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SYNTHESIS OF α- HYDROXY-β, γ-UNSATURATED ESTERS: HClO4-SiO2 CATALYZED ISOMERISATION OF GLYCIDIC ESTERS TO α-HYDROXY- β, γ-UNSATURATED ESTERS

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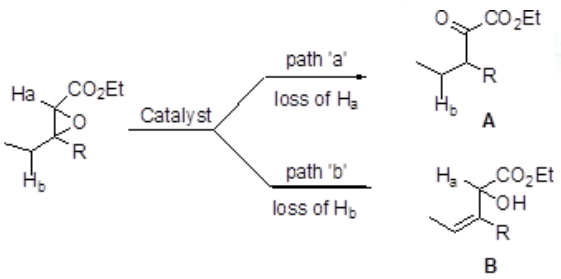
ABSTRACT **–** α-hydroxy-β, γ-unsaturated esters are important building blocks of bioactive compounds, natural products, achiral and chiral vinyl epoxides. These could be easily obtained by isomerization of glycidic esters. In this paper we have reported easy and convenient way of synthesis of α-hydroxy-β, γ-unsaturated esters by isomerisation of glycidic esters using inexpensive catalyst HClO4-SiO2 and eco-friendly ionic liquid. Moderate to good yields with lower reaction times reported.

Keywords: *α-hydroxy-β, γ-unsaturated esters, glycidic esters, ionic liquid, per-chloric acid, Chemistry Studies*

I. Introduction

Glycidic esters are the compounds having an epoxy and an ester group in conjugation where the compounds have two unsaturated groups. Because of this relation, they can either be rearranged or reacted with a variety of reagents to give synthetic intermediates for natural products eg., α-hydroxy-β,γ-unsaturated esters. These are versatile building blocks for the synthesis of bio-active compounds,[1] liquid crystals,[2] achiral and chiral vinyl epoxides.[3]

Glycidic esters, depending on their structure and the catalyst employed, undergo mainly two types of isomerisations as shown in Scheme 1. When the proton H_a α to the ester moiety is lost, the product formed is an α-keto ester **A**. On the other hand, when H_b is lost, α-hydroxy-β,γ-unsaturated ester **B** is formed.



Scheme 1

For the isomerisation of glycidic esters to α-hydroxy-β,γ-unsaturated esters **B** (path 'b', Scheme 1), one of the first reports in literature[4] dealt with α-alkyl substituted glycidate (equation i). This led to the synthesis of **4** through a few subsequent steps from the isomerised glycidic ester i.e., ethyl 2-hydroxy-3-alkenoate **2** (equation i). Absence of hydrogen atom α to the ester group allowed the observed regioselective isomerisation. It was found that glycidic esters having a hydrogen atom α to the ester moiety could also undergo isomerization via path B. For this purpose, Hartman and Rickborn[5] employed $LiClO_4$ as a catalyst and obtained α-hydroxy-β,γ-unsaturated esters **6** (equation ii).

In an effort to improve isomerisation of glycidic esters, Vankar et al.[6] have reported that α-hydroxy-β,γ-unsaturated esters **8** could be obtained in high yields if $BF_3.Et_2O$ is employed as a catalyst at 0°C (equation iii). Apart from the above described isomerisations, glycidic esters have also been found to undergo many other reactions, where the oxirane ring is regioselectively opened by various nucleophiles to give products of diverse synthetic utility.[7,8]

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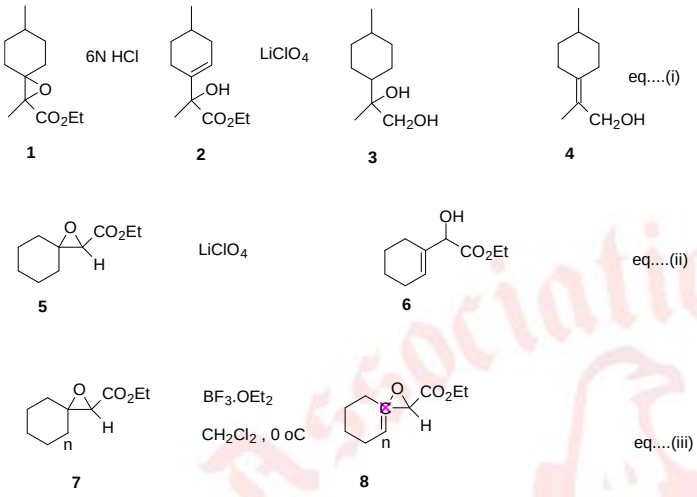


