HYDROLYSIS OF FATTY ESTERS IN DICHLOROMETHANE/ METHANOL

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Abstract: The preparation of cinnamic acid, palmitic acid and acid carboxylate of 14,16-hentriacontanedione were studied in dichloromethane/ methanol and 2-methyl tetrahydrofuran/ methanol (DCM/MeOH and 2-mTHF/MeOH). Hence, this paper demonstrated the alkaline hydrolysis (using NaOH and KOH) of esters in organic solvents (DCM/MeOH and 2-mTHF/MeOH). Although the aromatic ester methyl cinnamate was more readily hydrolysed, however same condition at longer time gave complete hydrolysis of the methyl palmitate and methyl acrylate and dimethyl itaconate modified 14,16-hentriacontanedione. Therefore, DCM/MeOH and 2-mTHF/DCM are quite suitable for the hydrolysis of fatty esters.

Keywords: Fatty esters, greener solvent, hydrolysis, solubility

Introduction

Alkaline hydrolysis is an important reaction process; the alkaline hydrolysed products are applied in soap making, pharmaceutical, paint, dying of items, food additive, and so on (Ahmad *et al*., 2013). The process of the alkaline hydrolysis is also called saponification (Ahmad *et al.,* 2013). The hydrolysis of ester is commonly performed with acid or base (Koshikari, 2012). Classical hydrolysis conditions for esters involve the use of NaOH, KOH, or LiOH in pure H_2O, MeOH, EtOH or MeOH/H_2O and EtOH/H_2O solvents (Salimon *et al*., 2011; Ikhazuangbe & Oni 2015; Sivasubramanian *et al.*, 2007).Alkaline system (usually KOH and NaOH) hydrolysis is carried out with a slight excess of base in ethanol. This is a sufficiently mild procedure that most fatty acids are unaltered (Salimon *et al*., 2011). According to Salimon *et al.* (2011), 1.75M of ethanolic KOH at 65^{o}C for 2 h was used to hydrolyse Jatropha curcas seed oil. According to Deshayes (2001), potassium carbonate (K_2CO_3) although weak could be used for the hydrolysis of esters using the solvent methanol. Gupta and Ho, 1977 reported the hydrolysis of methyl paraben and propyl paraben esters with 10% KOH in alcohol: water (80:20). Furthermore, Khurana *et al.* (2004) reported that methanol is the solvent of choice for rapid hydrolysis of esters at ambient condition with KOH, whereas hydrolysis of esters with KOH-ethanol and KOH-n-propanol are poor. This is because KOH is more soluble in methanol than the ethanol and n-propanol. Also that addition of water as co-solvent slows the hydrolysis and reactions were incomplete even after 6 h at 35^{o}C (Khurana *et al*., 2004). In addition, Lovric *et al.* (2007) reported the conversion of different esters into carboxylic acid with sodium and potassium trimethylsilanolate in the medium of tetrahydrofuran (THF).

Esters of aromatic acids readily give a solid metal carboxylate within few minutes of the reaction unlike esters of aliphatic acids. It had been observed that methyl esters hydrolysed quicker than esters with bulkier alkyl group (Khurana *et al*., 2004). Aliphatic esters with alpha hydrogens are not readily hydrolysed, like aromatic esters due to competing aldol type condensations and the tendency to form stabilized anion after deprotonation (Khurana *et al*., 2004). Recently, Theodorou *et al.* (2007) reported the hydrolysis of series of ester in dichloromethane/methanol (DCM/MeOH). In addition, Anderson *et al.* (2004) reported non-aqueous work-up hydrolysis of alkyl esters with barium hydroxide octahydrate in methanol followed by protonation with anhydrous hydrogen chloride. Generally, such studies are rare. Therefore, this paper deals with the hydrolysis of cinnamate, palmitate and methyl acrylate and dimethyl itaconate modified biobased β-diketone in DCM/MeOH.

Materials and Methods

Materials

KOH, NaOH, dichloromethane and methanol were obtained from Fisher Scientific UK, Limited. Then 2-methyl tetrahydrofuran, methyl *trans*-cinnamate and methyl palmitate were purchased from Sigma-Aldrich. Whereas methyl acrylate and dimethyl itaconate modified 14,16-hentriacontanedione were prepared prior to the hydrolysis.

