Pergamon

Tetrahedron Vol. 50, No. 30, pp. 9145-9156, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4020/94 $7.00+0.00

0040-4020(94)00512-5

Cobalt Catalyzed Regioselective Allylation of 1,3-Dicarbonyl Compounds

Golak C. Maikap, M. Madhava Reddy, Manoj Mukhopadhyay,
Beena Bhatia and Javed Iqbal*

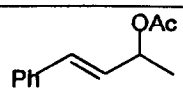
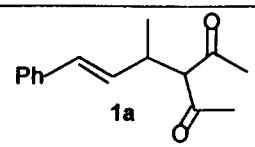
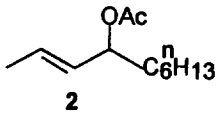
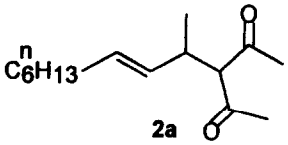
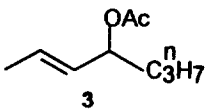
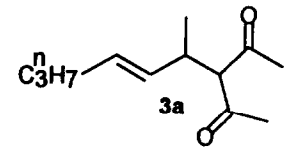
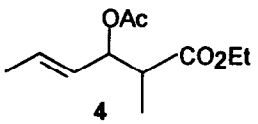
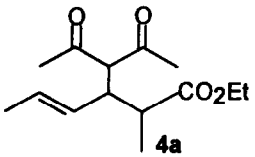
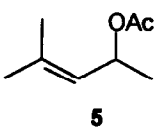
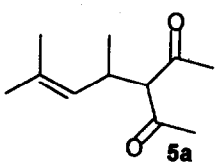
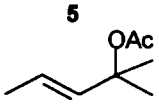
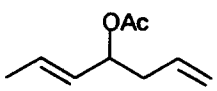
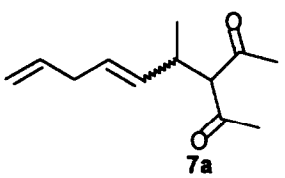
Department of Chemistry
Indian Institute of Technology, Kanpur
INDIA 208 016

Abstract: *Catalytic amount of Cobalt(II) chloride in 1,2-dichloroethane promotes the allylation of 1,3-dicarbonyl compounds with allyl acetates in high yields. The allylation of pentane-2,4-dione is highly regioselective as compared with methylacetoacetate and ethyl 2-oxocyclopentanecarboxylate.*

The formation of carbon-carbon bond involving high degree of regio and stereo control has been a challenging task for synthetic organic chemist over the last few decades. Among the various methodologies that are developed to date, the Palladium[1] and Molybdenum[2] catalyzed allylation of 1,3-dicarbonyl compounds with allylic substrates has emerged as an outstanding transformation for achieving high degree of regio and stereo selectivities. One of the major limitations with Palladium and Molybdenum catalysed allylation is that they are performed under basic conditions using stabilised anions derived from 1,3-dicarbonyl compounds. These reaction conditions are not compatable with base sensitive organic substrates and therefore bond formation on the latter using Palladium or Molybdenum π-allyl protocol suffers from a great disadvantage. In a recent preliminary communication we have described[3] that allylation of 1,3-dicarbonyl compounds can be achieved with allyl acetates without mandatory formation of enolates in the presence of catalytic amount of cobalt(II) chloride. This paper describes our further studies on the regiochemical aspect of this transformation.

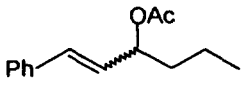
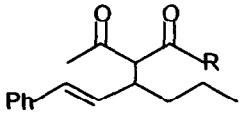
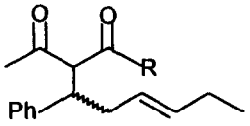
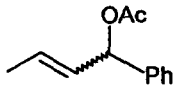
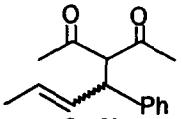
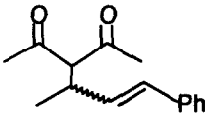
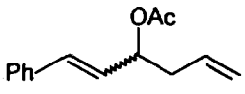
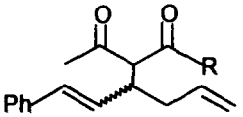
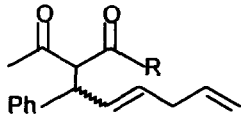
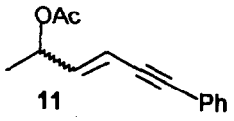
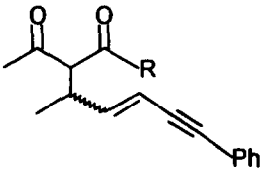
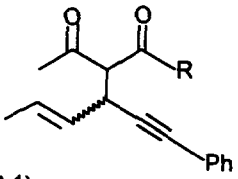
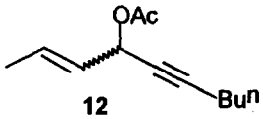
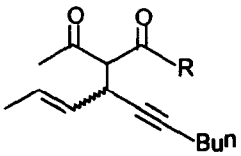
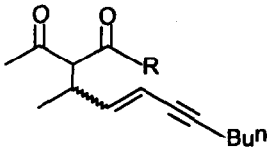
The reaction of 2,4-pentanedione with different allyl acetates in the presence of a catalytic amount of cobalt(II) chloride in 1,2-dichloroethane at 70°C afforded the corresponding allylated products in good yields. These reactions are highly regioselective as mainly one regioisomer is obtained as the major product (table 1). In certain cases the alkylation proceeds via allylic rearrangement (table 1, entries 2, 3, 6, 7) whereas for some it occurs without any transposition (table 1, entries 1, 4 and 5). These allylated products are obtained as a mixture of geometrical isomers in

