

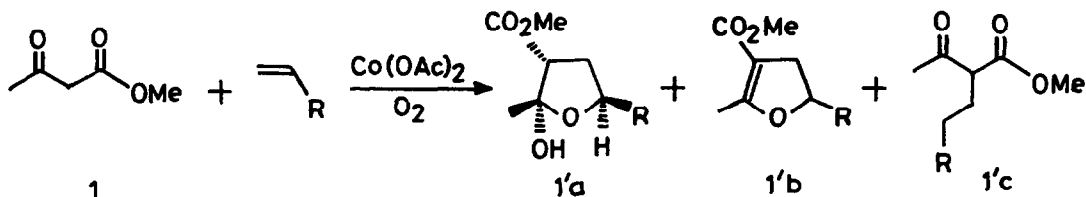
COBALT(II)ACETATE PROMOTED OXIDATIVE ADDITION OF 1,3-DICARBONYL COMPOUNDS TO ALKENES UNDER AEROBIC CONDITIONS

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Abstract : The reaction of 1,3-dicarbonyl compounds with various alkenes in presence of $\text{Co}(\text{OAc})_2 \cdot \text{XH}_2\text{O}$ under aerobic conditions gives dihydrofurans in moderate to good yields.² The role of dioxygen is discussed by comparing these reactions under anerobic conditions.

We recently reported the oxidative addition¹ of acetoacetates to terminal alkenes in the presence of one equivalent of cobalt(II)acetate to give 2-hydroxy-2-methyl-3-methoxycarbonyl-5-alkyl-tetrahydrofurans 1'a. This reaction proceeds smoothly in the presence of dioxygen and only one diastereomer of 1'a is obtained alongwith minor amounts of dihydrofuran 1'b and the alkylated product 1'c (Scheme 1). The hemi-ketal 1'a is precipitated immediately as a fluffy solid from the crude reaction mixture and any attempts to purify it by flash column chromatography led to the formation of dihydrofuran 1'b along with the minor unidentified products. The present study describes our detailed results on the reaction of various alkenes with 1,3-dicarbonyl compounds in the presence of cobalt(II)acetate and dioxygen.

