

# Synthesis of $\alpha,\beta$ -Unsaturated Aldehydes by 1,3-Carbonyl Transposition through One Carbon Homologation. Part 2†

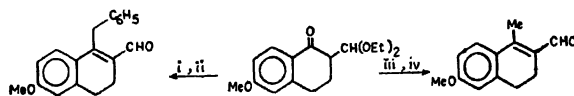
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The easily accessible 2-(diethoxymethyl)-6-methoxy-1-tetralone (1) on condensation with methylmagnesium iodide and benzylmagnesium chloride followed by treatment with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  affords 6-methoxy-1-methyl-3,4-dihydro-2-naphthaldehyde (2) and 1-benzyl-6-methoxy-3,4-dihydro-2-naphthaldehyde (3), respectively. The carbinols derived from the reaction of 2-(diethoxymethyl)-1-indanones (4a-4c) with methyl lithium undergo smooth transformations to the respective 3-methyl-1*H*-indene-2-aldehydes (5a-5c). *endo*-2-(*p*-Methoxyphenyl)-5-methylbicyclo[3.2.1]octan-6-en-7-aldehyde (14) has been prepared from *endo*-2-(*p*-methoxyphenyl)-5-methylbicyclo[3.2.1]octan-6-one (12) through the respective diethoxymethyl derivative (12) by sodium borohydride reduction followed by acid-catalysed rearrangement of the resulting diacetal carbinol.

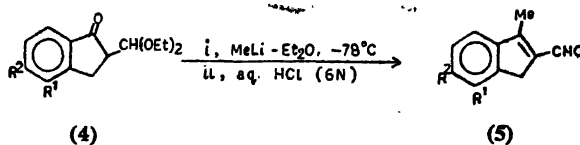
VARIOUS forms of transposition of carbonyl groups, important from a synthetic organic chemist's view point, are 1,2-carbonyl transposition<sup>1</sup>, 1,3-carbonyl transposition<sup>2-6</sup> and 1,4-carbonyl transposition<sup>7</sup>. The synthetic operations requiring 1,3-carbonyl transposition with one carbon homologation for the generation of  $\alpha,\beta$ -unsaturated aldehydes are also important. The earlier methods, of which the most common one involves the homologation of carbocyclic or aromatic conjugated cyclic and acyclic ketones with a general structure (A) having an active methylene group, to the  $\alpha,\beta$ -unsaturated aldehydes (C) has been achieved<sup>8-12</sup> through acid-catalysed rearrangement of the respective 2-(alkylthio)methylene carbinols (B), derived from the ketones in several steps, however, strong basic reagents are required for introduction of the functionalised  $\beta$ -carbon residue into the ketones. The other common method, *i.e.* Vilsmeier reaction<sup>13</sup>, also has certain limitations. In a recent paper<sup>1</sup> we have reported an alternate and simple approach to the transformations of cyclic and acyclic ketones having the general structure (A) to the respective  $\alpha,\beta$ -unsaturated aldehydes (C) through the easily accessible  $\beta$ -keto acetals (D) under mild reaction conditions<sup>14</sup>.

the unsaturated aldehyde 2 in 60% yield. Repeating the reaction of 1 with benzylmagnesium chloride leads to the known<sup>15</sup> aldehyde 3 in good yield.



Scheme 1: Reagents: i,  $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$ ,  $\text{Et}_2\text{O}$ ,  $-5-0^\circ$ ; ii,  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ,  $\text{CH}_2\text{Cl}_2$ ; iii,  $\text{MeMgI}$ ,  $\text{Et}_2\text{O}$ ,  $-5-0^\circ$ ; iv,  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ,  $\text{CH}_2\text{Cl}_2$ .

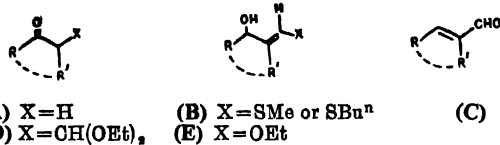
In the 1-indanone series the crude carbinols arising from condensation of the  $\beta$ -ketoacetals (4a-4c) with methyl lithium in ether at  $-78^\circ$ , followed by treatment with aqueous acid afford the  $\beta$ -methyl unsaturated aldehydes (5a-5c).