II. Result and Discussion

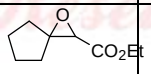
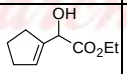
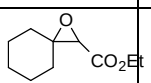
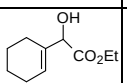
As discussed in the introduction part, α-hydroxy-β,γ-unsaturated esters are useful intermediates in the synthesis of some natural products and vinyl epoxides. Although many methods have been developed to synthesize these intermediates in a facile manner, but still there is a need to develop new catalysts, which work under mild reaction conditions and do not require the use of solvents that are detrimental to environment.

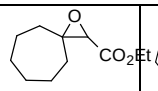
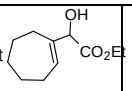
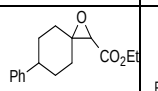
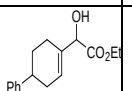
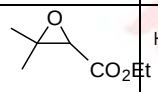
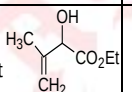
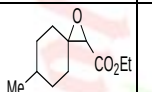
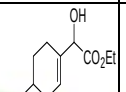
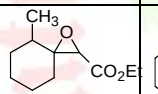
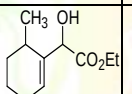
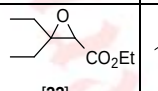
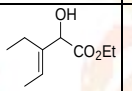
In that direction, we focussed our attention to use perchloric acid adsorbed silica gel ($HClO_4$–SiO_2)[9] as a catalyst to carry out the isomerisation of glycidic esters to α-hydroxy-β,γ-unsaturated esters since $HClO_4$–SiO_2 catalyst is cheap, less toxic, easier to make and handle.

On the other hand, ionic liquids are a new class of compounds entirely composed of ions and are used as an environmentally friendly alternatives for conventional solvents has gained much attention recently. Ionic liquids are known[10] to be non-volatile, non-toxic, reusable and convenient for many organic reactions. Among the well-known moisture- and air-stable room temperature ionic liquids, [bmim] [BF_4] is water soluble, [bmim] [PF_6] is water insoluble. These ionic liquids form a binary phase with the organic solvents and make the extraction of the products from reaction medium easier. we planned to use this solvent for isomerisation of glycidic esters to α-hydroxy-β,γ-unsaturated esters.

Our results are shown in the Table 1. To test the potentiality of $HClO_4$-SiO_2 system, we first took 100 mg of glycidic ester **9** (entry 1, Table 1) in 2 mL of freshly distilled dry dichloromethane under N_2. To this stirring solution was added weight equivalent of $HClO_4$-SiO_2 system at ambient temperature and the progress of the reaction was monitored by TLC. The reaction took 45 min to complete. The catalyst was filtered off and the crude product was purified by column chromatography to get the isomerised α-hydroxy-β,γ-unsaturated ester **10** as a colorless liquid in 60% yield. Its ^1H NMR (400 MHz, $CDCl_3$) spectrum showed peaks at δ 5.75 (br s, 1H) corresponding to vinylic proton, another broad singlet at δ 4.62 corresponding to methine proton, and a hydroxy proton at 2.97 (br s, 1H) confirming the formation of the α-hydroxy-β,γ-unsaturated ester **10**. The other protons appeared at δ 1.35 (t, J = 7.00 Hz, 3H) corresponding to -CH_3 of ester, 1.4-2.62 (m, 6H) corresponding to allylic and the other methylene protons of cyclopentene ring system and at 4.25 (q, 2H) corresponding to the –CH_2- of ester group. Further, its IR spectrum (neat) showed absorptions at 3494 cm^{-1} and 1732 cm^{-1} corresponding to the hydroxy and ester functionalities, respectively. The same was compared with the available literature data[8] and was found to be the same.