Table 1: Cobalt(II) Chloride Catalysed Allylation of 2,4-Pentanedione with Allylacetates.

Entry	Allyl acetate	Products(Yield%)[a,b]	Stereoselectivity (E:Z)
1	 **1**	 **1a**	(83) (100:0)
2	 **2**	 **2a**	(76) (80:20)
3	 **3**	 **3a**	(68)[c] (75:25)
4	 **4**	 **4a**	(69) (90:10)
5	 **5**	 **5a**	(35)
6	 **6**	**5a**	(54)
7	 **7**	 **7a**	(46)

a) Yield of the isolated products . (b) Only the major isomer is isolated as the other was found to be less than 15% for most of these reactions . (c) Obtained as a mixture of diastereomers .

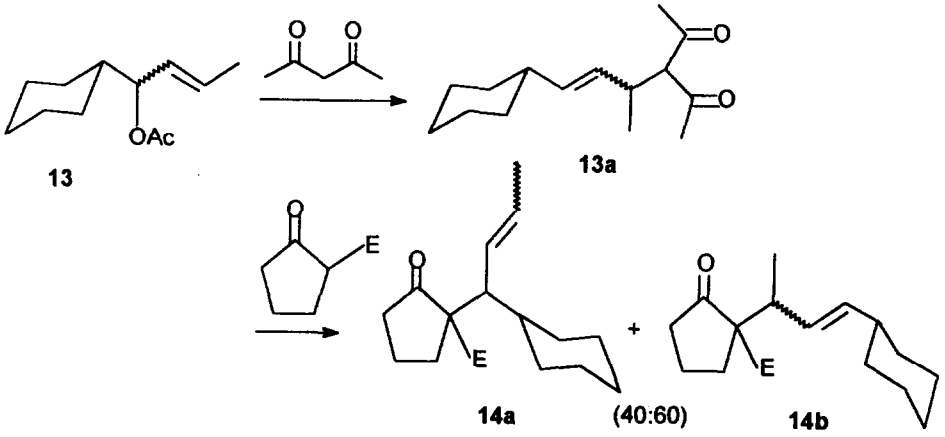
Table 2: Cobalt(II) Catalyzed Allylation of 2,4-Pentanedione and Methylacetoacetate: A Comparative Study.

Entry	Allyl acetate	R	Products(ratio)[a,b]		Yield(%)
1	 **8**				
		OMe	**8a:8b**	(1:2.5)	76
		Me	**8c:8d**	(10:1)	83
2	 **9**				
		OMe	**9a:9b**	(2:1)	49
		Me	**9c:9d**	(1:8)	61
3	 **10**				
		OMe	**10a:10b**	(1:2.2)	62
		Me	**10c:10d**	(4:1)	64
4	 **11**				
		OMe	**11a:11b**	(2:1)	32
		Me	**11c:11d**	(1:4)	55
5	 **12**				
		OMe	**12a:12b**	(1:1.5)	24
		Me	**12c:12d**	(6:1)	68

a) Isolated yield of the product . (b) Reaction with methylacetoacetate gave a mixture of diastereomers .