Preparation of cinnamic and palmitic acids

About 0.21 g methyl *trans*-cinnamate and KOH (3 mole equivalents) plus mixture of 2 mL DCM/ 3 mL MeOH in a 10 mL vial with a screw cap and stirred at 30^{o}C for 2 h 30 min. An intense white lump was formed with NaOH in the course of the reaction. Thereafter, the reaction mixture was concentrated and 10 mL water added and the mixture acidified to pH of 2 with concentrated HCl. The product was filtered off, and dried under vacuum as previously reported (Khurana *et al*., 2004). It was analysed with GC-FID and ^{1}HNMR. The reaction was repeated using NaOH and mixture of 2 mL 2-methyl tetrahydrofuran (2-mTHF)/ 3 mL MeOH.

About 0.20 g methyl palmitate and NaOH (3 mole equivalents) were measured and poured into a mixture of 1.5 mL DCM/ 2 mL MeOH in a 10 mL screw cap vial, covered and stirred at 30^{o}C for 2 h 30 min, 5 and 24 h, respectively. White lump was formed in the course of the reaction. The reaction was stopped at the appropriate times as earlier specified and concentrated under vaccum. Then, 10 mL distilled water added and the mixture acidified to pH of 2 with concentrated HCl. The product was filtered and analysed with GC-FID.

Preparation of acid carboxylate of the modified 14,16-hentriacontanedione

The hydrolysis of the modified lipophilic 14,16-hentriacontanedione was performed as previously reported (Theodorou *et al.,* 2007). About 0.0479 g of the methyl acrylate modified biobased β-diketone was dissolve into 0.2 mL DCM in a 50 mL vial, followed by 0.0175 g NaOH (i.e. 5 mole equivalents) in 0.3 mL MeOH and this was stirred overnight (24 h) at 30^{o}C. The reaction mixture turned into a white lump at the end of the reaction implying sodium carboxylate of the modified β-diketone was formed. The reaction was stopped and the solvent removed under vaccum. The mixture was then dissolved in 10 mL distilled water and acidified with HCl to pH of 2. The product was then extracted with 10 mL DCM and concentrated. The carboxylate of the

dimethyl itaconate was prepared as earlier described using 0.0692 g of the dimethyl itaconate modified biobased β-diketone. The recovered yield was 83%.

Results and Discussion

The key NMR and FTIR for the acid carboxylates of the modified β-diketone are as presented in Table 1. Table 2 shows the % formation of the palmitic acid from methyl palmitate; whereas, Fig. 1 represents the % conversion of methyl cinnamate into cinnamic acid.

Table 1: Key FTIR and NMR information for the acid carboxylates of the modified β-diketone

FTIR	Acid carboxylate of the methyl acrylate modified β-diketone	Acid carboxylate of the dimethyl itaconate modified β-diketone	Interpretation
O – H	3400 – 2400 cm^{-1}	3400 - 2500 cm^{-1}	Broad stretching vibration for intermolecular H-bonding for acid carboxylate.
C = O	1700 cm^{-1}	1694 cm^{-1}	Strong vibration for acid carboxylate
^{1}H-NMR (400 MHz, $CDCl_3$) δ	**Absence of chemical shift at about 3.66 ppm**	**Absence of chemical shift at about 3.66 ppm**	**Presence of acid carboxylate group**
^{13}C-NMR (101 MHz, $CDCl_3$) δ	**179.01 ppm**	**180.86 ppm**	**Carbon of carboxylic acid functional group**

Table 2: % formation of palmitic acid from methyl palmitate in the presence of NaOH

time of reaction	% formation of the palmitic acid
30 minute	5.75
5 hour	73.24
24 hour	99.25