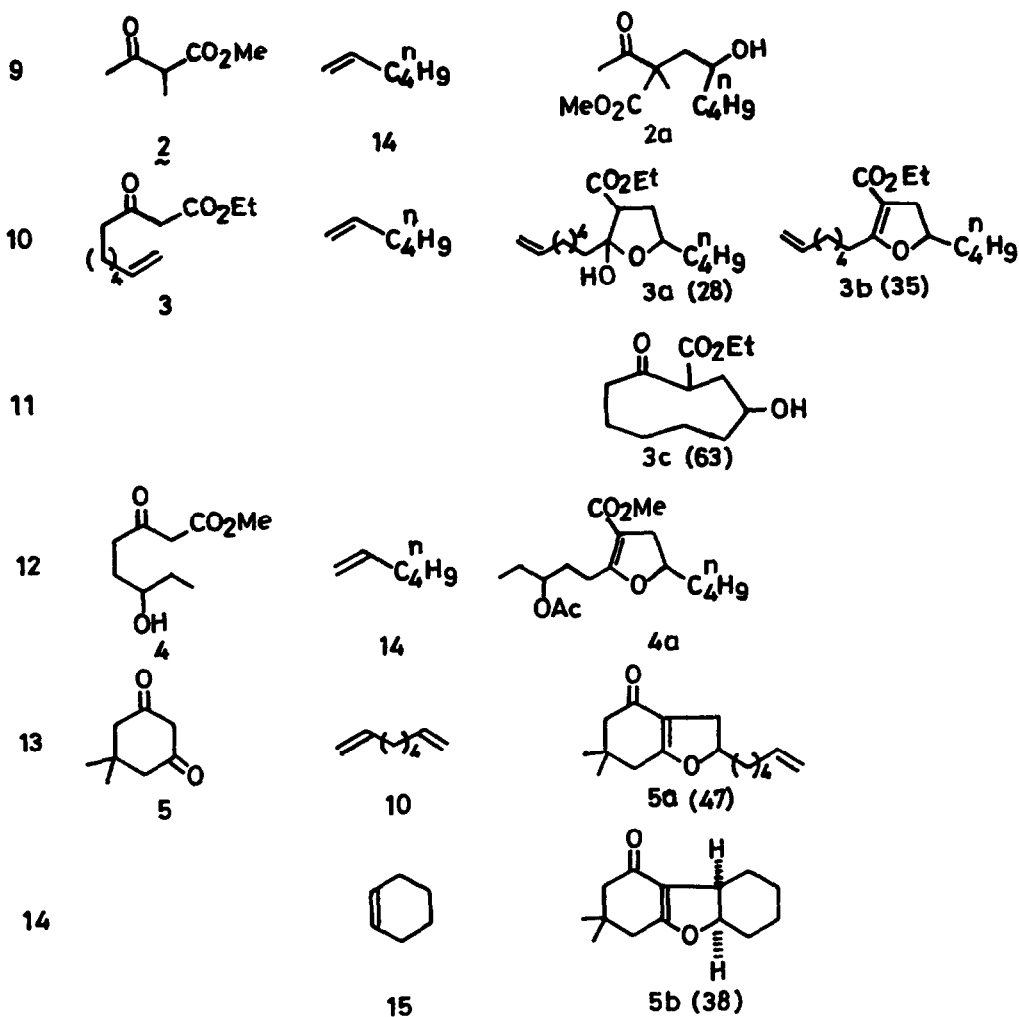


(Scheme 1)

Typically, cobalt(II)acetate (10 mmol), the 1,3-dicarbonyl compound (10 mmol) and the olefin (15-20 mmol) are dissolved in glacial acetic acid and the resulting solution is purged² with dioxygen and heated to 60-70°C for 8-12 hours. The work-up and flash column chromatography yielded dihydrofurans as the major products. The results of these reactions are compiled in Table 1. The reaction is highly regioselective as only one regioisomer 1a is obtained from olefin 6 (Table 1, entry 1). The trisubstituted olefin 7 underwent a highly regioselective reaction to yield 1b (Table 1, entry 2) as the only product. A mixture of hemi-

Table 1

Entry	Ketoester	Olefin	Products (Yield %)
1			
2			
3			
4			
5			
6			
7			
8			

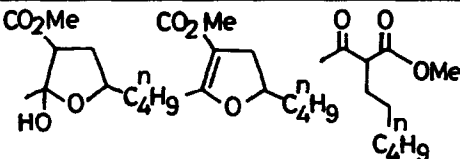
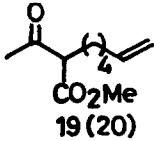
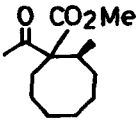


-ketal 1c and dihydrofuran 1d were obtained from alkene 8. Interestingly, only one double bond of a terminal diene reacted chemoselectively to yield the corresponding dihydrofurans (Table 1, entries 4, 5 and 13). The homoallyl alcohol 11 and allyl alcohol 12 react smoothly and give the corresponding dihydrofurans 1g and 1h respectively in good yields. The hydroxy group in alcohol 11 is acetylated under these conditions³. The γ -hexenylacetoacetate 3 reacts intermolecularly with excess of 1-hexene to give the hydroxy compound 3a and the dihydrofuran 3b as the sole products (Table 1, entry 10). No trace of any product arising

due to intramolecular cyclisation was noticed in this reaction. However, in absence of an olefin the compound 3 reacted intramolecularly to give the nine membered cyclic ketone 3c as the only product (Table 1, entry 11). The functionalised 1,3-dicarbonyl compounds like methyl (6-hydroxy-3-oxo)-octanoate 4 also undergo this reaction to yield the corresponding dihydrofuran 4a where the hydroxy group is acetylated during this process. Dimedone 5 also reacts chemoselectively with one double bond of 1,7-octadiene 10 to give the corresponding dihydrofuran 5a in good yields. The reaction of cyclohexene and dimedone give only one diastereomer of the tricyclic compound (Table 1, entry 14).