(a)  $\text{R}^1 = \text{OMe}$ ;  $\text{R}^2 = \text{H}$   
(b)  $\text{R}^1 = \text{Me}$ ;  $\text{R}^2 = \text{H}$   
(c)  $\text{R}^1 = \text{H}$ ;  $\text{R}^2 = \text{OMe}$

Scheme 2

With the successful development of the facile synthesis of  $\alpha,\beta$ -unsaturated aldehydes from aromatic conjugated ketones, the method has been extended to alicyclic ketones. The known  $\beta$ -ketoacetals 8 and 9, prepared according to Mock and Tsou<sup>14</sup> from the respective ketones 6 and 7, on reduction with sodium borohydride and subsequent acidic treatment produced the unstable unsaturated aldehydes 10 and 11 in *ca.* 50% yields, (characterised by spectral data).



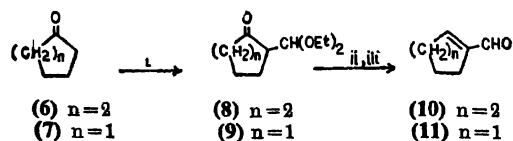
(A)  $\text{X} = \text{H}$   
(D)  $\text{X} = \text{CH}(\text{OEt})_2$ , (E)  $\text{X} = \text{OEt}$

(B)  $\text{X} = \text{SMe}$  or  $\text{SBU}^n$

(C)

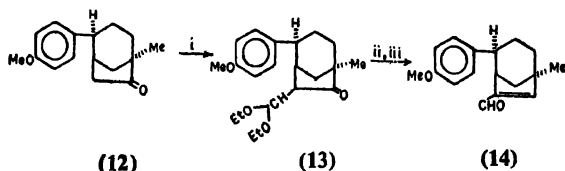
In continuation to this work, the introduction of an alkyl-substituent at the site of the ketone group in  $\beta$ -ketoacetals has been examined. Thus, the crude carbinol resulting from condensation of  $\beta$ -diethoxymethyl ketone (1) with methylmagnesium iodide in ether followed by treatment with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  affords

† Part 1, Ref. 1.



Scheme 3. Reagents: i,  $\text{OH}(\text{OEt})_2$ ,  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ,  $(i\text{-Pr})_3\text{NEt}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $-78$  to  $-10^\circ$ ; ii,  $\text{NaBH}_4$ - $\text{MeOH}$ ; iii, aq.  $\text{HCl}$  (6 *N*).

This two-step sequence has also been shown to be quite efficient with the bridged ketone (12)<sup>15</sup>, which leads to the respective  $\alpha,\beta$ -unsaturated aldehyde (14) through the respective  $\beta$ -ketoacetal (13), in good yield.



Scheme 4. Reagents: i,  $\text{OH}(\text{OEt})_2$ ,  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ,  $(i\text{-Pr})_3\text{NEt}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $-78$  to  $-10^\circ$ ; ii,  $\text{NaBH}_4$ - $\text{MeOH}$ ; iii, *p*- $\text{TsOH}$ ,  $\text{C}_6\text{H}_6$ .

The simplicity and mild reaction conditions of the present method, and the ease with which it can be applied to the preparation of unsubstituted and  $\beta$ -substituted  $\alpha,\beta$ -unsaturated aldehydes by one carbon homologation with 1,3-carbonyl transposition suggests that it will be the method of choice for such synthetic operation.

### Experimental

IR spectra were recorded on a Perkin-Elmer, PE 298 spectrometer. Unless otherwise stated the  $^1\text{H}$  NMR spectra were recorded at 200 MHz on a Varian XL-200 FT spectrometer in  $\text{CDCl}_3$  solutions with tetramethylsilane as internal standard. Petroleum and light petroleum refer to the fractions of b.p.  $60\text{-}80^\circ$  and  $40\text{-}60^\circ$ , respectively.

