Ytterbium triflate (and trimethylsilyl triflate) catalyzed isomerization of glycidic esters to α-hydroxy-β, γ-unsaturated esters and their conversion into cyclopentanoids using Johnson-Claisen rearrangement[1]

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This paper is respectfully dedicated to Prof. S.V. Kessar on the occasion of his 70th birthday

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Abstract

A variety of glycidic esters undergo smooth isomerization to the corresponding α–hydroxy-β, γ-unsaturated esters upon reaction with $Yb(OTf)_3$ or TMSOTf. These α-hydroxy-β, γ-unsaturated esters undergo Johnson-Claisen rearrangement to appropriately substituted diesters, some of which are converted into cyclopentanoids.

Keywords: Glycidic esters, $Yb(OTf)_3$, TMSOTf, α-hydroxy-β, γ-unsaturated esters, cyclopentanoids, Johnson-Claisen rearrangment

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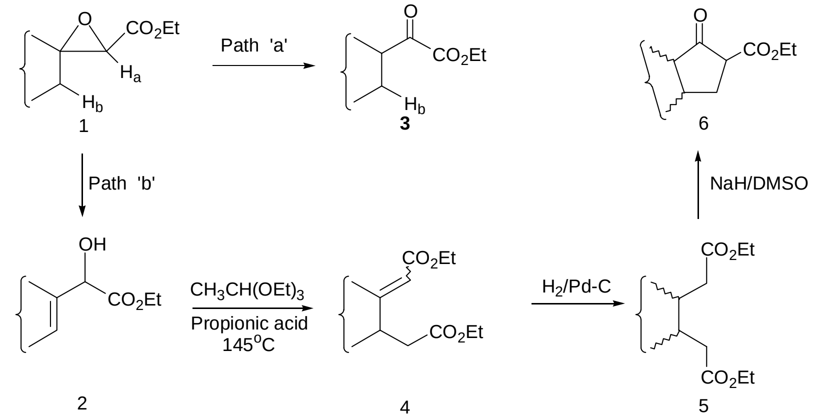
Introduction

α-Hydroxy-β, γ-unsaturated esters are readily derived from the corresponding glycidic esters[2,3] using protic or Lewis acids via their regioselective isomerizations. Out of the two possible isomerizations (path 'a' and path 'b', Scheme 1) of glycidic esters, the one leading predominantly to α-hydroxy-β, γ-unsaturated esters involves use of catalysts such as H_2SO_4,[3] HCl,[4] $BF_3.Et_2O$,[5] $LiClO_4$,[6] zeolite H ZSM-5,[7] and Nafion-H.[8] However, with stronger protic (H_2SO_4)[3] or Lewis acids ($BF_3.Et_2O$),[5] varying degrees of both kinds of isomerization are reported and appear to be a function of temperature.

Ytterbium triflate is known[9] to be a useful mild Lewis acid and has gained importance in recent years. Therefore, it occurred to us that it may permit isomerization of glycidic esters by either path 'a' or 'b.' Indeed, it was found that $Yb(OTf)_3$ readily converts a variety of glycidic esters **1** (Scheme 1) into the corresponding α-hydroxy-β, γ-unsaturated esters **2** (path 'b') at room temperature with no trace of α-keto esters **3** being formed via path 'a'. Our results are summarized in Table 1. We have also found that trimethylsilyl triflate (TMSOTf) allows similar isomerization (Table 1), albeit, at low temperature (-40^{o} C) and in some cases giving small amount (≈ 5-10%) of α-keto esters.