Table 1 : Isomerisation of glycidic esters to α-hydroxy-β, γ-unsaturated esters using $HClO_4$-SiO_2

	Substrate	Product	Dichloromethane as a solvent		[bmim] [PF_6] as a solvent	
			Time (min)	Yield %	Time (min)	Yield %
1.	 [9]	 [10]	45	60	30	50
2.	 [11]	 [12]	60	83	300	82

3.	 [13]	 [14]	45	64	60	64
4.	 [15]	 [16]	30	86	60	62
5.	 [17]	 [18]	60	50	30	44
6.	 [19]	 [20]	50	55	120	50
7.	 [21]	 [22]	20	52	300	75
8.	 [23]	 [24]	45	65	60	54

[a] Dihydroxy compound (see Table 2).

[b] Based on the starting material recovered.

With these encouraging results, we applied the $HClO_4$-SiO_2 reagent system to other glycidic esters. Thus, the glycidic ester **11** under above mentioned reaction conditions gave the isomerised α-hydroxy-β,γ-unsaturated ester **12** in 83% yield. The reaction went to completion in 60 min. Its ^{1}H NMR (400 MHz, $CDCl_3$) spectrum showed peaks at δ 1.26-1.31 (t, *J* = 7.08 Hz, 3H) corresponding to $–CH_3$ of ester, 3.06 (d, *J* = 5.60 Hz) corresponding to hydroxyl, 4.45-4.47 (d, *J* = 5.60 Hz, methine) and 5.82 (br s, 1H) corresponding to vinylic proton suggesting the formation of α-hydroxy-β,γ-unsaturated ester **12**. Further, its IR spectrum showed absorptions at 1729 cm^{-1} and 3513 cm^{-1} corresponding to ester and hydroxy functionalities, respectively. This data was compared with the literature-reported data.

Similarly, the glycidic esters **13**, **15**, **19** (derived from substituted cycloalkanones) and **17** underwent smooth isomerisation to produce α-hydroxy-β,γ-unsaturated esters **14**, **16**, **20** and **18**, respectively with moderate to good yields as shown in the Table 1. Reactions took 30-60 min for completion.

To test the regioselectivity of the isomerisation of glycidic esters by $HClO_4$-SiO_2 system, 2-methylcyclohexanone based glycidic ester **21** was chosen. Under the above-mentioned reaction conditions, **21** reacted smoothly to produce the desired product **22** in 52% yield. The isomerisation took place regioselectively to produce less substituted olefin. This is based on the fact that in its ^{1}H NMR (400 MHz, $CDCl_3$) spectrum a broad singlet at δ 5.65 was observed which corresponds to the olefinic proton. This can be expected only when the isomerisation takes place producing the less substituted double bond. Otherwise, the signal for the olefinic proton would not have been found. Further, a doublet at δ 1.25 (*J* = 8.00 Hz, 3H) corresponding to the methyl group attached to the cyclohexene ring system represents the formation of less substituted double bond. Otherwise, the methyl group would have appeared as a singlet at around δ 2.0. The other protons appear at δ 1.25-1.34 (m, t, *J* = 7.00 Hz, 3H, $-OCH_3$), 1.40-2.51 (m, 7H, allylic, 2[$-C\underline{H}_2-$] and $–C\underline{H}$-Me), 2.74-76 (d, *J* = 4.88 Hz, 1H, -OH), 4.18-4.55 (m, 3H, $-CH_2-$, $-C\underline{H}$-OH). Further, its IR spectrum showed absorptions at 1730 cm^{-1} and 3480 cm^{-1} corresponding to ester and hydroxy functionalities, respectively.

We also planned to explore the potentiality of the environmentally friendly, air stable ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate [bmim] [PF_6] in this isomerisation of glycidic esters. Comparatively, there was a lesser reaction time, but a little difference in the yield by using the ionic liquid.