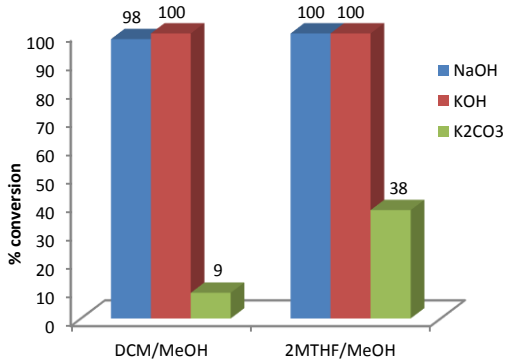
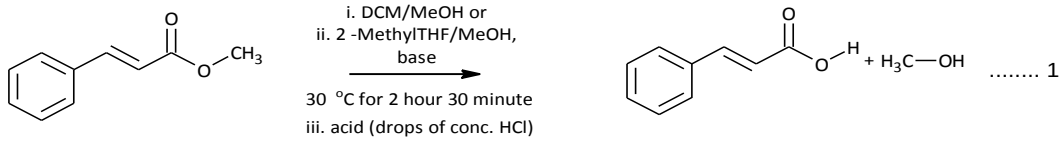


Fig. 1: % conversion of methyl cinnamate into cinnamic acid

Hydrolyses of the cinnamate were firstly investigated as described in in Equation 1. As the reaction progresses, the clear mixture turned into a white lump of the metal carboxylate salt. That is at about 2 h the conversion of methyl cinnamate into cinnamic acid was completed under these specified conditions. It has been also reported that use of polar aprotic solvents for base hydrolysis of ester makes the reaction goes faster (Theodorou *et al*., 2007). Similarly the hydrolysis of methyl cinnamate with KOH and NaOH in DCM/ MeOH and 2-MTHF/ MeOH gave a complete conversion as presented in Fig. 1. However, the use of K_2CO_3 resulted into an incomplete hydrolysis at same conditions. But Deshayes (2001) observed that potassium carbonate (K_2CO_3) although weak could be used for the hydrolysis of esters using the solvent methanol.



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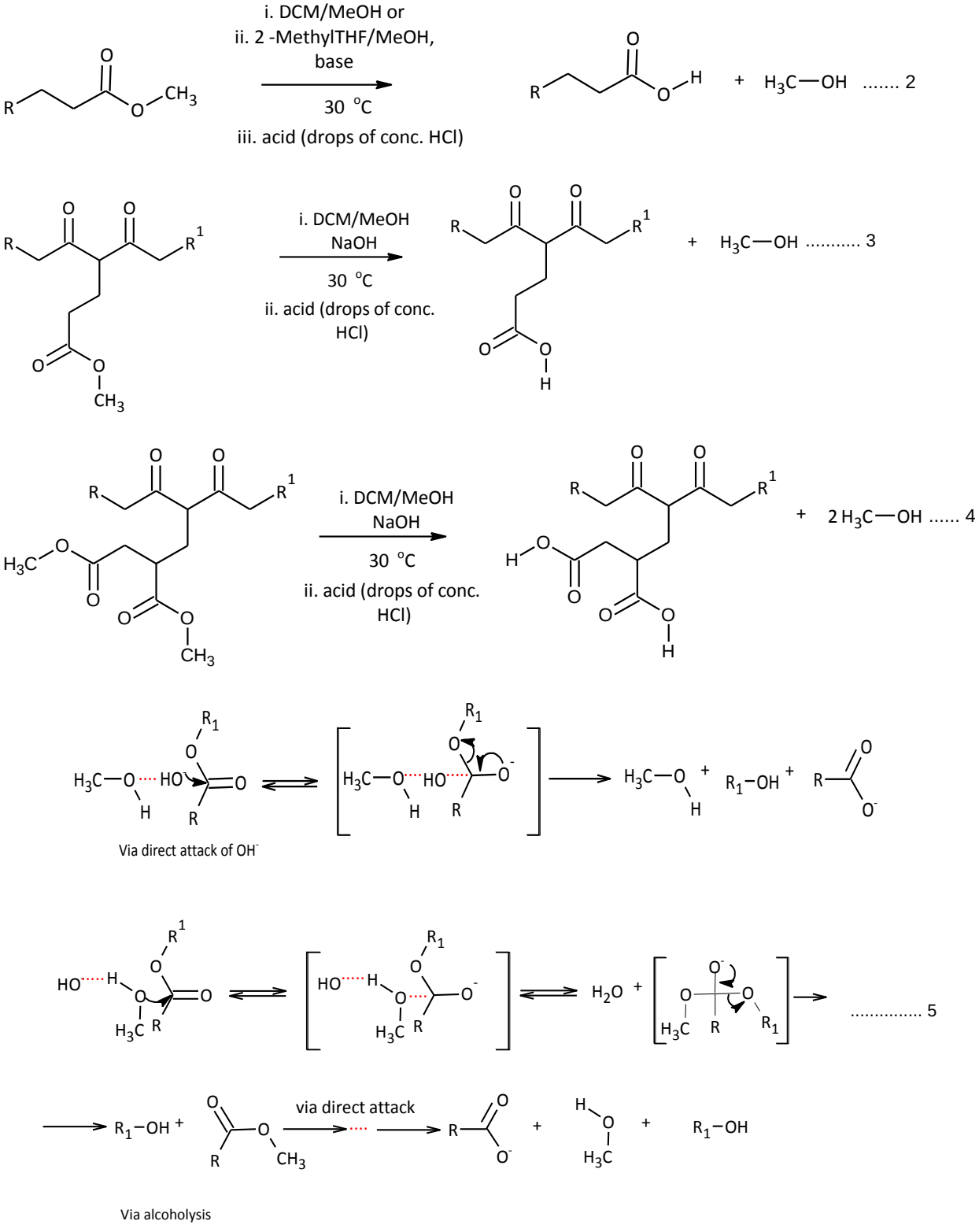
Furthermore, these results of the hydrolysis of methyl cinnamate in DCM/MeOH and 2-MTHF/MeOH suggest that 2-MTHF/MeOH has an edge above DCM/MeOH when K_2CO_3 was used as the base. This may have been due to the solubility of K_2CO_3 in 2-MTHF/MeOH solvents being more than DCM/MeOH. Thus the % formation of cinnamic acid with K_2CO_3 in 2-MTHF/MeOH was four times that of DCM/MeOH solvents. 2-MTHF is a greener solvent compared to DCM; therefore, the 2-MTHF/MeOH solvents should be used as a greener solvents system for the hydrolysis of hydrophobic esters.