Scheme 1

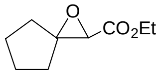
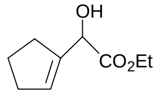
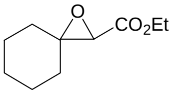
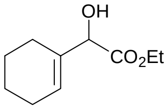
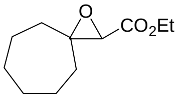
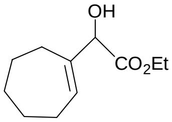
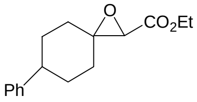
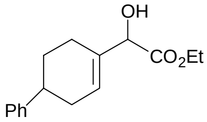
Results and Discussion

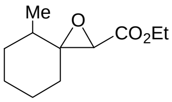
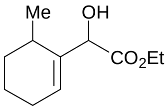
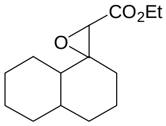
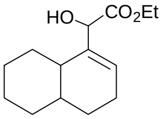
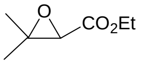
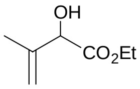
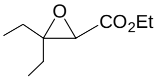
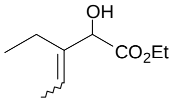
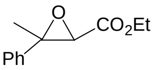
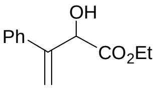
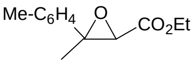
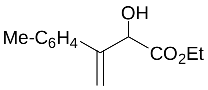
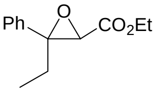
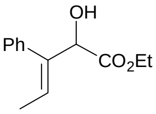
α,β-Unsaturated pyruvate esters, obtained via oxidation of α-hydroxy-β, γ-unsaturated esters, have been found to be excellent Michael acceptors[5] and dienophiles in Diels-Alder reactions.[5,10] We have shown[11] that α-hydroxy-β, γ-unsaturated esters are useful in the preparation of several vinylic epoxides. It was further shown by us[12] that enzymatic resolution of α-hydroxy-β, γ-unsaturated esters as well as isomerization of (-)-menthyl group bearing glycidic esters eventually lead to the formation of chiral vinylic epoxides. In continuation to explore the potential of α-hydroxy-β, γ-unsaturated esters we have now found that they serve as excellent precursors for the synthesis of cyclopentanoids (Scheme 1) via Johnson-Claisen rearrangement,[13] which occurs in a facile manner to form the corresponding diesters **4** (Table 2). These partly unsaturated diesters upon hydrogenation led to the corresponding fully saturated diesters **5,** some of which were converted into cyclopentanoids **6** via Dieckman cyclization.[14]

The saturated diesters **5** were obtained as a mixture of cis-trans isomers with predominance of the trans isomer. These isomers, however, could not be separated by column chromatography. The diester **7c** (Scheme 2), derived from cyclopentanone glycidic ester, was reluctant to undergo Dieckman cyclization to form **19** even at higher temperatures due to the trans stereochemistry[18] at the junction. On the other hand, the corresponding diester **8c** from cyclohexanone readily cyclized to form the hydrindane system **20** as a mixture of cis and trans isomers (40:60).[18,19] The bicyclic system **18a**[7] led to the formation of the corresponding diester **18b** upon Johnson-Claisen rearrangement via the ketene acetal intermediate **A,** which subsequently underwent smooth hydrogenation followed by Dieckman cyclization to form the angularly fused tricyclic system **21/22** as a 1:1 mixture.

In an attempt to make use of this type of cyclopentanoid formation in the synthesis of tricyclopentanoids, the bicyclo (3.3.0) system **23**[20] was converted into the corresponding diester **27** via the same sequence of reactions as described above (Scheme-2), however, it did not undergo cyclization to form the tricyclopentanoid systems **28/29** possibly again due to the resultant trans geometry at the junction after hydrogenation. If reduction of the double bond leads to a cis junction, it is possible to make use of the present methodology for the synthesis of tricyclopentanoids. In view of several tricyclopentanoids such as hirsutene,[21] coriolic acid,[22] isocomene[23] etc being important targets it is worth exploring the present synthetic strategy for their syntheses. Work towards this line is in progress. It is clear that the presence of an ester group in the original α-hydroxy–β, γ-unsaturated esters is responsible for permitting the eventual Dieckman cyclization en-route to cyclopentanoids. We hope, therefore, that this strategy will be useful in organic synthesis.