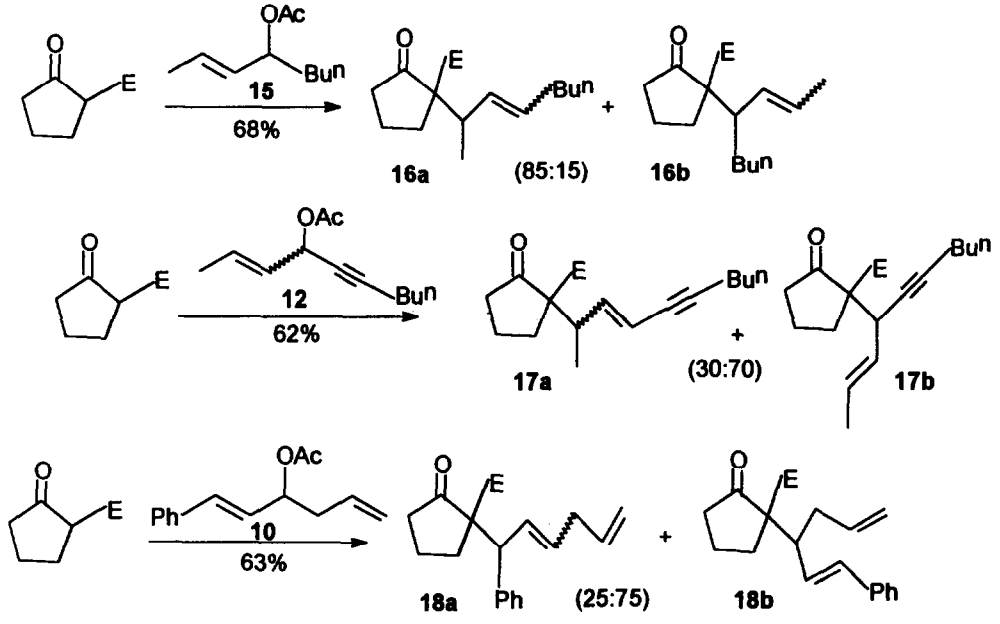
which the (E)-isomer predominates. Since the regioselective allylation is taking place at the less hindered carbon atom it indicates that the reaction may be controlled by steric factors. However, in the case where it is proceeding without any rearrangement it may be the electronic factor that governs the regioselectivity. Thus a comparative study of this reaction with different allyl acetates and methylacetoacetate or ethyl-2-oxocyclopentanecarboxylate was carried out to address the regiochemical issues related to this reaction. Interestingly, methylacetoacetate exhibited a poor regioselectivity with different allyl acetates (table 2). The reaction of aromatic allylacetates **8** and **9** with methylacetoacetate provided a mixture of regioisomers **8a-b** and **9a-b** respectively in which the product arising due to attack at the benzylic position was found to be the major. On the other hand, high regioselectivity was observed in favour of the regioisomer **8c** and **9c** respectively in the case of allylation with 2,4-pentanedione (table 2, entries 1 and 2). Similarly, in the case of diene acetate **10**, the alkylation at the benzylic position (i.e. **9a**) was again favoured when methylacetoacetate was used as the nucleophile whereas the alkylation of 2,4-pentanedione gave the other regioisomer **10c** as the major product (table 2, entry 3). It is worth mentioning that the regioselectivity is very high in the case of 2,4-pentanedione as compared[4] with the alkylation of methylacetoacetate. A similar trend is observed for the alkylation using enyne acetate **11** and **12** where once again 2,4-pentanedione underwent allylation to give one regioisomer predominantly (table 2, entries 4 and 5). It is also noteworthy that the chemical yields are low for the allylation of methylacetoacetate as compared with 2,4-pentanedione. It is interesting to note that methylacetoacetate shows a preference for reaction at the benzylic position during allylation with acetates **8-10** whereas on the other hand 2,4-pentanedione mainly reacts at nonbenzylic position or the propargylic position. This difference in the regioselective preference of methylacetoacetate and 2,4-pentanedione is highly interesting as it provides an important clue to the diverse nature of the reacting species derived from 1,3-dicarbonyl compounds. A comparison between 2,4-pentanedione and ethyl 2-oxo-cyclopentane-carboxylate with acetate **13** showed that the former undergoes highly regioselective allylation to give **13a** whereas a 40:60 mixture of allylated products **14a** and **14b** were obtained for the latter (Scheme 1).

The reaction of 2,4-pentanedione was also stereoselective as it gives (E)-isomer as the major product whereas allylation with cyclopentanecarboxylate afforded a mixture of geometrical as well as diastereomers. The regioselectivity in the allylation of ethyl



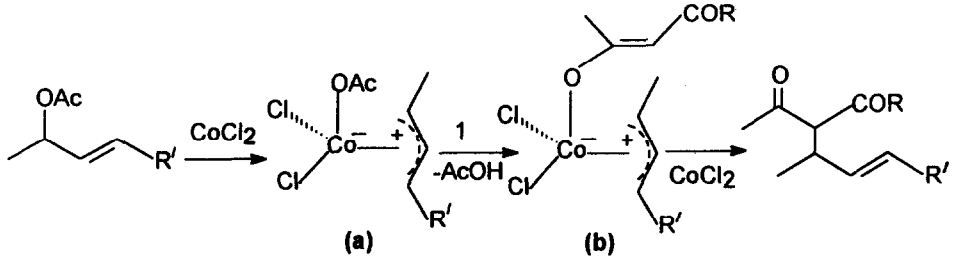
(Scheme 1)

