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SHORT COMMUNICATION

Trimerization of aldehydes with one α-hydrogen catalyzed by sodium hydroxide

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Trimerization of 2-methylpropanal (isobutyraldehyde) is a simple and effective method to synthesize 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate and 2,2,4-trimethyl-1,3-pentanediol-3-monoisobutyrate which are often used as film forming auxiliaries in paints. The use of solid sodium hydroxide as a catalyst provides an excellent yield of above 85 % after the optimization of the reaction time and the catalyst dosage. Furthermore, trimerization of four other aldehydes with one α-hydrogen catalyzed by solid sodium hydroxide can also take place and the yield of 1,3-diol monoesters reaches 50–70 %. Trimerization of aldehydes with one α-hydrogen can be explained by a three-step reaction mechanism: (i) aldol condensation of aldehyde; (ii) crossed Cannizzaro reaction; and (iii) esterification of carboxylic acid and alcohol.

Keywords: trimerization, isobutyraldehyde, aldehydes, sodium hydroxide

Trimerization of aliphatic aldehydes with one α-hydrogen is of fundamental importance in synthetic organic chemistry granting access to 1,3-diol monoesters widely used as coalescing agents in the paint industry (Törmäkangas & Koskinen, 2001; Gallagher et al., 2008). Our work was focused on 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (*Va*) and its isomers (2,2,4-trimethyl-1,3-pentanediol-3-monoisobutyrate; *VIa*) synthesized by the trimerization of 2-methylpropanal (isobutyraldehyde). Since *Va* is a glycol ester with a high boiling point and it is hardly soluble in water, it has drawn attention as a solvent and plasticizer having remarkable properties such as very good miscibility with resins, low solidifying point, excellent viscosity stability, and low soiling property in latex emulsions and paints (Takasu et al., 1972; Duccini et al., 2007). In recent years, it has been used as a film forming auxiliary in paints (Swan, 2005). *VIa* has the same industrial applications as *Va* and it is not necessary to separate them in industrial scale.

With the field of applications widening, the development of general and efficient methods for the synthesis of *Va* is an active area of research. Self-condensation of isobutyraldehyde catalyzed by various catalysts is a convenient method and the reaction with high atom economy is friendly to the environment. However, the catalysts used to promote the self-condensation of isobutyraldehyde are usually expensive and not easily accessible, $[Al(OC_2H_5)_4]_2Mg$, $[Al(OC_3H_7)_4]_2Mg$, $[Al(OC_4H_9)_4]_2Mg$ (Kulpinski & Nord, 1943; Villani & Nord, 1947), $LiWO_2$ (Villacorta & Filippo, 1983), 1,3-diol monoalcoholates (Törmäkangas & Koskinen, 2001), $Fe_3(CO)_{12}$ (Ito et al., 1983), $Cp^*_2Sm(thf)_2$ (Miyano et al., 1998). Preparation of the above-mentioned catalysts is usually complicated and costly which limits their industrial application. Jian et al. (2003a) disclosed a method to obtain *Va*. The reaction was carried out in two steps in the presence of a 45 mass % sodium hydroxide solution. The condensation reaction was conducted at temperatures in the range of 20–30 °C for 3 h, and at 60 °C for 2 h in the second step. After the removal of the aqueous phase by delamination, the organic phase was purified by fractional distillation under reduced pressure. Tic et al. (2012) introduced a method of continuous production of isobutyraldehyde. The reaction

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