Table 1. Isomerisation of Glycidic Esters with Yb(OTf)$_3$ and with Me$_3$SiOTf

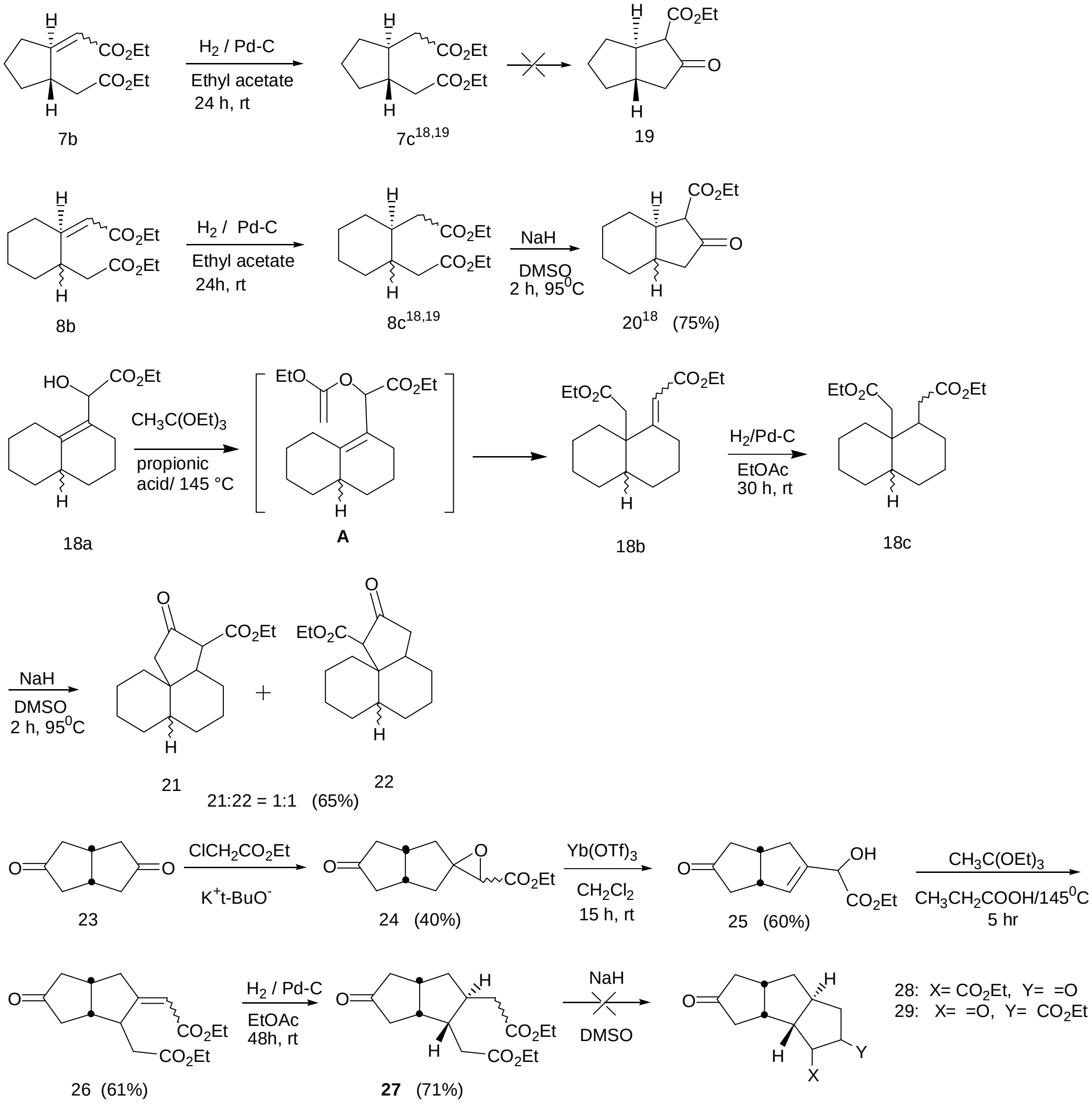
Entry	Glycidic ester	α-Hydroxy-β, γ-unsaturated ester	Using Yb(OTf)$_3$		Using TMSOTf	
			Reaction time (h)	Yield (%)	Reaction time (h)	Yield (%)
1	 7[6]	 7a[6]	12	70	1	60
2	 8[6]	 8a[6]	12	80	1	75
3	 9[6]	 9a[6]	10	82	1	80
4	 10[7]	 10a[7]	24	78	1.5	70