The hydrolysis of the methyl palmitate was conducted as described in Equation 2 similar to hydrolysis of methyl cinnamate. From previous studies, longer time is required for hydrolysis of non-aromatic esters. Therefore, different times

of 30 min, 5 and 24 h time were used for the hydrolysis of methyl palmitate for optimisation. Longer time of 24 h produced almost complete conversion of palmitate into palmitic acid. Table 2 shows the GC percentages formation of palmitic acid from methyl palmitate at these different times.



The complete hydrolysis of methyl palmitate took longer time than methyl cinnamate as reported by Khurana *et al*. (2004). Unlike previous reports, the hydrolysis of the methyl palmitate showed less co-products (Khurana *et al*., 2004). This condition used for the hydrolysis of the methyl cinnamate and palmitate were then applied for the hydrolysis of the esters of the methyl acrylate and dimethyl itaconate modified biobased β-diketones overnight as described in Equations 3 and 4. About 78% recovered yield was found. It is worthy to note that alkaline hydrolysis as was observed are

better performed at low KOH or NaOH concentration; and also at low temperatures as previous reported (Sarkar *et al*., 2012). Sarkar *et al.* (2012) also showed that saponification of carotenoid esters at high temperatures and high concentrations of alkali resulted into decomposition of the esters. Furthermore *et al.* (2005) reported that both monoesters and diesters can be hydrolysed in protic and aprotic solvents, but the hydrolysis is faster in aprotic solvents than protic solvent (Rao and Gajanan, 2005). Therefore, the mechanism for this hydrolysis of these esters in DCM/MeOH is expressed in Equation 5.

Conclusion

This paper demonstrated the hydrolysis of some lipophilic esters in organic solvents (DCM/MeOH and 2-mTHF/MeOH). Since 2-mTHF is a greener solvent than DCM, the alkaline hydrolysis of fatty esters using 2-mTHF/MeOH would be safer and more viable. Although the aromatic ester methyl cinnamate was more readily hydrolysed, same condition at longer time was appropriate for the hydrolysis of palmitate, methyl acrylate and dimethyl itaconate modified 14,16-hentriacontanedione.

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