**2-(Diethoxymethyl)-6-methoxy-1-tetralone (1):** A solution of freshly distilled boron trifluoride etherate (1.84 ml, 15 mmol) in dichloromethane was added dropwise to freshly distilled triethyl orthoformate (2.0 ml, 12 mmol) with stirring at  $-30^\circ$ . The mixture was then warmed to  $0^\circ$  and allowed to stand at the temperature for 15 min. It was then cooled to  $-78^\circ$  and a solution of 6-methoxy-1-tetralone (1.05 g, 6 mmol) was added dropwise followed by addition of *N,N*-diisopropylethylamine (4.8 ml, 18 mmol) over a period of 10 min. The mixture was then stirred at  $-10$  to  $-20^\circ$  for 2 h and then added to a saturated solution of sodium bicarbonate (50 ml). After usual work-up, followed by evaporation of solvent left the diethoxyl methyl ketone (1) as a deep red thick liquid (1.5 g, 90%);  $\nu_{\text{max}}$  (neat) 1 660 and 1 610  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CCl}_4$ ) 0.93-1.37 (6H, m,  $\text{OCH}_2\text{CH}_3$ ), 2.0-2.4 (1H, m, COCH), 2.41-3.27 (4H, m), 3.3-3.9 (4H, m,  $\text{OCH}_2\text{CH}_3$ ), 3.8 (3H, s,  $\text{ArOCH}_3$ ), 5.03 (1H, d, COCHCH(OEt)<sub>2</sub>), 6.46-6.83

(2H, m, ArH) and 7.83 (1H, d, *J* 9 Hz, ArH). This was used for the subsequent reactions without further purification.

**2-(Diethoxymethyl)-4-methoxy-1-indanone (4a):** It was obtained in 83% yield starting from 4-methoxyindan-1-one in the same way as above;  $\nu_{\text{max}}$  (neat) 1 700 and 1 610  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CCl}_4$ ) 0.83-1.47 (6H, m,  $2 \times \text{OCH}_2\text{CH}_3$ ), 2.7-3.26 (3H, m), 3.3-3.8 (4H, m,  $2 \times \text{OCH}_2\text{CH}_3$ ), 3.83 (3H, s,  $\text{ArOCH}_3$ ), 4.83 (1H, d, *J* 4 Hz, COCHCH(OEt)<sub>2</sub>), 6.7-7.33 (3H, m, ArH).

**2-(Diethoxymethyl)-4-methyl-1-indanone (4b):** It was prepared in 80% yield from 4-methylindan-1-one as in the aforementioned way;  $\nu_{\text{max}}$  (neat) 1 700 and 1 600  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CCl}_4$ ) 0.8-1.43 (6H, m,  $2 \times \text{OCH}_2\text{CH}_3$ ), 2.33 (3H, s,  $\text{ArCH}_3$ ), 2.67-3.9 (7H, m), 4.83 (1H, d, *J* 4 Hz, COCHCH(OEt)<sub>2</sub>) and 6.93-7.5 (3H, m, ArH).

**2-(Diethoxymethyl)-5-methoxy-1-indanone (4c):** It was obtained in 95% yield starting from 5-methoxyindan-1-one;  $\nu_{\text{max}}$  (neat) 1 700 and 1 610  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CCl}_4$ ) 0.83-1.47 (6H, m,  $2 \times \text{OCH}_2\text{CH}_3$ ), 2.77-3.7 (7H, m), 3.87 (3H, s,  $\text{ArOCH}_3$ ), 4.83 (1H, d, *J* 4 Hz, COCHCH(OEt)<sub>2</sub>), 6.7-6.96 (2H, m, ArH) and 7.43-7.67 (1H, m, ArH).

**7-(Diethoxymethyl)-endo-2-(*p*-methoxyphenyl)-5-methylbicyclo[3.2.1]octan-6-one (13):** It was obtained in 85% yield starting from the bridged ketone (12)<sup>15</sup>;  $\nu_{\text{max}}$  (neat) 1 735 and 1 605  $\text{cm}^{-1}$ ;  $\delta$  0.98 (3H, t, *J* 8 Hz,  $\text{OCH}_2\text{CH}_3$ ), 1.04 (3H, s,  $\text{CH}_3$ ), 1.08 (3H, t, *J* 8 Hz,  $\text{OCH}_2\text{CH}_3$ ), 1.54-1.78 (3H, m), 2.0 (1H, m), 2.22-2.44 (2H, m), 2.82-3.0 (3H, m), 3.5-3.74 (4H, m,  $2 \times \text{OCH}_2\text{CH}_3$ ), 3.80 (3H, s,  $\text{ArOCH}_3$ ), 4.62 (1H, d, *J* 4 Hz, COCHCH(OEt)<sub>2</sub>), 6.9 (2H, d, *J* 8 Hz, ArH), 7.28 (2H, d, *J* 8 Hz, ArH).