5	 11[7]	 11a[7]	24	67	1	65
6	 12[7]	 12a[8]	14	52	1.5	50
7	 13[15]	 13a[15]	8	40	1	35
8	 14[6]	 14a[6]	6	64	1	60
9	 15[16]	 15a[16]	4	70	1	65
10	 16[17]	 16a	5	80	1	70
11	 17	 17a	5	75	1	69

Experimental Section

General Procedures. Infrared spectra were recorded on Bruker FT/IR Vector 22 spectrometer as neat liquids. ^{1}H NMR were recorded on Jeol JNM-PMX 60, Bruker WP-80 and Jeol LA-400 NMR spectrometers using tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on Jeol LA-400 NMR spectrometer in solution of $CDCl_3$ using TMS as internal standard. Mass spectra were obtained using Jeol SX102/DA-6000 spectrometer. Elemental analysis were carried out using Thermo Quest EA 1110 (model) CE instruments C, H, N, O, S analyzer. Column chromatography was performed on silica gel (100-200 mesh, s.d.fine-chem Ltd. India).

Glycidic esters. Compounds **7**[6], **8**[6], **9**[6], **10**[7], **11**[7], **12**[7], **13**[15], **14**[6], **15**[16], **16**[17] are known in the literature and were prepared according to the reported procedures.[2,3]

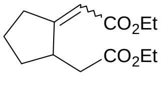
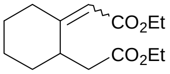
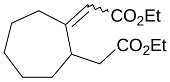
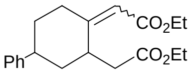
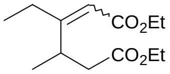
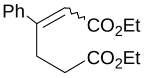
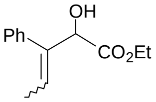
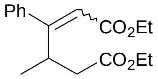
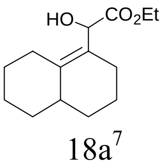
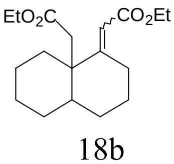


Scheme 2

3-Ethyl-3-phenyl-oxirane-2-carboxylic acid ethyl ester (17). Yield: 50%. IR (neat) ν_{max}: 1750, 1730 cm^{-1}. ^{1}H NMR (CCl$_4$, 60 MHz): δ 0.8 and 0.93 (2t, 3H, J = 7, 7 Hz), 1.3 (t, 3H, J = 8 Hz) 1.6-2.43 (m, 2H), 3.13 and 3.53 (2s, 1H), 3.8 and 4.26 (2q, 2H, J = 7, 6.5 Hz), 7.3 (s, 5H). MS (m/z): 220 (M$^+$). Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%. Found: C, 70.79; H, 7.14%.
Glycidic ester 24. IR (neat) ν_{max}: 1752, 1730, cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.31 (m, 3H), 1.64-1.82 (m, 2H), 2.19-2.65 (2m, 6H), 2.75-2.9 (m, 2H), 3.50 (s, 1H), 4.11-4.30 (m, 2H). ^{13}C NMR (CDCl$_3$, 100 MHz): 14.16, 35.00, 38.80, 38.96, 43.56, 43.74, 55.66, 61.45, 70.20,

115.97, 168.46, 219.03. Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19%. Found: C, 64.23; H, 7.11%.

