An Efficient One Pot Synthesis of Bicyclic Dienones

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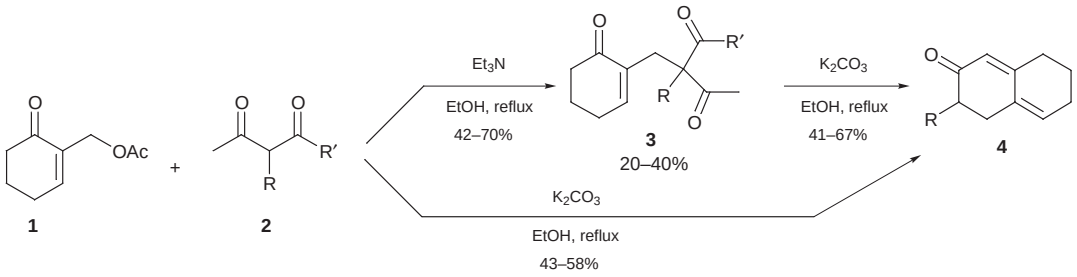
Bicyclic dienones **4** are prepared in a one pot process from the reaction of 2-(acetoxymethyl)cyclohex-2-enone **1** with 1,3-dicarbonyl compounds **2** in the presence of K_2CO_3 in refluxing absolute ethanol.

Synthetic methods for dienones **4** are fairly sparse.[1–3] We have recently reported[4] that cyclization of intermediates **3**, obtained from the reaction of 2-(acetoxymethyl)cyclohex-2-enone **1**[5,6] with 1,3-dicarbonyl compounds **2** in the presence of Et_3N, afforded compounds **4** (Scheme 1). The overall yield of this Robinson annulation,[7] effected in a two-step sequence, is *ca.* 20–40%.

As an improvement to this method, we report herein a direct access to dienones **4** in satisfactory yields.

2-(Acetoxymethyl)cyclohex-2-enone **1** reacts with 1,3-dicarbonyl compounds **2**[9] in the presence of a large excess (4 equiv.) of anhydrous K_2CO_3 in refluxing absolute ethanol by an S_N2 type reaction to give products **3**. These intermediates generate, *in situ, via* cleavage followed by cyclization, the target bicyclic dienones **4** in 43–58% overall yield (Scheme 1).

In summary, we have developed a simple one-step method for the preparation of bicyclic dienones **4** in overall yield higher than those obtained in our previous paper.[4]



3	**3a**	**3b**	**3c**	**3d**[8]	**3e**[8]
R	H	Me	Et	H	H
R′	Me	Me	Me	OMe	OEt
Yield of **4** (%)	48	58	52	43	46

Scheme 1

Experimental

^{1}H NMR spectra were recorded in $CDCl_3$ solutions at 60 or 300 MHz with tetramethylsilane as an internal reference. ^{13}C NMR were recorded at 75 MHz with $CDCl_3$ as the internal reference. Chemical shifts are given in ppm (δ) and coupling constants J are reported in Hz. IR spectra were obtained on a Perkin Elmer Paragon 1000 PC IR spectrometer. Mass spectra were measured on a Hewlett-Packard 5890 spectrometer at 70 eV (EI). Column chromatography was performed using silica gel 60 (70–230 mesh).

Preparation of Dienones **4**.—A representative experimental procedure for the preparation of **4a** is described. A mixture of 2-(acetoxymethyl)cyclohex-2-enone **1** (1.00 g, 6 mmol), pentane-2,4-dione (0.684 g, 6 mmol), commercial anhydrous potassium carbonate (3.32 g, 24 mmol) and 20 ml of absolute ethanol, was refluxed for 2 h. The solvent was evaporated *in vacuo* and the reaction mixture was partitioned between water (25 ml) and diethyl ether (50 ml). Aqueous 2M HCl (5 ml) was added to dissolve salts and the mixture was extracted with diethyl ether (3 × 20 ml). The ether extracts were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography [1 : 4 then 4 : 1 diethyl ether–light petroleum (bp 40–60 °C).

Dienone **4a** yellow oil; IR ($CHCl_3$): 1659, 1630, 1589 cm^{-1}; δ_H(300 MHz, $CDCl_3$): 6.10–5.93 (m, 1H), 5.75 (s, 1H), 2.65 (t, 2H, J = 7 Hz), 2.50–2.45 (m, 4H) 2.29–2.27 (m, 2H), 1.85–1.76 (m, 2H); δ_C (75 MHz, $CDCl_3$): 199.3, 155.9, 131.8, 131.7, 123.1, 37.3, 30.8, 29.4, 25.8, 22.0; MS: *m/z* 148 (M^+, 69), 133 (12), 120 (43), 105 (37), 91 (100), 77 (22), 65 (20), 51 (21) (Found: C, 81.2; H, 8.1. $C_{10}H_{12}O$ requires C, 81.08; H, 8.11%).

Dienone **4b** yellow oil; IR ($CHCl_3$): 1659, 1630, 1591 cm^{-1}; δ_H(60 MHz, $CDCl_3$): 6.17–5.90 (m, 1H), 5.67 (s, 1H), 2.77–2.10 (m, 7H), 2.01–1.54 (m, 2H), 1.23–1.04 (m, 3H); δ_C (75 MHz, $CDCl_3$): 202.0, 155.0, 131.8, 131.7, 122.2, 41.0, 37.6, 30.4, 25.7, 22.0, 15.4; MS: *m/z* 162 (M^+, 100), 147 (21), 134 (74), 119 (51), 105 (22), 91 (53) (Found: C, 81.4; H, 8.6. $C_{10}H_{14}O$ requires C, 81.48; H, 8.64%).

Dienone **4c** yellow oil; δ_H(300 MHz, $CDCl_3$): 6.00–5.98 (m, 1H), 5.57 (s, 1H), 2.64–2.59 (m, 1H), 2.38–2.33 (m, 3H), 2.20–2.15 (m, 3H), 1.72–1.66 (m, 3H), 1.33-1.29 (m, 1H), 0.84 (t, 3H, J = 6 Hz); δ_C (75 MHz, $CDCl_3$): 201.9, 154.8, 132.1, 131.7, 122.4, 47.8, 34.5, 30.5, 26.0, 23.2, 22.2, 11.5; MS: *m/z* 176 (M^+, 16), 148 (100), 120 (76), 91 (63), 77 (24) (Found: C, 81.9; H, 9.0. $C_{12}H_{16}O$ requires C, 81.82; H, 9.09%).

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