2-oxocyclopentanecarboxylate is quite dependent upon the nature of allyl acetate. Thus its allylation with acetate **15** afforded the major regioisomer **16a** derived from the attack at sterically less hindered position, whereas the reaction with enyne acetate **12** led to the major product **17b** resulting due to attack at hindered propargylic position. Similarly the reaction with diene acetate **10** afforded the branched alkylated product **18b** as the major product (Scheme 2).



(Scheme 2)

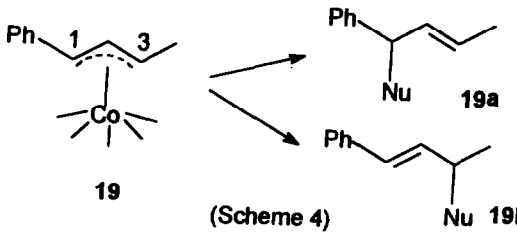
The mechanism for this reaction may be explained by assuming the formation of a π-allyl cobalt complex[5] (a) or an ion pair obtained as a result of the interaction between allyl acetate and cobalt(II) chloride (Scheme 3). The reaction of 1,3-dicarbonyl compounds via a redox process



(Scheme 3)

may give a cobalt-enolate (b), which will undergo an intramolecular carbon-carbon bond formation to afford the allylated product. We have earlier proposed[6] a similar model for the reaction of vinyl ethers with methylacetoacetate. The high regioselectivity in the case of 2,4-pentanedione or ethyl 2-oxocyclopentane carboxylate, which will readily form an enolate, may be arising due to this intramolecular reaction.

The source of divergence in regioselectivity between 1,3-dicarbonyl compound appear to stem from an intricate balance between charge distribution in the π-allyl species and the reactivity of 1,3-dicarbonyl compound. In an unsymmetrical complex **19** from aromatic allyl acetate, C-1 would be more electron[2b] deficient than C-3 (Scheme 4). The higher reactivity of the cobalt enolate of methyl acetoacetate compared to that of 2,4-pentanedione enolate would encourage the attack at C-1 to give major product **19a** due to attack at benzylic position, whereas, the low reactivity of the enolate from 2,4-pentanedione diminishes the importance of the charge distribution and provides the major product **19b** arising due to the thermodynamically controlled pathway (table 2, entries 1-3). The reactivity profile of ethyl 2-oxo-cyclopentanecarboxylate is similar to



(Scheme 4)

that of 2,4-pentanedione, however, the regioselectivity in the case of former is low as compared with the latter. The low yield and regioselectivity observed in the case of methylacetoacetate may be

attributed to the sluggishness in forming the cobalt enolate as compared to the reactions involving 2,4-pentanedione which will readily form the enolate. These results demonstrate that by a suitable choice of nucleophile, high regiochemical control can be exercised in cobalt-catalyzed allylation with allylacetates. This methodology provides a viable alternative to palladium or molybdenum catalysed allylic alkylation.

EXPERIMENTAL

Materials and Methods

1,2-Dichloroethane, THF and ether were purified by standard procedures. Acetylacetone, methylacetoacetate, alkyl halides and aldehydes were purchased and purified prior to use. $CoCl_2$ was purchased from LOBA India Ltd., Bombay and dried at 120°C for 2-3h before the reaction. Column chromatography was performed on ACME silicagel (60-120 mesh) using petroleum ether-ethylacetate as the eluent. ^{1}H-NMR spectra were recorded at 60, 80 and 400 MHz in $CDCl_3$ or CCl_4. Elemental analyses were conducted using Coleman automatic C, H and N analyser. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 Mass Spectrometer Data System using Argon (6 kV, 10 mA) as the FAB gas.

All the known compounds were characterised by comparing the data from the literature.

General Procedure for the Synthesis of Allylacetates

Alcohols were prepared either by $NaBH_4$ reduction of the corresponding carbonyl compounds or by the reaction of Grignard reagent with the corresponding carbonyl compounds or by the reaction of allylbromide with α, β-unsaturated aldehydes[7]. These alcohols were acylated with acetic anhydride and triethylamine in the presence of 4-N,N-dimethylaminopyridine[8]. Preparation of some of the representative examples are given below.