Table 2. Johnson-Claisen Rearrangement of α-hydroxy-β, γ-unsaturated Esters

Entry	α-Hydroxy-β,γ-unsaturated esters	Rearranged diesters	Reaction Time (h)	Yield (%)
1	7a	 7b	1	64
2	8a	 8b	1	62
3	9a	 9b	1	86
4	10a	 10b	4	58
5	14a	 14b	1	82
6	15a	 15b	1	75
7	 17a	 17b	1.5	72
8	 18a[7]	 18b	6	60

Isomerisation of Glycidic esters to α-Hydroxy-β,γ–unsaturated esters

General procedure

using Yb(OTf)$_3$: To a stirred solution of a glycidic ester (1 mmol) in dry CH_2Cl_2 (2 mL) was added a catalytic amount of Yb(OTf)$_3$ (15 mg) under N_2 at room temperature and stirring continued. After the reaction was complete (TLC monitoring), the reaction mixture was quenched with saturated $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 x15 mL). The combined organic layer was washed with water (2 x 10 mL), brine (1 x 10 mL) and dried over anhydrous Na_2SO_4. Removal of solvent gave a crude product, which was purified by column chromatography (SiO_2).

Using TMSOTf: To a solution of a glycidic ester (1 mmol) in dry CH_2Cl_2 (2 mL) was added TMSOTf in catalytic amount (1 drop) under N_2 at –40°C. The reaction mixture was stirred at that temperature and progress of the reaction was monitored by TLC. The reaction mixture was quenched by $NaHCO_3$ solution (10 mL) and extracted with CH_2Cl_2 (3 x 20 mL). Usual work-up gave a crude product, which was purified by column chromatography (SiO_2).

Compounds **7a**[6], **8a**[6], **9a**[6], **10a**[7], **11a**[7], **12a**[8], **13a**[15], **14a**[6], **15a**[16] are known in the literature and their spectral and physical data were comparable with the compounds obtained by us.

2-Hydroxy-3-p-tolyl-but-3-enoic acid ethyl ester (16a). IR (neat) ν_{max}: 3500, 1720 cm^{-1}. ^1H NMR (CCl_4, 60 MHz) : δ 1.26 (t, 3H, J = 7 Hz), 2.46 (s, 3H), 3.29 (brs, 1H), 4.06-4.39 (q, 2H, J = 7 Hz), 5.0 (s, 1H), 5.46 (s, 2H), 7.0-7.52 (m, 4H). Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89, H, 7.32%. Found: C, 70.78; H, 7.26%.

2-Hydroxy-3-phenyl-pent-3-enoic acid ethyl ester (17a). Yield: 65%. IR (neat) ν_{max}: 3500, 1720 cm^{-1}. ^1H NMR (CCl_4, 60 MHz) : δ 0.9 and 1.2 (2t, 3H, J = 7 Hz), 1.57 and 1.87 (2d, 3H, J = 7, 7 Hz), 3.4 (brs, 1H), 4.0 (q, 2H, J = 7 Hz), 4.63 and 5.13 (2 brs, 1H), 5.83 (q, 1H, J = 7 Hz), 7.13 (s, 5H). Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89, H, 7.32%. Found: C, 70.81; H, 7.19%.

Hydroxy-(5-oxo-1,3a,4,5,6,6a-hexahydro-pentalen-2-yl)-acetic acid ethyl ester (25). IR (neat) ν_{max}: 3470, 1720, cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.27-1.32 (m, 3H), 1.90-2.12 (m, 2H), 2.2-2.55 (m, 4H), 2.75-3.10 (m, 2H), 3.48 (brs, 1H), 4.21-4.32 (m, 2H), 4.7 (brs, 1H,), 5.72 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.20, 37.67, 38.96, 42.27, 44.63, 45.99, 62.19, 70.05, 132.34, 140.75, 172.92, 219.44. Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19%. Found: C, 64.20; H, 7.08%.

