Synthesis of substituted hexa-3,5-dienoic acid methyl esters from conjugated dienones

Rishan Lang Nongkhlaw, Ridaphun Nongrum and Bekington Myrboh *

Department of Chemistry, North Eastern Hill University, Shillong-793022, Meghalaya, India

Received (in Cambridge, UK) 7th February 2001, Accepted 4th April 2001
First published as an Advance Article on the web 4th May 2001

Substituted hexa-3,5-dienoic acid methyl esters (**2**) were conveniently prepared in one step by 1,2-carbonyl transposition of the corresponding dienones (**1**) using lead(IV) acetate and boron trifluoride–diethyl ether in benzene at room temperature.

Introduction

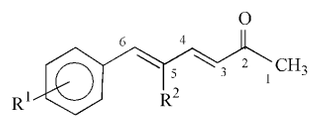
Hexa-3,5-dienoic acid methyl esters are important synthons in organic synthesis. The unsubstituted diene is one of the key intermediates used for the synthesis of the "southern" half of vitamin B_{12}.[1] It has also been used as an intermediate in the synthesis of the alkaloid lycorine.[2] Although there is a vast amount of literature on the synthesis of its conjugated analogs, our literature survey showed that there are only few reports that describe the synthesis of this class of compounds. Some of the reported methods include the following: (i) the Rh-catalysed C–C coupling of allene with but-3-enoic acid to give a mixture of esters of hexa-3,5-dienoic acid in a 9 : 1 ratio;[3] (ii) the transition-metal-catalysed reaction of styrene with but-3-enoic acid;[4] and (iii) the reaction of allylic alcohols with acetylene, CO and MeOH (as described in an Italian patent) in the presence of an $NiBr_2$–phosphine complex to yield two products, one of which is the title compound.[5] Other methods include the use of Li–diisopropylamide–HMPA in THF to deconjugate methyl sorbate to the corresponding diene.[6]

Previously we have illustrated the successful use of lead(IV) acetate in combination with Lewis acids to effect a 1,2-carbonyl transposition in acetophenones[7] and acyclic α,β-unsaturated ketones[8] and a ring contraction in cyclic α,β-unsaturated ketones and related systems.[9a–c] As part of our continuing work to test the effectiveness of this reagent combination, we inserted one more double bond between the carbonyl and the benzylidene system to see whether the presence of the doubly conjugated moiety in the ketone (**1**) would also facilitate a 1,2-carbonyl shift.

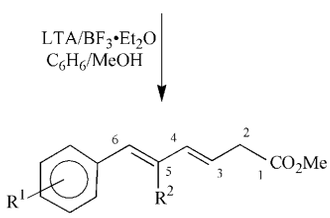
Results and discussion

We wish to report here a simple method for the synthesis of 5-alkyl-6-arylhexa-3,5-dienoic acid methyl ester (**2**) by transformation of 5-alkyl-6-arylhexa-3,5-dien-2-one (**1**) assisted by lead(IV) acetate and boron trifluoride–diethyl ether (Scheme 1). The reactions proceeded smoothly at low temperature (−30 °C) to give the products in yields varying between 35 and 50%.

The mechanism for this transformation (Scheme 2) appears to involve an initial Lewis acid-catalysed enolisation of ketone **1** to give enolate **3**, which then undergoes an oxyplumbation reaction in the presence of lead(IV) acetate and MeOH to give the organometallic intermediate **4** (not isolated). The elimination of lead(II) acetate, evidently assisted by neighboring group participation of the adjacent π electrons, resulted in the generation of a carbocation stabilized by the conjugated π system, which, in the presence of MeOH, rearranges to the more stable product **2**.



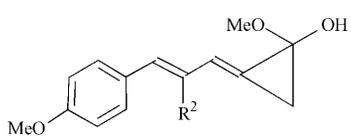
1



2

Scheme 1

^{1}H NMR analysis of two reaction mixtures in which R^1 = OMe and R^2 = Me, CH_2Me showed the presence of methylene protons as multiplets at *ca.* δ 1.87 and 1.71, while ^{13}C NMR showed a resonance at *ca.* δ 12.3, suggesting the presence of the cyclopropyl intermediate **6**, which evidently rearranges to the more stable product **2** during work-up.