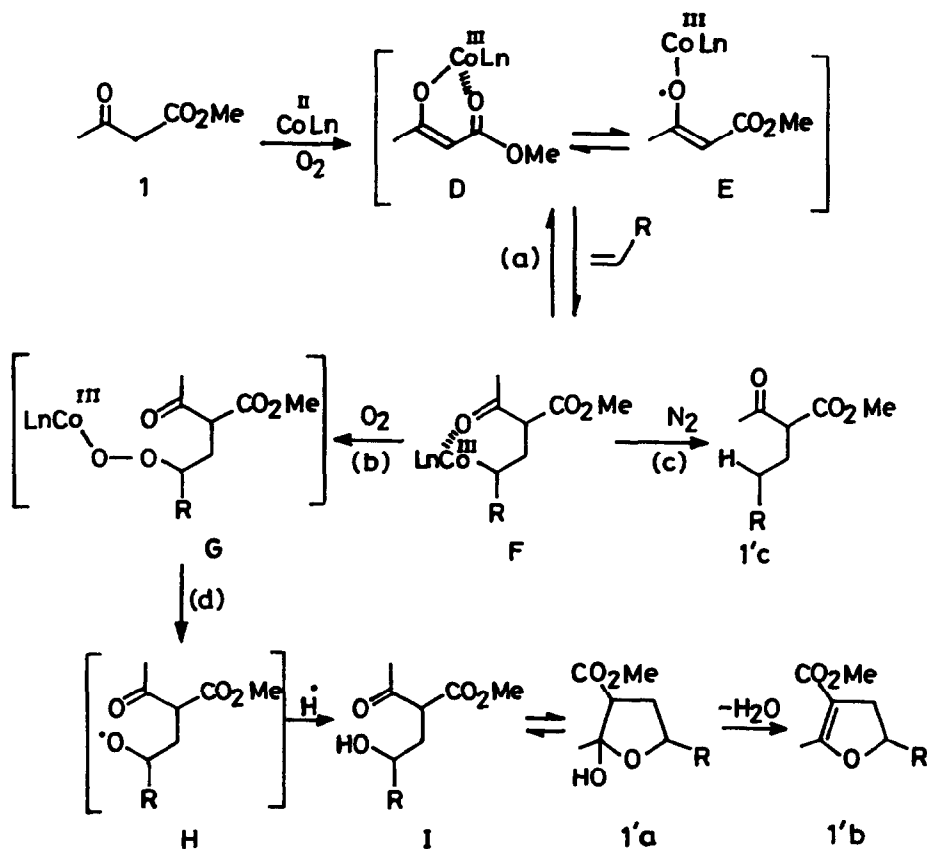
The dihydrofurans 1'b are formed by the elimination^{4a,b} of water from the corresponding hemi-ketal (i.e. 1'a) and the formation of the later is dependent upon the presence of dioxygen during these reactions. This fact is demonstrated by conducting the reaction under anerobic conditions. Thus, the reaction between methyl acetoacetate and 1-hexene under nitrogen did not yield any hemi-ketal or dihydrofuran instead the alkylated product 18 was formed as the major product (Table 2, entries 1 and 2). This reaction also leads to the formation of small amount (~ 10%) of oligomeric product. The reaction with 1,5-hexadiene under nitrogen yielded only the alkylated product in low yields (Table 2,

Table 2: Reaction of Methylacetoacetate with Alkenes under Nitrogen

Entry	Olefin	Reaction conditions	Products (Yield %)
1	14	Co (II) (OAc) ₂ , O ₂ , 80°C, 14h	 16 (68) 17 (8) 18 (5)
2	14	Co (OAc) ₂ , N ₂ , 75 - 80°C 25-30h	18 (75)
3	9	— do —	 19 (20)
4	10	— do —	 20 (35)

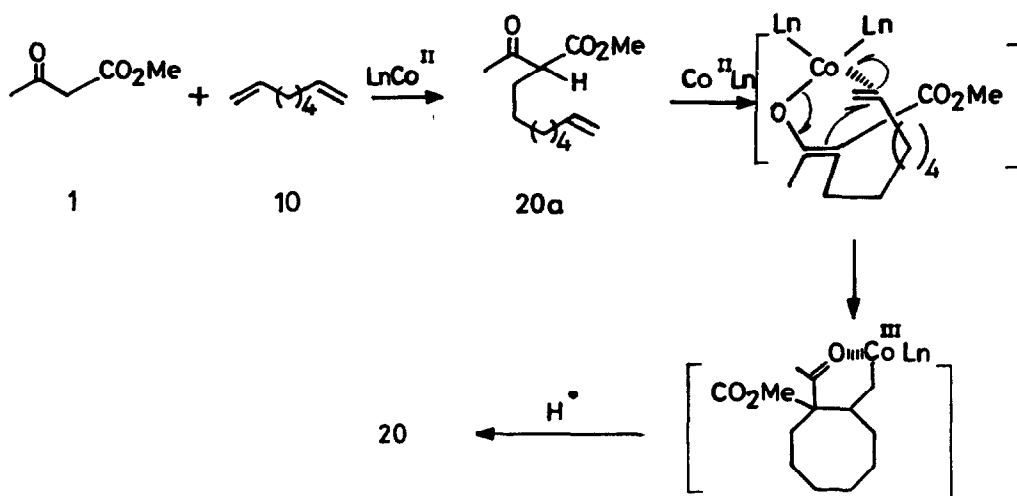
entry 3) whereas the same reaction under dioxygen gave the dihydrofuran 1e as the major product (Table 1, entry 4). Similarly the reaction with 1,7-octadiene gave the cyclic compound in low yields which is again in contrast with results of the same reaction under dioxygen atmosphere (Table 1, entry 5). These experiments clearly indicate that the hemi-ketal 1'a is formed due to the incorporation of dioxygen during these reactions. In view of the results obtained under aerobic and anaerobic conditions, we propose the following mechanistic pathway for the reaction carried out in presence of dioxygen.