**6-Methoxy-1-methyl-3,4-dihydro-2-naphthaldehyde (2):** To a stirred solution of the acetal (1; 556 mg, 2 mmol) in ether (10 ml) kept at  $0$  to  $-5^\circ$  was added a solution of methylmagnesium iodide in ether (prepared from 750 mg Mg, 1 ml MeI, and 25 ml ether) dropwise with stirring under nitrogen. The reaction mixture was stirred at that temperature for 2 h, followed by 2 h at room temperature and then left overnight. Finally, the reaction mixture was refluxed for 2 h, cooled and decomposed with ice-cold saturated  $\text{NH}_4\text{Cl}$  solution. The ether layer was separated and the aqueous layer was extracted with ether ( $3 \times 20$  ml). The combined organic layer was washed with 5%  $\text{Na}_2\text{S}_2\text{O}_3$  solution ( $2 \times 15$  ml) followed by brine and then dried. Removal of solvent left crude carbinol as a red viscous liquid, which was taken in dry  $\text{CH}_2\text{Cl}_2$  (6 ml) and treated with freshly distilled boron trifluoride etherate (0.2 ml) with stirring under  $\text{N}_2$  at  $-5$  to  $0^\circ$ . The stirring was continued for an additional 1 h in the cold, followed by 1 h at room temperature and then worked-up in the usual way. Removal of solvent left a red mass which on chromatography over silica gel (7 g) and elution with benzene-petroleum (1:9) furnished aldehyde (2) (240 mg, 60%), m.p.  $62^\circ$  (light petroleum) (Found: C, 77.48; H, 7.04.  $\text{C}_{13}\text{H}_{14}\text{O}_2$  requires: C, 77.20;

H, 6.98%);  $\lambda_{\max}$  244 (4.11) and 340 nm ( $\log \epsilon$  4.40);  $\nu_{\max}$  (KBr) 2 920, 1 640, 1 600, 1 560, 1 425, 1 300 and 1 280  $\text{cm}^{-1}$ ;  $\delta$  2.5 (3H, s,  $\text{CH}_3$ ), 2.5-2.54 (2H, m), 2.7-2.74 (2H, m), 3.84 (3H, s,  $\text{ArOCH}_3$ ), 6.75-6.8 (2H, m, ArH), 7.48 (1H, d,  $J$  8 Hz, ArH) and 10.3 (1H, s, CHO).

**1-Benzyl-6-methoxy-3,4-dihydro-2-naphthaldehyde (3)**: To a cold ( $-5$  to  $0^\circ$ ) stirred solution of the acetal (**1**; 500 mg, 1.8 mmol) in ether (15 ml) was added a solution of benzylmagnesium chloride prepared from magnesium (400 mg), benzyl chloride (1.0 g, 8 mmol) in ether (30 ml) under  $\text{N}_2$ . The reaction mixture was stirred at the same temperature for 2 h followed by 12 h at room temperature. It was decomposed with ice-cold aqueous ammonium chloride solution and extracted with ether ( $3 \times 50$  ml), washed with brine and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent afforded an oil, which was taken in dry methylene chloride (7 ml) and stirred with boron trifluoride etherate (0.1 ml) under  $\text{N}_2$  for 0.5 h. It was decomposed with 5% aqueous sodium bicarbonate solution (50 ml), extracted with methylene chloride ( $3 \times 30$  ml), washed with brine and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of solvent afforded a gummy mass, which on chromatography over silica gel (7 g) and elution with benzene-petroleum (1:9) afforded the aldehyde (**3**) (325 mg, 69%), m.p.  $116^\circ$  (light petroleum) (lit.<sup>19</sup>  $116$ - $117^\circ$ );  $\lambda_{\max}$  203.75 (4.87), 245.4 (4.0) and 343.6 nm ( $\log \epsilon$  4.17);  $\nu_{\max}$  (KBr) 1 675, 1 640 and 1 605  $\text{cm}^{-1}$ ;  $\delta$  2.66 (2H, m), 2.80 (2H, m), 3.80 (3H, s,  $\text{ArOCH}_3$ ), 4.4 (2H, s,  $\text{ArCH}_2$ ), 6.66-6.8 (2H, m, ArH); 7.26 (5H, brs, ArH), 7.4 (1H, d,  $J$  8 Hz, ArH) and 10.15 (1H, s, CHO).