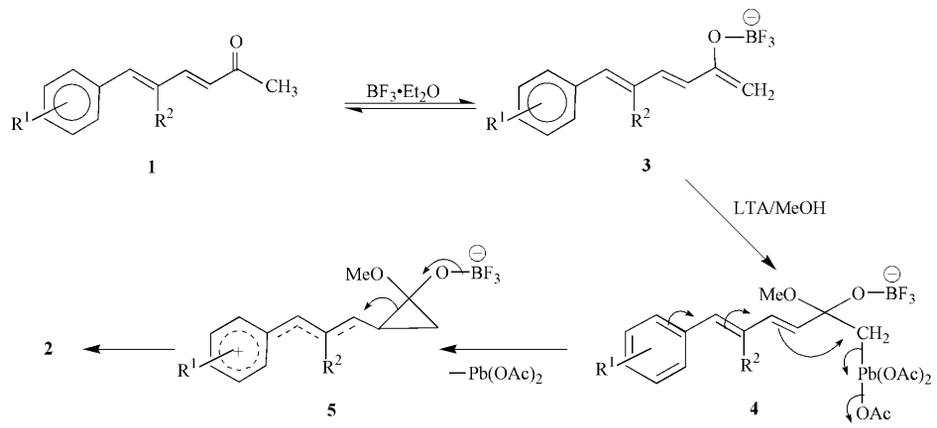


6

R^2 = —CH_3, —CH_2CH_3

For this investigation we have chosen ketones **1** (Table 1), which were prepared in two steps by successive condensation of an aromatic aldehyde with an aliphatic aldehyde and then with an aliphatic ketone. At each step the products were purified by column chromatography before proceeding to the next reaction. Thus, the starting material (**1**), which possesses an *E* geometry at the 3-position, reacts with lead(IV) acetate in the presence of boron trifluoride–diethyl ether and methanol in benzene at −30 °C to give the product **2** in which the stereochemistry is retained or changed depending on the nature of the substituent R^2. As R^2 becomes increasingly bulky the concentration of the *E* isomer (**3*E***) becomes greater and only a trace amount of the *Z* (**3*Z***) isomer is obtained. The stereochemistry of the double bond at the 3-position was assigned on the basis of the coupling constant and also on the basis of the CH_2COOR signal, which is generally at lower field for *Z* than for the corresponding *E* compounds.[10]

 DOI: 10.1039/b101242h



Scheme 2

Table 1 Preparation of substituted hexa-3,5-dienoic acid methyl esters

Entry	Products[a]	R^1	R^2	Time/h	Yield (%)[b] Z[c]	Yield (%)[b] E[c]
1	**2a**	H	H	24	10	40
2	**2b**[d]	H	CH_3	17	7	40
3	**2c**	H	CH_2CH_3	24	0	35
4	**2d**	*p*-CH_3	H	24	10	38
5	**2e**	*p*-CH_3	CH_3	12	7	40
6	**2f**	*p*-CH_3	CH_2CH_3	24	0	47
7	**2g**	*p*-Cl	CH_3	24	0	45
8	**2h**	*p*-Cl	CH_2CH_3	24	0	40
9	**2i**	*p*-OCH_3	CH_3	20	8	35
10	**2j**	*p*-OCH_3	CH_2CH_3	24	0	42
11	**2k**	3,4-di-OCH_3	CH_3	24	0	38
12	**2l**	3,4-di-OCH_3	CH_2CH_3	24	0	35
13	**2m**	*p*-NO_2	CH_3	24	0	0

[a] Products are characterized by IR, ^{1}H NMR and ^{13}C NMR. [b] Refer to isolated yields. [c] Based on H–H coupling constants. [d] The data match those reported in the literature.[3]

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 instrument using $CDCl_3$ as the solvent. Chemical shifts are reported in ppm from internal tetramethylsilane and are given on the δ scale. J values are given in Hz. IR spectra were recorded on a Perkin-Elmer 297 spectrophotometer. CHN analyses were recorded in a Vario EL analyzer. Mass spectra were recorded on a JEOL D-300 (EI) mass spectrometer. Freshly prepared lead tetraacetate[11] was used in all reactions. Column chromatography was performed by using silica gel (60–120 mesh, Merck).