Cobalt(II) acetate will oxidise the acetoacetate to give an cobalt(II) enolate⁵ D. The enolate D, which is likely to behave as an enol radical E, will add to the alkene to yield a organocobalt compound F (Scheme 2). The carbon-cobalt bond in F will behave⁶ as a radical due to homolysis of this bond. Therefore the insertion of dioxygen^{7a} in the



(Scheme 2)

carbon-cobalt bond of **F** will give the peroxy-cobalt(III) complex **G** (step b) which on homolytic cleavage of oxygen-oxygen bond may give rise to the corresponding alkoxy radical **H**. The radical **H** will abstract a hydrogen atom to give the hydroxy compound **I** which may undergo an intramolecular ketalisation to yield the hemi-ketal **1'a**. The oxidation of alkenes by dioxygen and cobalt(II) complexes have been recently shown to occur^{7b,8} via peroxy-cobalt complexes. Under anaerobic condition there is no driving force for the formation of the alkyl-cobalt intermediate **F** as it can not be intercepted by dioxygen. Therefore the equilibrium in step (a) will shift towards complex **D** & **E** (a more stable radical than **F**) and this equilibrium will cause the reaction to proceed extremely slowly (see Table 2). Thus, in the absence of dioxygen the alkyl-cobalt intermediate **F** (a potential carbon centred radical) will abstract (step c) a hydrogen atom to give the mono alkylated acetoacetate **1'c**. The formation of cyclic compound **20** may occur via the intramolecular radical cyclisation of the initially formed mono alkylated product **20a** from methyl

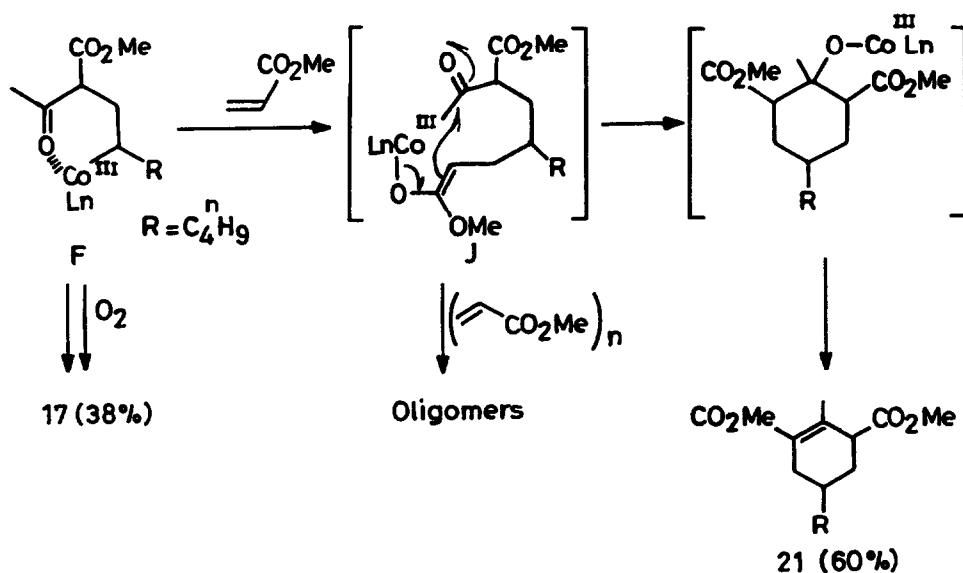


(Scheme 3)

acetoacetate and 1,7-octadiene (Scheme 3).