**7-Methoxy-3-methyl-1H-indene-2-aldehyde (5a)**: Methylolithium (6.5 ml of 1.2 M solution in ether, 8 mmol) was added dropwise to a stirred solution of the acetal (**4a**; 500 mg, 2 mmol) in ether (10 ml) at  $-78^\circ$ . The reaction mixture was stirred at that temperature for 3 h and then left overnight. Next day ice-cold 6 N HCl solution (30 ml) was added to the reaction mixture and stirred for 2 h. It was extracted with ether ( $3 \times 30$  ml) washed with 5%  $\text{Na}_2\text{S}_2\text{O}_8$  solution, brine and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of solvent afforded the crude aldehyde, which was chromatographed over silica gel (5 g) to give in the benzene-petroleum (1:9) elutes the aldehyde (**5a**) (260 mg, 70%), m.p.  $128$ - $129^\circ$  (light petroleum) (Found: C, 76.50; H, 6.50.  $\text{C}_{12}\text{H}_{12}\text{O}_2$  requires: C, 76.57; H, 6.43%);  $\lambda_{\max}$  245 (3.90) and 310 nm ( $\log \epsilon$  4.10);  $\nu_{\max}$  (KBr) 2 900, 2 820, 1 645, 1 600, 1 575, 1 480, 1 440, 1 400, 1 385 and 1 345  $\text{cm}^{-1}$ ;  $\delta$  2.54 (3H, t,  $J$  0.01 Hz,  $\text{CH}_3$ ), 3.58 (2H,  $J$  0.01 Hz,  $\text{ArCH}_2$ ), 3.905 (3H, s,  $\text{ArOCH}_3$ ), 6.92 (1H, d,  $J$  8 Hz, ArH), 7.22 (1H, d,  $J$  8 Hz, ArH), 7.37 (1H, t,  $J$  8 Hz, ArH), 10.20 (1H, s, CHO).

**3,7-Dimethyl-1H-indene-2-aldehyde (5b)**: To a stirred solution of the acetal (**4b**; 470 mg, 2 mmol) in ether (10 ml) at  $-78^\circ$  was added a solution of methylolithium (6.5 ml, 1.2 M solution in ether, 8 mmol) under  $\text{N}_2$  and stirred at that temperature

for 3 h and left overnight. It was then decomposed with ice-cold 6 N HCl solution and stirred for an additional 2 h. Usual work-up, followed by removal of the solvent gave a solid product, which was purified by chromatography over silica gel (5 g) and elution with petroleum. Crystallisation of the solid from light petroleum gave the pure aldehyde (**5b**) (215 mg, 63%), m.p.  $118^\circ$  (Found: C, 83.92; H, 6.87.  $\text{C}_{12}\text{H}_{12}\text{O}$  requires: C, 83.69; H, 7.02%);  $\lambda_{\max}$  236 (3.69) and 310 nm ( $\log \epsilon$  4.07),  $\nu_{\max}$  (KBr) 1 645, 1 600 1 515, 1 440, 1 430, 1 385 and 1 350  $\text{cm}^{-1}$ ;  $\delta$  2.39 (3H, s,  $\text{ArCH}_3$ ), 2.56 (3H, t,  $J$  0.01 Hz,  $\text{CH}_3$ ), 3.53 (2H, uq,  $J$  0.01 Hz,  $\text{ArCH}_2$ ), 7.29-7.36 (2H, m, ArH), 7.43 (1H, d,  $J$  8 Hz, ArH) and 10.23 (1H, s, CHO).