Ethyl-3-acetoxy-2-methyl hex-4-enoate (4)

Crotonaldehyde (9.0 mmol) and ethyl bromopropionate (7.5 mmol) and Zn powder (0.58g) were taken in benzene (40 mL) and ether (10 mL). The reaction mixture was refluxed for 30 min. on a water bath and then cooled to ice-bath temperature followed by addition of cold 10% H_2SO_4 (50 mL) with vigorous stirring. The organic layer was extracted with benzene (3x50 mL) and this extract was washed with 5% H_2SO_4 (2x20 mL), 10% aquous Na_2CO_3 (25 mL) and finally with water and then dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the alcohol which was acylated with acetic anhydride and triethylamine in the presence of dimethylaminopyridine. The acetate was purified by column chromatography on

silica gel. ^{1}H-NMR ($CDCl_3$) : δ 5.5 (m, 2H), 4.0 (q, J = 6 Hz, 2H), 2.5 (t J = 6 Hz, 1H), 2.0 (m, 1H), 1.85 (s, 3H), 1.65 (d, J = 6.5 Hz, 3H), 1.1 (t, J = 6.5 Hz, 3H), 0.9 (d, J = 7 Hz, 3H).

4-Acetoxy-dec-2-ene 5-yne (12)

To a solution of 1-hexyne (1 mol equiv.) in dry THF, n-butyl lithium (1.2 mol equiv.) was added at -20°C. Reaction mixture was stirred at room temperature for 0.5h. A THF solution of crotonaldehyde (1.2 mol equiv.) was added dropwise to the reaction mixture at 0°C and stirred for 1h and then warmed to ~50°C. The reaction mixture was quenched with saturated NH_4Cl solution and extracted with ethylacetate (3x50 mL). The organic layer was washed with saturated NH_4Cl solution and brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the alcohol which was acylated with acetic anhydride and triethylamine in the presence of DMAP. The acetate was purified by column chromatography (pet. ether - ethylacetate) on silicagel. ^{1}H-NMR ($CDCl_3$) : δ 6.0-5.2 (m, 2H), 3.2 (t, J = 6.5 Hz, 2H), 2.4-2.0 (m, 1H), 1.9 (s, 3H), 1.5 (d, J = 7 Hz, 3H), 1.4-1.0 (m, 4H), 0.9 (t, J = 6.5 Hz, 3H).

General Procedure for the Allylation of 1,3-dicarbonyl compounds

Allylacetate (5 mmol) and 1,3-dicarbonyl compound (5 mmol) were heated at 70°C while stirring in 1,2-dichloroethane (30 mL) in the presence of catalytic amount of dry cobalt(II) chloride (~30 mg) for 8-25h. Removal of the solvent gave a residue which was taken into ethylacetate and washed successively with saturated $NaHCO_3$ solution (3x25 mL), water (2x20 mL) and brine (1x25 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue which was chromatographed over silicagel to give the products.

3-Acetyl 4-methyl dodec-5-ene-2-one (2a)

Allylacetate **2** (5 mmol, 0.99g), pentane 2,4-dione (5.2 mmol, 0.52g) and cobalt(II) chloride (30 mg) in 1,2-dichloroethane (30 mL) were heated at 70°C for 22h. The usual work-up followed by column chromatography afforded **2a** (0.85g, 76%) as a mixture of regioisomers. The major isomer was found to have the following spectral data. ^{1}H-NMR ($CDCl_3$) δ : 5.6 (m, 1H), 5.2 (dd, J = 13 and 7 Hz, 1H), 3.3 (d, J = 6 Hz, 1H), 3.15-2.5 (m, 1H), 2.15 (s, 3H), 2.0 (s, 3H), 1.85 (m, 2H), 1.65-1.05 (m, 11H), 1.0 (d, J = 6 Hz, 3H). IR (Thin film) ν_{max} : 2940, 1710, 1690, 1350 cm^{-1}.

Ethyl 2-methyl-3(3'-pentane-2,4-dione)hex-4-enoate (4a)

Allylacetate **4** (5 mmol, 1.07g), pentane 2,4-dione (5.2 mmol, 0.52g) were heated at 70°C in 1,2-dichloroethane (30 mL) in the presence of

cobalt(II) chloride (30 mg) for 25h. The usual workup followed by column chromatography afforded **4a** (0.87g, 69%) as a mixture of regioisomers. ^{1}H-NMR ($CDCl_3$) : δ 5.9-5.1 (m, 2H), 4.0 (q, J = 6.5 Hz, 2H), 3.7 (d, J = 6.2 Hz, 1H), 2.31 (m, 1H), 2.1 (m, 1H), 2.0 (s, 3H), 1.95 (s, 3H), 1.70 (d, J = 6.5 Hz, 3H), 1.2 (t, J = 6.5 Hz, 3H), 1.0 (d, J = 6.5 Hz, 3H). IR (thinfilm) : ν_{max} 2940, 1735, 1705, 1470, 1460, 1365 cm^{-1}, m/z (f.a.b) 155 (base peak, M^+-99), 73 ($C_3H_5O^+$), 43 ($C_2H_3O^+$).