The presence of a carbon-cobalt bond in **F** is also inferred from a competitive reaction. Thus, the Co(OAC)_2 mediated reaction of methyl acetoacetate in presence of 1-hexene (1 equivalent) and methyl acrylate (1 equivalent) under dioxygen lead to the formation of dihydrofuran **17** and a cyclic product **21** arising due to a sequential incorporation of 1-hexene and methyl acrylate (Scheme 4). The intermediate **F** will give

dihydrofuran 17 on insertion with dioxygen. Alternatively, it may add to the methyl acrylate to give a cobalt enolate J which will undergo an intramolecular aldol condensation followed by elimination to yield compound 21 and small amount of oligomeric products. This experiment clearly shows that the intermediate F can be intercepted by dioxygen as well as by a more reactive (compared to 1-hexene) olefin like methylacrylate⁹. The formation of 21 as the major product indicates that the intermediate F prefers to react with methyl acrylate than dioxygen. The addition of organo-cobalt complexes to deactivated olefins is quite well known¹⁰ from the work of Pattenden et.al.



In conclusion, the cobalt(II)acetate mediated reaction of 1,3-dicarbonyl compound with alkenes in presence of dioxygen leads to the formation of dihydrofuran in good yields. These reaction are proceeding via incorporation of dioxygen as indicated by the results obtained under anerobic condition.

EXPERIMENTAL

Methods and Materials :

Infra red spectra were recorded on a Perkin Elmer 1320 spectrometer. The proton NMR spectra were recorded on Bruker WP-80, Jeol PMX-60 and Bruker WP-400 spectrometer. Elemental analysis was conducted using

coleman automatic C, H and N analyser. Analytical thin layer chromatography was performed on silica gel (Acme) coated glass plates. Column chromatography was performed using 100-200 mesh (Acme) silica gel. The purity of compounds was checked on Shimadzu LC-6A high performance liquid chromatography.

Methyl acetoacetate and alkenes 6-10, 12, 14 and 15 were purchased commercially and purified before use. The β -ketoesters 2-4 were prepared according to the literature procedure¹¹. Cobalt(II)acetate was purchased from Loba (India), Bombay and it was heated at 120°C for 3 h and crushed to powder before use.

General procedure for the cobalt(II)acetate promoted addition of 1,3-dicarbonyl compounds to alkenes :

Cobalt(II)acetate (10 mmol), the 1,3-dicarbonyl compound (10 mmol) and alkene (15-20 mmol) were dissolved in glacial acetic acid and the resulting solution is purged with dioxygen and heated to 70-80°C for 8-15 hours. Acetic acid is removed under vacuuo to give a residue which is taken into ether and the organic layer is washed successively with saturated solution of sodium bicarbonate (3x20 ml), ammonium chloride (2x15 ml) and water (2x15 ml). The ether layer is dried (MgSO₄) and evaporated to give a liquid which was subjected to column chromatography over silica gel using ethylacetate-petroleum ether as the eluant.

2-4-Dimethyl-3-methoxycarbonyl-5-pentanyl-4,5-dihydrofuran 1a :

Isolated as a clear, colorless oil in 58% yield by flash chromatography on silica gel (2:1 petroleum ether - EtOAc). ¹H-NMR(CCl₄) δ 4.22 (dt, J = 3 and 9 Hz, 1 H), 3.51 (s, 3 H), 2.75 (dq, J = 4 and 8 Hz, 1 H), 2.02 (s, 3 H), 1.12-1.7 (m, 8 H), 1.10 (d, J = 7 Hz, 3 H), 0.89 (t, J = 6.8 Hz, 3 H). IR(CH₂Cl₂) : 1710, 1652 cm⁻¹. Anal. Calcd. for C₁₃H₂₂O₃: C, 69.03; H, 9.73. Found : C, 69.23; H, 9.98.

