywords: 4-methylcatechol dimethylacetate, MCDA, KI, catalysis, Calone1951® synthesis, synthesis process

Introduction

Calone 1951®, 7-methyl-2*H*-benzo-1,5-dioxepin-3(4*H*)-one, is a member of the benzodioxepinone family with a pleasant fragrance redolent of watermelon (Drevermann et al., 2005). The synthesis of Calone 1951® reported in the literature can be categorised into four procedures according to the starting materials. The starting materials for the first procedure are 4-methylcatechol and chloroacetonitrile (Rooney et al., 1975), from which Calone 1951® is synthesised via consecutive etherification, condensation, and acidification reactions with the product yield as high as 51 %. The second procedure starts from 4-methylcatechol and 1,3-dichloro-2-propanol (Rosnati & De Marchi, 1962), from which 7-methyl-3,4-dihydro-2*H*-benzo[*b*][1,4]dioxepin-3-ol is first synthesised, then oxidised to Calone 1951®. The product yield achieved by this procedure is low (4 %). In the third procedure, Calone 1951® is synthesised from 4-methylcatechol and 1,3-dichloroacetone via a cyclic condensation and a rearrangement reaction, successively (Shi, 2006; Zhang, 2010; Lin et al., 2009). This procedure can achieve a product yield of 50 %. However, 1,3-dichloroacetone is highly toxic and corrosive. The fourth procedure for synthesising Calone 1951® starts from 4-methylcatechol and methyl bromoacetate (Drevermann et al., 2005, 2007a, 2007b; Beere-

*Corresponding author, e-mail: lcdong72@cqu.edu.cn