Methyl 2-acetyl 3-phenyl oct-4-enoate (8a)

The reaction was carried out as above using allylacetate **8** (0.95g, 4.36 mmol), methylacetoacetate (0.58g, 5.0 mmol), $CoCl_2$ (~30 mg) in dry 1,2-dichloroethane (30 mL). The crude product mixture was chromatographed to give **8b** (0.60g, 54%). ^{1}H-NMR : δ 7.3 (s, 5H), 6.25 (d, J = 16 Hz, 1H), 5.6 (dd, J = 16 and 8 Hz, 1H), 3.80 (s, 3H), 3.6 (d, J = 10 Hz, 1H), 3.2-2.6 (m, 1H), 2.15 (s, 3H), 2.0-1.75 (m, 2H), 1.65-1.01 (m, 2H), 0.85 (t, J = 6.5 Hz, 3H). IR (thinfilm) : ν_{max} 3040, 1740, 1715, 1490, 1430, 1350 cm^{-1}.

Methyl 2-acetyl 4-^{n}propyl 5-phenyl pent-4-ene-2-one (8b)

This was separated from the above reaction mixture as a minor product (0.24g, 22%). ^{1}H-NMR ($CDCl_3$) : δ 7.1 (s, 5H), 6.25 (d, J = 16 Hz, 1H), 5.6 (dd, J = 16 and 8 Hz, 1H), 3.8 (s, 3H), 3.5 (d, J = 10 Hz, 1H), 3.2-2.6 (m, 1H), 2.08 (s, 3H), 1.3 (m, 4H), 0.9 (t, J = 6.5 Hz, 3H). IR (thinfilm) : ν_{max} 2980, 1750, 1730, 1490, 1430 cm^{-1}.

3-Acetyl 4-^{n}propyl 6-phenyl hex-5-ene-2-one (8c)

This compound was prepared as described above by the reaction of allylacetate **8** (0.95g, 4.36 mmol), acetylacetone (0.52g, 5.23 mmol) and dry $CoCl_2$ (~30 mg) in dry 1,2--dichloroethane (30 mL). Purification by column chromatography afforded **8c** (0.849g, 75%). ^{1}H-NMR ($CDCl_3$) : δ 7.1 (s, 5H), 6.25 (d, J = 16 Hz, 1H), 5.6 (dd, J = 16 and 8 Hz, 1H), 3.6 (d, J = 10 Hz, 1H), 3.2-2.6 (m, 1H), 2.15 (s, 3H), 2.0 (s, 3H), 1.3 (m, 4H), 0.9 (t, J = 6.5 Hz, 3H). IR (thinfilm) : ν_{max} 3020, 1710, 1690, 1350 cm^{-1}. Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.08; H, 8.52 Found : C, 79.23, H, 8.56.

3-Acetyl 4-phenyl non-5-ene-2-one (8d)

This compound was isolated from the reaction mixture as described for **8c** (0.096g) in 9% yield. ^{1}H-NMR ($CDCl_3$) : δ 7.0 (s, 5H), 5.45-5.15 (m, 2H), 3.95 (m, 2H), 2.05 (s, 3H), 2.0-1.75 (m, 2H), 1.7 (s, 3H), 1.65-1.01 (m, 2H), 0.85 (t, J = 6.5 Hz, 3H). IR (CCl_4) : ν_{max} 3020, 1710, 1690 cm^{-1}.

4[2'(methyl-3'-oxo-butonoate)]-dec-2-ene-yne (12a)

This reaction was carried out as above using the allylacetate **12** (0.97g, 5 mmol), methylacetoacetate (0.60g, 5.2 mmol), $CoCl_2$ (~30 mg) and dry 1,2-dichloroethane (30 mL). The crude product was chromatographed to yield **12a** (0.125g, 10%). ^{1}H-NMR ($CDCl_3$) : δ 5.9-5.1 (m, 2H), 3.5 (s, 3H), 3.2 (d, J = 6 Hz, 1H), 3.1 (m, 1H), 2.2 (t, J = 6.2 Hz, 2H), 2.15 (s, 3H), 1.7 (d, J = 8 Hz, 3H), 1.5-1.15 (m, 4H), 0.9 (t, J = 6 Hz, 3H). IR (thinfilm) : ν_{max} 2935, 2220, 1735, 1715, 1445 cm^{-1}.