4-Ethyl-3-methoxycarbonyl-2,5,5-trimethyl-4,5-dihydrofuran 1b :

Isolated as an oil in 68% yield by flash chromatography on silica gel (2:1 petroleum ether - EtOAc). ¹H-NMR(CDCl₃) δ 3.53 (s, 3 H), 2.53 (m, 1 H), 2.0 (s, 3 H), 1.57 (m, 2 H), 1.15 (s, 6 H), 0.87 (t, J = 6.8 Hz, 3 H). IR(CH₂Cl₂) : 1710, 1650 cm⁻¹. Anal. Calcd. for C₁₁H₁₈O₃: C, 66.64; H, 9.0. Found : C, 66.22; H, 8.95.

2,5-Dimethyl-3-methoxycarbonyl-5-neopentyl-4,5-dihydrofuran 1d :

Isolated as a gum in 35% yield by flash chromatography on silica gel (2:1 petroleum ether - EtOAc). ¹H-NMR (CCl₄) δ 3.48 (s, 3 H), 2.5 (m, 2 H), 2.03 (t, J = 1.5 Hz, 3 H), 1.58 (s, 2 H), 1.29 (s, 3 H), 0.92

(s, 3 H). IR (thin film) : 1708, 1655 cm^{-1} . Anal. Calcd. for $\text{C}_{13}\text{H}_{22}\text{O}_3$: C, 69.02; H, 9.73. Found : C, 69.27; H, 10.22.

2,5-Dimethyl-2-hydroxy-3-methoxycarbonyl-5-neopentyltetrahydrofuran 1c :

Isolated as an oil in 23% yield by flash chromatography on silica gel (2:1 petroleum ether - EtOAc). $^1\text{H-NMR}(\text{CCl}_4)\delta$ 3.60 (s, 3 H), 2.9-2.0 (m, 3 H), 1.38 (s, 3H), 1.35 (s, 2 H), 1.21 (s, 3 H), 0.98 (s, 9 H). IR (CH_2Cl_2) : 3455, 1745 cm^{-1} . Anal. Calcd. for $\text{C}_{13}\text{H}_{24}\text{O}_4$: C, 63.93; H, 9.83. Found : C, 64.27; H, 10.59.

5-(But-3'-enyl)-3-methoxycarbonyl-2-methyl-4,5-dihydrofuran 1e :

Isolated as an oil in 62% yield by flash chromatography on silica gel (3:1 petroleum ether - EtOAc). $^1\text{H-NMR}(\text{CCl}_4)\delta$ 5.95 - 5.21 (m, 1 H), 4.92 - 4.62 (m, 2 H), 4.30 (m, 1 H), 3.53 (s, 3 H), 2.98 - 2.13 (m, 2 H), 2.0 (t, $J = 1.5$ Hz, 3 H), 1.89 (m, 2 H), 1.56 (m, 2 H). IR (CH_2Cl_2) : 1705, 1650 cm^{-1} . Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{O}_3$: C, 67.32; H, 8.16. Found : C, 67.51; H, 8.50.

5-(Hex-5'-enyl)-3-methoxycarbonyl-2-methyl-4,5-dihydrofuran 1f :

Isolated as a gum in 66% yield by flash chromatography on silica gel (2.5:1 petroleum ether - EtOAc). $^1\text{H-NMR}(\text{CCl}_4)\delta$ 5.95 - 5.19 (m, 1 H), 5.05 - 4.69 (m, 2 H), 4.35 (m, 1 H), 3.59 (s, 3 H), 2.97 - 2.18 (m, 2 H), 2.1 - 1.90 (m, 2 H), 2.01 (t, $J = 1.5$ Hz, 3 H), 1.7 - 1.18 (m, 6 H). IR (CH_2Cl_2) : 1702, 1654 cm^{-1} . Anal. Calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_3$: C, 69.65; H, 8.93. Found : C, 70.13; H, 9.27.

5-(2'-Acetoxyoctyl)-3-methoxycarbonyl-2-methyl-4,5-dihydrofuran 1g :

Isolated as an oil in 70% yield by flash chromatography on silica gel (2:1 petroleum ether - EtOAc). $^1\text{H-NMR}(\text{CCl}_4)\delta$ 4.85 (m, 1 H), 4.33 (m, 1 H), 3.52 (s, 3 h), 2.25 (d, $J = 7$ Hz, 2 H), 2.02 (bs, 3 H), 1.95 (s, 3 H), 1.8 - 1.05 (m, 12 H), 0.85 (t, $J = 6.5$ Hz, 3 H). IR (CH_2Cl_2) : 1735, 1700, 1650 cm^{-1} .