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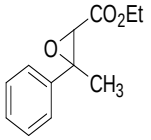
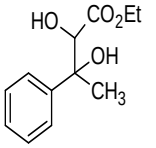
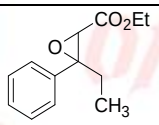
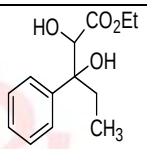
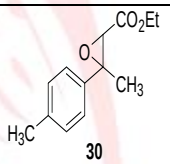
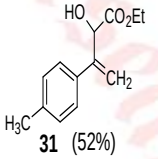
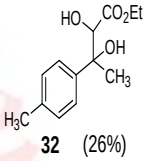
Other glycidic esters produced α-hydroxy-β,γ-unsaturated ester as the major product along with minor dihydroxy compound. It is observed that the reactions proceed slowly when ionic liquid is reused repeatedly.

As a test experiment, 100 mg of the glycidic ester **9** was dissolved in 2g of the ionic liquid, to this weight equivalent of $HClO_4$-SiO_2 was added at ambient temperature and the progress of the reaction monitored by TLC. The reaction took 30 min for completion. The product recovered from diethyl ether (3 x 2 mL) was concentrated and purified by column chromatography. The left-over ionic liquid was dissolved in acetone and residual SiO_2 was filtered off. The product *viz.*, α-hydroxy-β,γ-unsaturated ester **10**, was obtained in 50% yield. The ^1H NMR spectrum was compared with the authentic spectrum obtained when dichloromethane was used as the solvent. Comparatively, there was a lesser reaction time, but a little difference in the yield by using the ionic liquid. The same procedure was followed for the other glycidic esters. Glycidic esters **11**, **13, 15**, **17**, **19** and **23** gave the isomerised esters **12, 14**, **16**, **18**, **20** and **24**, respectively as shown in the Table 1. Interestingly, glycidic ester **21** took longer time and produced regioselectively less substituted double bond containing α-hydroxy-β,γ-unsaturated ester **22** in 75% yield.

The glycidic esters **25** and **27** are comparatively very reactive and exclusively gave dihydroxy compounds **26** and **28** respectively and other glycidic ester **30** produced α-hydroxy-β,γ-unsaturated ester **31** as the major product along with minor dihydroxy compound **32** as shown in Table 2. It was observed that the reactions proceed slowly when ionic liquid is reused repeatedly.

Table 2: Results of isomerisation of glycidic esters to dihydroxy compounds.

Entry	Substrate	Reaction time	Product	
			Major	Minor
1.	 **25**	10 min	 **26** (60%)	-----
2.	 **27**	90 min	 **28** (64%)	-----
3.	 **30**	90 min	 **31** (52%)	 **32** (26%)

In summary, we have developed an efficient method for the preparation of α-hydroxy-β,γ-unsaturated esters using $HClO_4$-SiO_2 reagent system in dichloromethane and also in ionic liquid (green solvent) [bmim] [PF_6] medium.

III. Experimental Section

A. General

All experiments were performed in oven dry glass apparatus. All the aldehydes used for the preparation of glycidic esters are commercially available and were purchased from different chemical companies. All the aldehydes and ethyl chloroacetate were freshly distilled before use. Dichloromethane was dried over anhydrous $CaCl_2$ and freshly distilled over CaH_2 prior to use. CH_3CN was dried over P_2O_5 and freshly distilled over CaH_2 before using. All reactions were carried out under an inert nitrogen atmosphere. All compounds were purified by silica gel column chromatography (100-200 mesh) using petroleum ether and ethyl acetate as the solvents. Reaction mixtures were magnetically stirred, unless otherwise specified. IR spectra were recorded on Perkin Elmer 1320 spectrometer and the absorption bands were reported in reciprocal centimeter (cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on Jeol LA-400NMR spectrometer in $CDCl_3$ using tetramethyl

silane as an internal standard. FAB mass spectra were obtained using Jeol SX 102/DA-6000 spectrometer and peak positions of principal fragments have been reported in m/z. Elemental analysis was carried out in Coleman automatic carbon, hydrogen and nitrogen analyzer.