General procedure for the preparation of 5-alkyl-6-arylhexa-3,5-dien-2-one 1

Step 1: preparation of 3-arylpropenaldehyde. To a cooled (0 °C), stirred solution of freshly distilled aromatic aldehyde (50 mmol) and aliphatic aldehyde (50 mmol), 2 ml of 10% sodium hydroxide solution were added dropwise. The mixture was brought to room temperature and further stirred for another 4 hours. The solution was then rendered acidic to litmus by the addition of dilute hydrochloric acid and extracted with diethyl ether. The organic layer was separated, dried and evaporated under reduced pressure to give a brown oil that was purified by column chromatography on silica gel, using hexane as the eluent, to give the 3-arylpropenaldehyde in yields ranging from 50 to 67%. The product obtained was then used in the next step.

Step 2: preparation of 5-alkyl-6-arylhexa-3,5-dien-2-one 1. To a cooled (0 °C), stirred solution of 3-arylpropenaldehyde (30 mmol), obtained as above, dry acetone (30 mmol) was added followed by dropwise addition of 10% sodium hydroxide solution (1.5 ml). The mixture was further stirred at room temperature for another 4 hours, rendered acidic to litmus by the addition of dilute hydrochloric acid and extracted with diethyl ether. The organic layer was separated, dried and evaporated under reduced pressure to give a brown oil. Chromatography on silica gel using hexane as the eluent yielded the *dienone* (43–58%).

General procedure for the preparation of methyl 5-alkyl-6-arylhexa-3,5-dienoate 2

In a typical procedure, a stirred suspension of lead(IV) acetate (10.5 mmol) in benzene (30 ml) was purged with nitrogen and cooled to −30 °C. A solution of the dienone (**1**) (10 mmol) was then added in one lot followed by MeOH (5 ml) and $BF_3{\cdot}Et_2O$ (3 ml). The reaction mixture was allowed to warm to room temperature and stirring was continued under nitrogen for 17–24 hours. The precipitated lead(II) acetate was filtered off and the filtrate successively washed with saturated $NaHCO_3$ solution, water and brine, dried over Na_2SO_4 and the solvent removed *in vacuo*. The crude product was purified by column chromatography using silica gel as the solid phase and hexane as eluent to give the pure products (**2**) in varying yields (Table 1).

Spectroscopic data

6-Phenylhexa-3,5-dien-2-one 1a.[12] IR (neat): 1674 cm^{-1}; ^{1}H NMR: δ 2.24 (s, 3H, COCH_3), 5.96 (d, 1H, J 15.2, H-3), 6.28 (dd, 1H, J 15.2, 10.1, H-5), 6.31 (d, 1H, J 15.2, H-6), 6.42 (dd, 1H, J 15.2, 10.1, H-4), 7.25–7.48 (m, 4H, Ar-H); ^{13}C NMR: δ 31.2, 130.1, 132.4, 134.3, 137.4, 137.8, 139.5, 139.7, 143.2, 193.3; MS (EI) *m*/*z* (%): 172 (M$^+$, 23), 129 (74), 77 (65), 43 (100). Anal. Calcd. for $C_{12}H_{12}O$ (172): C, 83.72; H, 6.97. Found: C, 83.80; H, 6.95%.

Methyl (*E*,*E*)-6-phenylhexa-3,5-dienoate 2a. IR (neat): 1738 cm^{-1}; ^{1}H NMR: δ 3.20 (d, 2H, J 7.2, CH_2CO), 3.68 (s, 3H, OCH_3), 5.88 (m, 1H, H-3), 6.29 (dd, 1H, J 15.2, 10.1, H-4), 6.36 (dd, 1H, J 15.2, 10.1, H-5), 6.42 (d, 1H, J 15.2, H-6), 7.21–7.53 (m, 5H, Ar-H); ^{13}C NMR: δ 42.1, 51.3, 129.4, 131.0, 133.6, 136.0, 137.1, 138.1, 144.2, 172.7; MS (EI) *m*/*z* (%): 202 (M$^+$, 56), 171 (46), 143 (100), 77 (70), 59 (80). Anal. Calcd. for $C_{13}H_{14}O_2$ (202): C, 77.22; H, 6.93. Found: C, 77.30; H, 6.98%.