5-(1'-hydroxy-1'-methyl)ethyl-3-methoxycarbonyl-2-methyl-4,5-dihydrofuran 1h :

Isolated as an oil in 57% yield by flash column chromatography on silica gel (1.5:1 petroleum ether - EtOAc). $^1\text{H-NMR}(\text{CCl}_4)\delta$ 4.20 (t, $J = 7$ Hz, 1 H), 3.65 (s, 3 H), 2.85 - 2.20 (m, 2 H), 2.05 (t, $J = 1.2$ Hz, 3 H), 1.15 (s, 3 H), 1.12 (s, 3 H). IR (CH_2Cl_2) : 3450, 1700, 1650 cm^{-1} . Anal. Calcd. for $\text{C}_{10}\text{H}_{16}\text{O}_4$: C, 60.0; H, 8.0. Found : C, 59.57; H, 7.81.

5-Acetoxymethyl-3-methoxycarbonyl-2-methyl-4,5-dihydrofuran 1i :

Isolated as an oil in 51% yield by flash chromatography (2:1 petroleum

ether - EtOAc). $^1\text{H-NMR}$ (CCl_4) δ 4.33 (m, 1 H), 3.89 (d, $J = 6.2$ Hz, 2 H), 3.55 (s, 3 H), 2.89 - 2.2 (m, 2 H), 2.0 (t, $J = 1.2$ Hz, 3 H), 1.95 (s, 3 H). IR (CH_2Cl_2) : 1737, 1700, 1650 cm^{-1} . Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{O}_5$: C, 56.07; H, 6.54. Found : C, 56.65; H, 7.07.

Methyl(2-acetyl-4-hydroxy-2-methyl)octanoate 2a :

Isolated as an oil in 58% yield by flash chromatography (2:1 petroleum ether - EtOAc). $^1\text{H-NMR}$ (CCl_4) δ 3.89 (m, 1 H), 3.57 (s, 3 H), 2.05 (s, 3 H), 1.85 - 1.10 (m, 8 H), 1.12 (s, 3 H), 0.89 (t, $J = 6.5$ Hz, 3 H), IR (CH_2Cl_2) : 3470, 1740, 1729 cm^{-1} .

5-Butyl-2-(Hept-6'-enyl)-2-hydroxy-3-ethoxycarbonyltetrahydrofuran 3a :

Isolated as a gum in 28% yield by flash chromatography (2:1 petroleum ether - EtOAc). $^1\text{H-NMR}$ (CCl_4) δ 5.91 - 5.19 (m, 1 H), 4.98 - 4.45 (m, 2 H), 4.2 (q, $J = 6.8$ Hz, 2 H), 3.79 (m, 1 H), 2.87 - 2.11 (m, 3 H), 2.0 - 1.12 (m, 16 H), 1.10 (t, $J = 6.8$ Hz, 3 H), 0.90 (t, $J = 6.5$ Hz, 3 H). IR (CH_2Cl_2) : 3470, 1735, 1655 cm^{-1} . Anal. Calcd. for $\text{C}_{18}\text{H}_{32}\text{O}_4$: C, 69.23; H, 10.25. Found : C, 69.89; H, 10.91.

5-Butyl-3-ethoxycarbonyl-2-(Hept-6'-enyl)-4,5-dihydrofuran 3b :

Isolated as an oil in 35% yield by flash chromatography (2:1 petroleum ether - EtOAc). $^1\text{H-NMR}$ (CCl_4) δ 5.93 - 5.20 (m, 1 H), 4.96 - 4.40 (m, 2 H), 4.23 (q, $J = 6.8$ Hz, 2 H), 4.17 (m, 1 H), 2.95 - 2.05 (m, 6 H), 1.87 - 1.18 (m, 12 H), 1.15 (t, $J = 6.8$ Hz, 3 H), 0.88 (t, $J = 6.8$ Hz, 3 H). IR (CH_2Cl_2) : 1700, 1660, 1655 cm^{-1} . Anal. Calcd. for $\text{C}_{18}\text{H}_{30}\text{O}_3$: C, 73.46; H, 10.20. Found : C, 73.93; H, 10.89.