B. Preparation of glycidic esters

To a suspension of sodium sand (253 mg) in 3.5 mL of anhydrous xylene was slowly added a mixture of ketone (10 mmol) and ethyl chloroacetate (10.2 mmol) with stirring and cooling in an ice salt bath. The reaction mixture was then allowed to come to room temperature over additional 6 h. The red colored solution was then poured into 10 mL ice-cold water and extracted with ether (3 x 25 mL). The combined ether layer was washed with water (2 x 10 mL), brine (10 mL) and dried over anhydrous Na_2SO_4. After removal of ether using rotary evaporator, xylene was removed under reduced pressure. The crude product was purified by Kugelrhor distillation.

IV. Preparation of the catalyst $HClO_4$- SiO_2[9]

$HClO_4$ (1.25g, 12.5 mmol, as a 70% aqueous solution) was added to the suspension of silica gel (23.75 g, 200-400 mesh) in Et_2O. The mixture was concentrated and the residue heated at 100°C for 72 h under vacuum to afford $HClO_4$-SiO_2 as a free flowing powder.

A. Method A: $HClO_4$-SiO_2 in dichloromethane

General procedure

To a stirred solution of glycidic ester (1 mmol) in dry dichloromethane was added weight equivalent of $HClO_4$-SiO_2 catalyst under N_2 and the stirring was continued. Progress of the reaction was monitored by TLC. Once the reaction was over, $HClO_4$-SiO_2 was filtered off and the solvent evaporated under reduced pressure. The crude product was purified by column chromatography using 100-200 mesh SiO_2.

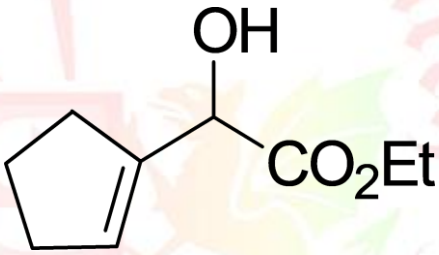
B. Method B: $HClO_4$-SiO_2 and [bmim] [PF_6] system

General procedure

To a solution of glycidic ester (1mmol) in 2g of [bmim] [PF_6] was added weight equivalent of $HClO_4$-SiO_2 under N_2 and stirring continued. Progress of the reaction was monitored by TLC. Once the reaction was over, the product was recovered with diethyl ether (3 x 2 mL). The combined organic layers were concentrated, and crude product was purified by column chromatography using 100-200 mesh SiO_2.

To the residual reaction solvent in the above process was added acetone (2 x 5 mL) and the whole mixture was filtered to remove the catalyst. After evaporation of acetone, the recovered ionic liquid was dried under high vacuum at 60 °C for 3-4 h and reused for the reaction.

(l) Ethyl 2-hydroxy-2-cyclopentenylacetate (10)

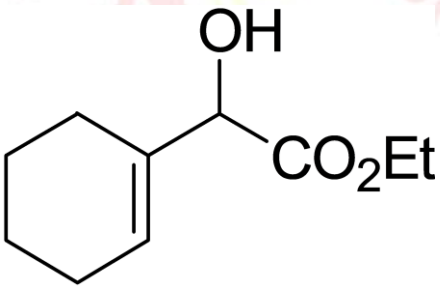


Yield: 60%

IR (CH_2Cl_2) ν_{max}: 3494, 1732 cm^{-1}

^1H NMR ($CDCl_3$, 400 MHz) δ 1.35 (t, *J* = 7.00 Hz, 3H, -OCH_2-CH_3), 1.46-2.62 (m, 6H, allylic and other methylene protons), 3.05 (br s, 1H, -OH), 4.25 (q, 2H, -OCH_2-), 4.62 (br s, 1H, -CHOH), 5.75 (br s, 1H, vinylic).