α,β-Unsaturated esters after the Johnson-Claisen rearrangement. The experimental procedure was followed as reported in the literature.[13]

(2-Ethoxycarbonylmethylene-cyclopentyl)-acetic acid ethyl ester (7b). IR (neat) ν_{max}: 1720, 1700, 1640 cm^{-1}. ^1H NMR (CCl_4, 60 MHz): δ 1.26 (t, 6H, J = 7 Hz), 1.53-2.18 (m, 4H), 2.43 (d, 2H, J = 6 Hz), 2.6-3.17 (m, 3H), 4.1 (q, 4H, J = 7 Hz), 5.63 (brs, 1H). MS (m/z): 240 (M^+), 194 (M^+ - 46), 167 (M^+- 73), 165 (M^+- 75). Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39%. Found: C, 64.89%; H, 8.34%.

(2-Ethoxycarbonylmethylene-cyclohexyl)-acetic acid ethyl ester (8b). IR (neat) ν_{max}: 1725, 1705, 1635 cm^{-1}. ^1H NMR (CCl_4, 60 MHz): δ 1.23 (t, 6H, J = 7 Hz), 1.46-2.0 (m, 6H), 2.2-2.93 (m, 4H), 2.93-3.5 (m, 1H), 4.1 (q, 4H, J = 7 Hz), 5.5 (s, 1H). MS (m/z): 254 (M^+), 208 (M^+ - 46), 179 (M^+- 75). Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.12%; H, 8.72%. Found: C, 66.04%; H, 8.73%.

(2-Ethoxycarbonylmethylene-cycloheptyl)-acetic acid ethyl ester (9b). IR (neat) ν_{max}: 1720, 1700, 1635 cm^{-1}. ^1H NMR (CCl_4, 60 MHz): δ 1.25 (t, 6H, J = 7 Hz), 1.46-2.13 (m, 8H), 2.3 (d, 2H), 2.53-2.97 (m, 2H),2.97-3.45 (m, 1H), 4.1 (q, 4H, J = 7 Hz), 5.65 (brs, 1H). MS (m/z): 268 (M^+), 222 (M^+ - 46), 195 (M^+- 73), 193 (M^+- 75). Anal. Calcd. for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01%. Found: C, 67.09; H, 8.91%.

(2-Ethoxycarbonylmethylene-5-phenyl-cyclohexyl)-acetic acid ethyl ester (10b). IR (neat) ν_{max}: 1705, 1720, 1630 cm^{-1}.^{1}H NMR (CCl_4, 60 MHz) : δ 1.22 (t, 6H, J = 7 Hz), 1.6-2.28 (m, 6H), 2.6 (d, 2H), 2.73-3.26 (m, 2H), 4.13 (q, 4H, J = 7 Hz), 5.3 (brs, 1H), 7.16 (s, 5H). MS (m/z): 330 (M^+), 284 (M^+ - 46), 256 (M^+- 74), 255 (M^+- 75). Anal. Calcd. for $C_{20}H_{26}O_4$ C, 72.70; H, 7.93%. Found: C, 72.66; H, 7.83%.

3-Ethyl-4-methyl-hex-2-enedioic acid diethyl ester (14b). IR (neat) ν_{max}: 1720, 1635 cm^{-1}. ^{1}H NMR (CCl_4, 60 MHz): δ 0.77-1.5 (m, 12H), 2.0-2.9 (m, 5H), 3.7-4.33 (m, 4H), 5.57 (s, 1H). MS (m/z): 242 (M^+), 169 (M^+- 73). Anal. Calcd. for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15%. Found: C, 64.35; H, 9.09%.