**6-Methoxy-3-methyl-1H-indene-2-aldehyde (5c)**: Methylolithium (6.5 ml of 1.2 M in ether, 8 mmol) was added dropwise to a cold ( $-78^\circ$ ) magnetically stirred solution of the acetal (**4c**; 500 mg, 2 mmol) in ether (10 ml). The reaction was carried out as above. Usual work-up afforded a solid product which was chromatographed over silica gel (5 g). The elutes with benzene-petroleum (1:9) afforded **5c** which was crystallised from light petroleum (270 mg, 72%), m.p.  $126$ - $127^\circ$  (Found: C, 76.41; H, 6.53.  $\text{C}_{12}\text{H}_{12}\text{O}_2$  requires: C, 76.57; H, 6.43%);  $\lambda_{\max}$  246 (3.93) and 336 nm ( $\log \epsilon$  4.30);  $\nu_{\max}$  (KBr) 2 970, 1 640, 1 635 (Fermi band), 1 600, 1 570, 1 480, 1 430 and 1 390  $\text{cm}^{-1}$ ;  $\delta$  2.51 (3H, t,  $J$  1.01 Hz,  $\text{CH}_3$ ), 3.58 (2H, uq,  $J$  0.01 Hz,  $\text{ArCH}_2$ ), 3.86 (3H, s,  $\text{ArOCH}_3$ ), 6.82 (1H, m, ArH), 7.04 (1H, brs, ArH), 7.45 (1H, d,  $J$  8 Hz, ArH) and 10.1 (1H, s, CHO).

**Cyclohexene-2-aldehyde (10)**: To a well stirred solution of the acetal (**8**)<sup>14</sup> (282 mg, 1.5 mmol) in methanol (5 ml) was added sodium borohydride (200 mg, 5.4 mmol) and the mixture was stirred for 12 h. The reaction mixture was decomposed with ice-cold 6 N HCl (50 ml), stirred for 1.5 h and worked-up in the usual way. Removal of solvent afforded a colourless liquid (**10**)<sup>16</sup> (85 mg, 50%);  $\nu_{\max}$  (neat) 1 695 and 1 650  $\text{cm}^{-1}$ ;  $\delta$  1.16-2.4 (8H, m), 6.86 (1H, m, olefinic H) and 9.44 (1H, s, CHO).

**Cyclopentene-2-aldehyde (11)**: The acetal (**9**)<sup>14</sup> was converted to the respective aldehyde (**11**)<sup>17</sup> in the usual way as above, but was found to contain some polymeric product as revealed by  $^1\text{H}$  nmr,  $\delta$  1.48-2.0 (6H, m), 6.92 (1H, brs, olefinic H), 9.82 (1H, s, CHO) and other high field protons.

**endo-2-(p-Methoxyphenyl)-5-methylbicyclo[3.2.1]-octan-6-en-7-aldehyde (14)**: To a well stirred solution of the acetal (**13**; 175 mg, 0.51 mmol) in methanol (5 ml) was added excess sodium borohydride (68 mg, 1.8 mmol) and stirred for 3 h. The reaction mixture was decomposed with ice-cold 2 N HCl (25 ml) and extracted with ether ( $3 \times 30$  ml), washed with brine and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of solvent afforded a liquid which was azeotropically refluxed with *p*-toluenesulphonic acid (50 mg) and benzene (50 ml) for 3 h under  $\text{N}_2$ . The reaction mixture was washed with 5% aqueous sodium bicarbonate solution, brine and dried ( $\text{Na}_2\text{SO}_4$ ).

Removal of solvent afforded a gummy mass, which on chromatography over silica gel (3 g) and elution with benzene-petroleum (1 : 9) afforded the desired aldehyde (14) (80 mg, 62%), which solidified on standing in refrigerator, m.p. 82-84° (light petroleum) (Found : C, 79.33 ; H, 7.66.  $C_{17}H_{20}O_2$  requires C, 79.65 ; H, 7.86%).  $\lambda_{max}$  202 (4.09) and 226 nm (log  $\epsilon$  4.15) ;  $\nu_{max}$  (KBr) 2 950, 1 675, 1 610, 1 510 and 1 460  $cm^{-1}$  ;  $\delta$  1.15 (3H, s,  $CH_3$ ), 1.36-2.07 (6H, m), 2.75 (1H, m), 3.07 (1H, m), 3.70 (3H, s,  $ArOCH_3$ ), 6.6-6.72 (3H, m,  $ArH$ , with olefinic  $H$ ), 6.90 (1H, d,  $J$  8 Hz,  $ArH$ ) and 9.47 (1H, s, CHO).

#### Acknowledgement

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