(2) Ethyl 2-hydroxy-2-cyclohexenylacetate (12)



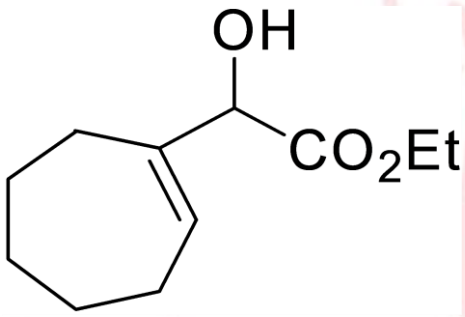
Yield: 83%

State: thick oil (Lit. b.p. 116-118 °C/10m.m)

IR (CH_2Cl_2) ν_{max}: 3513, 1729cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26-1.31 (t, *J* = 7.08 Hz, -CH_3), 1.54-2.14 (m, 8H, cyclohexyl protons), 3.06-3.07 (d, *J* = 5.60 Hz, 1H, -OH), 4.22-4.28 (m, 2H, -CH_2-), 4.45-4.47 (d, *J* = 5.60 Hz, methine), 5.82 (br s, 1H, vinylic proton).

(3) Ethyl 2-hydroxy-2-cycloheptenylacetate (14)



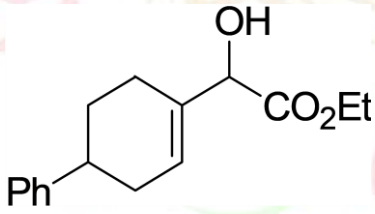
Yield: 64%

State: thick oil (Lit. b.p. 89 °C / 0.5m.m)

IR (CH_2Cl_2) ν_{max}: 3500, 1730 cm^{-1}

^{1}H NMR spectrum ($CDCl_3$, 400 MHz) δ 1.25-1.32 (dt, *J* = 7.08 Hz, 3H, -CH_3), 1.41-1.55 (m, 4H, 2 x -CH_2-), 1.70-1.76 (2H, d, *J* = 4.64 Hz, -OH), 4.20-4.31 (m, 2H, -C<u>H</u>$_2$-CH_3), 4.46-4.47 (d, *J* = 4.88, 1H, methine), 5.95-5.98 (t, *J* = 6.60 Hz, 1H, vinylic).

(4) Ethyl 2-hydroxy-2-(4-phenyl-1-cyclohexenyl) acetate (16)



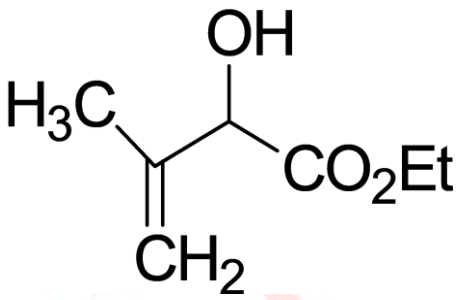
Yield: 86%

State: white crystalline solid (m.p.58 °C)

IR (CH_2Cl_2) ν_{max}: 3517, 1729 cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28-1.33 (t, *J* = 7.00 Hz, 3H, -CH_3), 1.73-2.36 (m, 6H, 3[-CH_2-]), 2.75-2.83 (m, 1H, -CH-Ph), 4.23-4.31 (q, *J* = 7.00 Hz, 2H, -C<u>H</u>$_2$-CH_3), 4.54 (br s, 1H, methine), 5.93 (br s, 1H, vinylic proton), 7.17-7.31 (m, 5H, aromatic).

(5) Ethyl 2-hydroxy-3-methyl-3-butenoate (18)

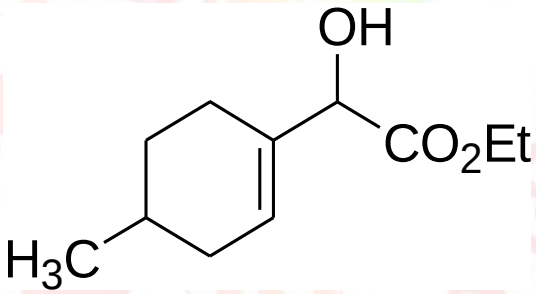


Yield: 50%

IR (CH_2Cl_2) ν_{max}: 3460, 1729 cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.25 (t, *J* = 7.08 Hz, 3H, -OC<u>H</u>$_2$-CH_3), 1.63 (m, 3H, =C(C<u>H</u>$_3$).CH-), 3.18 (br s, 1H, -OH), 4.13 (q, *J* = 7.00 Hz, 2H, -OCH_2-), 4.5 (s, 1H, -C<u>H</u>OH), 4.7-5.2 (m, 2H, vinylic).