3-Phenyl-hex-2-enedioic acid diethyl ester (15b). IR (neat) ν_{max}: 1705, 1720, 1620 cm^{-1}. ^{1}H NMR (CCl_4, 60 MHz): δ 1.2 and 1.3 (2t, 6H, J = 7, 7 Hz), 2.36 (t, 2H, J = 8 Hz), 3.36 (t, 2H, J = 8 Hz), 3.8-4.4 (m, 4H), 6.0 (s, 1H), 7.33 (s, 5H). MS (m/z): 276 (M^+), 203 (M^+- 73). Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.55; H, 7.29%. Found: C, 69.49; H, 7.20%.

4-Methyl-3-phenyl-hex-2-enedioic acid diethyl ester (17b). IR (neat) ν_{max}: 1710, 1720, 1635, 1625 cm^{-1}. ^{1}H NMR (CCl_4, 60 MHz) : δ 0.8-1.5 (m, 9H), 2.23, 2.36 (2d, 2H, J = 6Hz), 2.8-3.26 (m, 1H), 3.6-4.43 (m, 4H), 5.7 and 5.76 (2s, 1H), 6.93-7.42 (m, 5H). MS (m/z): 290 (M^+), 275 (M^+- 15), 217 (M^+- 73). Anal. Calcd. for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64%. Found: C, 70.22; H, 7.58%.

(8a-Ethoxycarbonylmethyl-octahydro-naphthalen-1-ylidene)-acetic acid ethyl ester (18b). IR (neat) ν_{max}: 1700, 1725, 1620 cm^{-1}. ^{1}H NMR (CCl_4, 60 MHz): δ 0.77-2.0 (m, 19H), 2.13 (m, 2H), 2.23-3.0 (m, 2H, J = 8 Hz), 4.1 (q, 4H, J = 7 Hz), 5.32 (brs, 1H). MS (m/z): 308 (M^+), 235 (M^+- 73). Anal. Calcd. for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15%. Found: C, 69.99; H, 9.16%.

(1-Ethoxycarbonylmethyl-5-oxo-hexahydro-pentalen-2-ylidene)-acetic acid ethyl ester (26). IR (neat) ν_{max}: 1720, 1700, 1640 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz):δ 1.18-1.32 (br t, 6H, J = 7 Hz), 2.00-2.35 (m, 4H), 2.36-2.65 (m, 5H), 2.75-3.00 (m, 2H), 3.15-3.37 (m, 1H), 4.04-4.23 (br q, 4H, J = 7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): (peaks for the major diastereomer) δ 218.61, 171.4, 167.6, 166.30, 114.6, 60.78, 59.87, 47.80, 45.14, 43.85, 42.87, 38.49, 38.27, 37.44, 14.26, 14.17. MS (m/z): 295 (M^+), 207 (M^+-88). Anal. Calcd. for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53%. Found; C, 65.21; H, 7.45%.

Saturated diesters after hydrogenation

(2-Ethoxycarbonylmethyl-cyclopentyl)-acetic acid ethyl ester (7c). IR (neat) ν_{max}: 1725 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.25 (t, 6H, J = 7.1 Hz), 1.18-1.95 (m, 8H), 2.19 (dd, 2H, J = 8.0 Hz, 15.1 Hz), 2.47 (dd, 2H, 3.9 Hz, 15.1 Hz), 4.13 (q, 4H, J =7.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (*trans isomer*): 172.88, 60.01, 39.09, 34.99, 31.93, 23.16, 14.05. (*cis isomer*):172.99, 60.08, 38.61, 34.35, 30.20, 21.99, 14.05. Anal. Calcd. for $C_{13}H_{22}O_4$: C, 64.43; H, 9.15%. Found: C, 64.33; H, 9.06%.