Compound (12b)

This compound was obtained from the above reaction (0.173g, 14%). ^{1}H-NMR ($CDCl_3$) : δ 5.8-5.2 (m, 2H), 3.5 (s, 3H), 3.20 (d, J = 6 Hz, 1H), 3.0-2.25 (m, 1H), 2.20 (t, J = 6.2 Hz, 2H), 2.15 (s, 3H), 1.5-1.15 (m, 4H), 1.2 (d, J = 8 Hz, 3H), 0.9 (t, J = 6.2 Hz, 3H). IR (thinfilm) : ν_{max} 2980, 2235, 1715, 1740, 1455, 1440 cm^{-1}.

Compound (12c)

A mixture of allylacetate 12 (0.97g, 5 mmol), acetylacetone (0.55g, 5.5 mmol), $CoCl_2$ (~30 mg) in dry 1,2-dichloroethane (30 mL) was heated at 70°C to give **12c** (0.67g, 58%). ^{1}H-NMR ($CDCl_3$) : δ 5.75 (dd, J = 12 and 6 Hz, 1H), 5.25 (dq, J = 18 and 6 Hz, 1H), 3.75 (d, J = 8 Hz, 1H), 2.35 (t, 6.2 Hz, 2H), 2.15 (s, 3H), 2.0 (s, 3H), 1.65 (d, J = 5 Hz, 3H), 1.6-1.1 (m, 4H), 0.9 (t, J = 6 Hz, 3H). IR (thinfilm) : ν_{max} 3450 (br), 2940, 2220, 1720, 1695, 1380, 1355; m/z (f.a.b.) 233 (M^+-1), 231 (M^+-3), 135 (M^+-99), 43 (base peak, $C_2H_3O^+$).

Compound (12d)

This was isolated from the above reaction mixture in 10% (0.11g) yield. ^{1}H-NMR (CCl_4) : δ 5.90 (d, J = 11 Hz, 1H), 5.75-5.45 (dd, J = 12 and 6 Hz, 1H), 3.4 (d, J = 11 Hz, 1H), 3.2-2.6 (m, 1H), 2.2 (t, J = 6.2 Hz, 2H), 2.15 (s, 3H), 2.0 (s, 3H), 1.7-1.05 (m, 4H), 1.0 (d, J = 6 Hz, 3H), 0.9 (t, J = 6.5 Hz, 3H). IR (thinfilm) : ν_{max} 2920, 2215, 1730, 1685, 1420 cm^{-1}.

Compound (13a)

A mixture of allylacetate **13** (1.18g, 6 mmol), acetylacetone (0.7g, 7 mmol) and $CoCl_2$ (~30 mg) in 1,2-dichloroethane (30 mL) was heated at 70°C for 8h. The crude product was chromatographed to yield **13a** (71%). ^{1}H-NMR ($CDCl_3$) : δ 5.37-5.12 (m, 2H), 3.53 (d, J = 12.5 Hz, 1H), 3.1-2.8 (m, 1H), 2.1 (s, 3H), 2.0 (s, 3H), 1.9-1.34 (m, 5H), 1.31-1.0 (m, 6H), 0.9 (d, J = 6.25 Hz, 3H). IR (thinfilm) : ν_{max} 1720, 1690, 1350 cm^{-1}. Anal. Calcd. for $C_{15}H_{24}O_2$: C, 76.28; H, 10.16 Found : C, 76.39; H, 10.23.

Compound (14b)

This compound was prepared as described above by the reaction of allylacetate **13** (1.36g, 7.3 mmol), ethyl-2--oxo-cyclopentane carboxylate (1.14g, 7.3 mmol) and $CoCl_2$ (~30 mg) in 1,2-dichloroethane (30 mL) at 70°C for 8h to give **14b** (1.57g, 74%). ^{1}H-NMR ($CDCl_3$) : δ 5.32 (t, J = 6 Hz, 2H), 4.2 (q, J = 7.5 Hz, 2H), 3.3-2.9 (m, 1H), 2.7-1.85 (m, 6H), 1.8-1.35 (m, 5H), 1.25-1.0 (m, 6H). ^{13}C NMR : 14.03, 15.92, 19.78, 25.91, 26.06, 33.02, 39.06, 61.33, 76.69, 77.01, 77.33, 169.97, 214.09. IR (thinfilm) : ν_{max} 1745, 1715, 1440, 1215 cm^{-1}. Anal. Calcd. for $C_{18}H_{28}O_3$: C, 73.99, H, 9.58 Found : C, 74.05; H, 9.64.