(6) Ethyl 2-hydroxy-2-(4-methyl-1-cyclohexenyl) acetate (20)

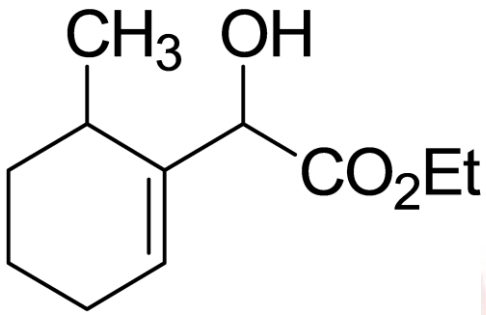


Yield: 50%

IR (CH_2Cl_2) ν_{max}: 3514, 1726 cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.88-0.98 (2d, *J* = 6.60 Hz, -CH-C<u>H</u>$_3$), 1.02-1.09 (t, 3H, -CH_3), 1.17-2.16 (m, 7H, cyclohexene ring protons), 3.05-3.10 (d, *J* = 5.36 Hz, 1H, -OH), 4.44 (br s, 1H, methine), 4.24-4.32 and 4.72-4.79 (m, 2H, -OC<u>H</u>$_2$-CH_3), 5.78 (br s, 1H, vinylic).

(7) Ethyl 2-hydroxy-2-(6-methylcyclohexa-1-enyl) acetate (22)



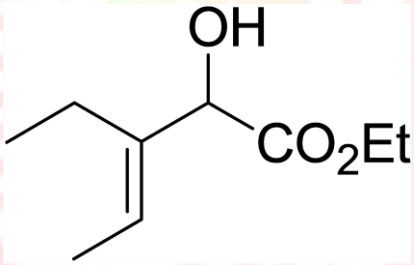
Yield: 52%

State: colorless thick liquid

IR (CH_2Cl_2) ν_{max}: 3480, 1730 cm^{-1}

^1H NMR ($CDCl_3$, 400 MHz) δ 1.25 (d, *J* = 8.00 Hz, 3H, -CH-C<u>H</u>$_3$), 1.25-1.34 (t, *J* = 7.00 Hz, 3H, -OC<u>H</u>$_3$), 1.40-2.51 (m, 7H, allylic, 2[-C<u>H</u>$_2$-] and –C<u>H</u>-Me), 2.74-76 (d, *J* = 4.88 Hz, 1H, -OH), 4.18-4.55 (m, 3H, -C<u>H</u>$_2$-, -C<u>H</u>-OH), 5.65 (br s, 1H, olefinic proton).

(8) Ethyl 2-hydroxy-3-ethyl-pent-3-enoate (24)



Yield: 65%

IR (CH_2Cl_2) ν_{max}: 3500, 1715 cm^{-1}

^1H NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, *J* = 7.00 Hz, 3H, -OCH$_2$.C<u>H</u>$_3$), 1.20 (t, 3H, -C<u>H</u>$_2$-CH$_3$), 1.53 and 1.59 (2d, 3H, CH$_3$-C=), 1.92 (t, *J* = 7.32 Hz, 3H, CH$_3$-C<u>H</u>$_2$-), 3.33 (br s, 1H, -OH), 4.03 (q, 2H, *J* = 7.00 Hz, -OCH$_2$.CH$_3$), 4.28 and 4.82 (2br s, 1H, -C<u>H</u>OH), 5.35 (q, *J* = 5.70 Hz, 1H, =C<u>H</u>-).

V. Acknowledgement

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VI. References

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