(2-Ethoxycarbonylmethyl-cyclohexyl)-acetic acid ethyl ester (8c). IR (neat) ν_{max}: 1725 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.08–1.8 (m, 10H), 1.26 (t, 6H, J = 7.0 Hz), 2.1 (dd, 1H, J = 7.8 Hz, 14.9 Hz), 2.15-2.3 (m, 2H), 2.48 (dd, 1H, J = 3.4 Hz, 14.9 Hz), 4.13 (q, 4H, J = 7.0 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz): δ (*trans isomer*): 173.17, 60.23, 39.21, 35.67, 32.29, 25.74, 14.21. (*cis isomer*): 173.2, 60.27, 39.02, 35.47, 28.72, 23.04, 14.21. MS (m/z): 210 (M$^+$-46). Anal. Calcd. for $C_{14}H_{24}O_4$: C,65.60; H, 9.44%. Found: C, 65.63; H, 9.36%.

(8a-Ethoxycarbonylmethyl-decahydro-naphthalen-1-yl)-acetic acid ethyl ester (18c). IR (neat) ν_{max}: 1725 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.8-2.0 (m, 16H), 1.25 (t, 6H, J = 7 Hz), 2.06-2.47 (m, 4H), 4.08 (q, 4H, J = 7 Hz). MS (m/z): 310 (M$^+$), 237 (M$^+$- 73). Anal. Calcd. for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74%. Found: C, 69.59; H, 9.63%.

(1-Ethoxycarbonylmethyl-5-oxo-octahydro-pentalen-2-yl)-acetic acid ethyl ester (27). IR (neat) ν_{max} : 1740 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.05-1.27 (br t, 6H, J = 7 Hz), 2.0-2.18 (m, 4H), 2.2-2.38 (m, 4H), 2.44-2.6 (m, 4H), 2.62-2.96 (m, 1H), 3.00-3.20 (m, 1H), 4.2-4.2 (m, 4H). ^{13}C NMR (CDCl$_3$, 100 MHz): (peaks for the major diastereomer) δ 219.63, 172.42, 172.31, 60.35, 60.25, 45.37, 44.31, 43.88, 43.14, 39.83, 37.67, 37.50, 37.34, 32.70, 14.14, 14.08. MS (m/z): 269 [(M$^+$+1)-28], 182 (M$^+$-116). Anal. Calcd. for $C_{16}H_{24}O_5$: C, 64.85; H, 8.16%, Found: C, 64.80; H, 8.11%.

General procedure for Dieckman cyclization[14]

A solution of a saturated diester (2 mmol) in DMSO (2 mL) was added to NaH (4 mmol) in DMSO (2 mL) and the resulting mixture was stirred at 95^0 C under N_2 atmosphere. After completion of the reaction (TLC monitoring), it was cooled to room temperature and quenched with 2 mL of saturated aqueous NH_4Cl solution. Usual work-up gave the crude product which was purified by column chromatography.

2-Oxo-octahydro-indene-1-carboxylic acid ethyl ester (20). IR (neat) ν_{max}: 1735, 1710 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.23 (t, 3H, J = 7.0 Hz), 1.1–2.0 (m, 8H), 2.35-2.45 (m, 2H), 2.80 (d, 2H, J = 12.2 Hz), 3.13 (d, 1H, J = 10.8 Hz), 4.15 (q, 2H, J = 7.0 Hz). MS (m/z): 210 (M$^+$), 169 (M$^+$-41), 139 (M$^+$-69). Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63%. Found: C, 68.48; H, 8.59%.

2-Oxo-dodecahydro-cyclopenta[*d*]naphthalene-3-carboxylic acid ethyl ester (21) and 2-Oxo-dodecahydro-cyclopenta[*d*]naphthalene-1-carboxylic acid ethyl ester (22). IR (neat) ν_{max}: 1730, 1710 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.2-2.1 (m, 18H), 2.1-2.6 and 2.77-3.03 (2m, 3H), 2.77 and 3.03 (2d, 2H, J = 13 Hz), 3.26-3.48 (2m, 1H), 4.15- 4.26 (m, 2H). MS (m/z): 264 (M$^+$). Anal. Calcd. for $C_{14}H_{24}O_3$: C, 72.69; H, 9.15%. Found: C, 72.65; H, 9.18%.

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