2-Ethoxycarbonyl-4-hydroxycyclononanone 3c :

Isolated as a semi-solid in 63% yield by flash chromatography (1:1 petroleum ether - EtOAc). $^1\text{H-NMR}$ (CDCl_3) δ 4.08 (q, $J = 6.8$ Hz, 2 H), 3.89 (m, 1 H), 3.48 (t, $J = 6.2$ Hz, 1 H), 2.8 - 1.18 (m, 12 H), 1.09 (t, $J = 6.5$ Hz, 3 H). IR (CH_2Cl_2) : 3550, 1735, 1708 cm^{-1} . Anal. Calcd. for $\text{C}_{12}\text{H}_{20}\text{O}_4$: C, 63.13; H, 8.77. Found : C, 63.42; H, 9.23.

2-(3'-Acetoxypentyl)-5-butyl-3-methoxycarbonyl-4,5-dihydrofuran 4a :

Isolated as a gum in 57% yield by flash chromatography (3:1 petroleum ether - EtOAc). $^1\text{H-NMR}$ (CCl_4) δ 4.62 (m, 1 H), 4.18 (m, 1 H), 3.55 (s, 3 H), 3.1 - 2.05 (m, 4 H), 1.92 (s, 3 H), 1.8 - 1.05 (m, 10 H), 0.97 (t, $J = 6.8$ Hz, 3 H), 0.90 (t, $J = 7$ Hz, 3 H). IR (CH_2Cl_2) : 1735, 1710 cm^{-1} . Anal. Calcd. for $\text{C}_{17}\text{H}_{28}\text{O}_5$: C, 62.82; H, 8.97. Found: C, 63.25; H, 9.38.

Dihydrofuran 5a :

Isolated as a solid (MP. 179-80°C) in 47% yield by flash chromatography

graphy (3:1 petroleum ether - EtOAc). $^1\text{H-NMR}(\text{CCl}_4)\delta$ 6.05 - 5.30 (m, 1 H), 5.09 - 4.70 (m, 2 H), 4.56 (m, 1 H), 3.01 - 2.21 (m, 4 H), 2.15 (s, 2 H), 2.11 (s, 2 H), 1.83 - 1.12 (m, 6 H), 1.05 (s, 6 H). IR (KBr) : 1716, 1695, 1609, 1583. Anal. Calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_2$: C, 68.63; H, 8.30. Found : C, 68.39; H, 8.76.

Dihydrofuran 5b :

Isolated as a gum in 38% yield by flash chromatography (2.5:1 petroleum ether - EtOAc). $^1\text{H-NMR}(\text{CCl}_4)\delta$ 4.47 (ddd, $J = 7, 3$ and 1.5 Hz, 1H), 2.95 - 2.19 (m, 1 H), 2.11 (s, 2 H), 2.01 (s, 2 H), 1.85 - 1.10 (m, 8 H), 1.05 (s, 6 H). IR (thin film) : 1710, 1629, 1466, 1450 cm^{-1} .

1-Acetyl-1-methoxycarbonyl-2-methylcyclooctane 20 :

Isolated as a gum in 35% yield by flash column chromatography (1:1 petroleum ether - Ether). $^1\text{H-NMR}(\text{CDCl}_3)\delta$ 3.65 (s, 3 H), 1.15 (s, 3 H), 1.89 (m, 1 H), 1.80 - 1.05 (m, 12 H), 0.92 (d, $J = 7$ Hz, 3 H). IR (thin film) : 2874 - 2961, 1718, 1654, 1636, 1508 and 1457 cm^{-1} . Anal. Calcd. for $\text{C}_{13}\text{H}_{22}\text{O}_2$: C, 74.24; H, 10.54. Found : C, 73.98; H, 10.32.

5-Butyl-1,3-dimethoxycarbonyl-2-methylcyclohex-1-ene 21 :

Isolated as an oil in 60% yield by flash chromatography (19:1 petroleum ether - EtOAc). $^1\text{H-NMR}(\text{CCl}_4)\delta$ 3.53 (s, 3 H), 3.47 (s, 4 H), 2.05 (m, 5 H), 1.7 - 1.00 (m, 9 H), 0.90 (t, $J = 6.8$ Hz, 3 H). IR (thin film) : 1737, 1646, 1437, 1360 and 1199 cm^{-1} .

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2. These reactions can also be carried out without purging the reaction flash with molecular oxygen. However, on a large scale (25-30 mmol) reaction the positive pressure of molecular oxygen is necessary.
3. We have recently noted that alcohols can be acetylated with acetic acid in presence of cobalt(II)acetate (unpublished results).
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