Compound (17b)

Allylacetate **12** (0.97g, 5 mmol), ethyl-2-oxo-cyclopentane carboxylate (1.0g, 7 mmol) and $CoCl_2$ (~30 mg) in dry 1,2-dichloroethane (30 mL) were subjected to the reaction conditions as described above. The usual workup followed by column chromatography afforded **17a** and **17b** (0.90g, 62%) as a mixture of diastereoisomer and geometrical isomer have the following spectral data. ^{1}H-NMR ($CDCl_3$) : δ 5.72 (m, 1H), 5.1-5.43 (m, 1H), 4.05 (q, J = 7Hz, 2H), 3.62 (m, 1H), 1.75-2.7 (m, 6H), 1.68 (d, J = 7.5 Hz, 3H), 1.05-1.5 (m, 6H), 1.02 (m, 3H), 0.85 (m, 3H) (m, 6H). ^{13}C NMR : 13.46, 13.98, 17.66, 18.29, 19.60, 21.75, 21.85, 29.16, 30.94, 38.63, 39.21, 61.62, 76.73, 77.04, 77.36, 126.04, 129.97, 213.02. IR (thinfilm) : ν_{max} 2230, 1750, 1720, 1470, 1450, 1230 cm^{-1}. Anal. Calcd. for $C_{18}H_{26}O_3$: C, 74.50, H, 8.96. Found : C, 74.59; H, 9.00.

Compound (18b)

Allylacetate **10** (1.0g, 4.6 mmol), ethyl-2-oxo-cyclopentane carboxylate (0.9g, 5.76 mmol) and $CoCl_2$ (~30 mg) in dry 1,2-dichloroethane (30 mL) were heated as described in the general procedure. The usual workup followed by column chromatography yielded a mixture of **18a** and **18b** (0.90g, 63%) as a mixture of diastereoisomers and geometrical isomers. The major isomer was found to have the following spectral data. ^{1}H-NMR ($CDCl_3$) : δ 7.3 (s, 5H), 6.35 (d, J = 18 Hz, 1H), 5.90 (dd, J = 6 and 18 Hz, 1H), 5.35 (m, 1H), 5.05 (m, 1H), 4.89 (m, 1H), 4.10 (q, J = 7.5 Hz, 2H), 3.21 (dt, J = 8 and 3 Hz, 1H), 2.65 (m, 2H), 2.35-1.80 (m, 6H), 1.25 (t, J = 7 Hz, 3H). IR (thinfilm) : ν_{max} 3080, 1745, 1720, 1630, 1595, 1490, 1445, 1225 cm^{-1}. Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.92; H, 7.69. Found : C, 77.00; H, 7.73.

REFERENCES

1. (a) Trost, B.M.; Tetrahedron, **1977**, 33, 2615. (b) Trost, B.M., Acc. Chem. Res., **1980**, 13, 385. (c) Palladium reagents in organic synthesis, Heck, R.F.; Academic Press: London, **1985**. (d) Godleski, S.A. in Comprehensive Organic Synthesis, Trost, B.M.; Ed. Pergamon, **1991**, Vol. 4, 585.

2. (a) Trost, B.M.; Lautens, M., J. Am. Chem. Soc., **1992**, 104, 5543. (b) Trost, B.M.; Lantens, M., J. Am. Chem. Soc., **1983**, 105, 3343. (c) Trost, B.M.; Merlic, C.A., J. Am. Chem. Soc., **1990**, 112, 9590.

3. Bhatia, B.; Reddy, M.M.; Iqbal, J., Tetrahedron Lett. **1993**, 34, 6301.

4. For alkylation of Pentane-2,4-dione through its Co(II) complex see : Vallribera, A.; Marquet, J.; Moreno-Manas, M.; Cayon, E. Tetrahedron, **1993**, 49, 6437.

5. For nucleophilic attack on cobalt complex see : Roustan, J.L.; Merour, J.Y.; Houlihan, F., Tetrahedron Lett., **1979**, 3721.

6. Cobalt(II) catalyzed formation of allyl cation from allylacetate has been proposed earlier : (a) Nayyar, N.K.; Reddy, M.M.; Iqbal, J., Tetrahedron Lett., **1991**, 32, 6965 (b) Iqbal, J.; Srivastava, R.R., Tetrahedron Lett., **1991**, 32, 1663.

7. Vogel's Text book of Practical Organic Chemistry, 4th Ed.; ELBS: England, **1984**.

8. Steglich, W.; Hofle, G. Angew. Chem. Int. Ed. Engl. **1969**, 8, 981.

(*Received in UK* 28 *April* 1994; *revised* 3 *June* 1994; *accepted* 10 *June* 1994)