Methyl (*Z*,*E*)-6-phenylhexa-3,5-dienoate 2a. IR (neat): 1741 cm^{-1}; ^{1}H NMR: δ 3.19 (d, 2H, J 7.2, CH_2CO), 3.69 (s, 3H, OCH_3), 5.90 (m, 1H, H-3), 6.31 (dd, 1H, J 11.5, 10.1, H-4), 6.35 (dd, 1H, J 15.2, 10.1, H-5), 6.40 (d, 1H, J 15.2, H-6), 7.21–7.51 (m, 5H, Ar-H); ^{13}C NMR: δ 40.2, 51.9, 131.2, 131.8, 134.0, 134.8, 136.1, 138.9, 143.4; MS (EI) *m*/*z* (%): 202 (M$^+$, 31), 171

(26), 143 (100), 77 (68), 59 (74). Anal. Calcd. for $C_{13}H_{14}O_2$ (202): C, 77.22; H, 6.93. Found: C, 77.32; H, 6.95%.

5-Methyl-6-phenylhexa-3,5-dien-2-one 1b. IR (neat): 1675 cm^{-1}; ^1H NMR: δ 1.94 (s, 3H, CH_3), 2.22 (s, 3H, COCH_3), 5.92 (d, 1H, *J* 15.2, H-3), 6.30 (s, 1H, H-6), 6.39 (d, 1H, *J* 15.2, H-4), 7.28–7.40 (m, 5H, Ar-H); ^{13}C NMR: δ 20.8, 29.8, 129.8, 130.1, 133.6, 136.8, 138.4, 138.7, 140.3, 142.8, 193.1; MS (EI) *m*/*z* (%): 186 (M^+, 62), 143 (36), 77 (68), 43 (100). Anal. Calcd. for $C_{13}H_{14}O$ (186): C, 83.87; H, 7.52. Found: C, 83.91; H, 7.56%.

Methyl (*E*,*E*)-5-methyl-6-phenylhexa-3,5-dienoate 2b. IR (neat): 1736 cm^{-1}; ^1H NMR: δ 1.95 (s, 3H, CH_3), 3.19 (d, 2H, *J* 7.2, CH_2CO), 3.70 (s, 3H,OCH_3), 5.86 (m, 1H, H-3), 6.30 (d, 1H, *J* 15.2, H-4), 6.45 (s, 1H, H-6), 7.18–7.42 (m, 5H, Ar-H); ^{13}C NMR: δ 21.6, 37.4, 51.8, 129.4, 130.2, 134.3, 135.6, 138.7, 139.6, 142.1, 172.5; MS (EI) *m*/*z* (%): 216 (M^+, 47), 157 (100), 77 (71), 59 (67). Anal Calcd. for $C_{14}H_{16}O_2$ (216): C, 77.77; H, 7.40. Found: C, 77.85; H, 7.51%.

Methyl (*Z*,*E*)-5-methyl-6-phenylhexa-3,5-dienoate 2b. IR (neat): 1738 cm^{-1}; ^1H NMR: δ 1.95 (s, 3H, CH_3), 3.18 (d, 2H, *J* 7.2, CH_2CO), 3.68 (s, 3H, OCH_3), 5.82 (m, 1H, H-3), 6.30 (d, 1H, *J* 11.5, H-4), 6.42 (s, 1H, H-6), 7.14–7.41 (m, 5H, Ar-H); ^{13}C NMR: δ 21.3, 40.8, 51.6, 126.8, 129.9, 130.1, 133.0, 134.5, 136.9, 138.5, 140.1, 171.7; MS (EI) *m*/*z* (%): 216 (M^+, 32), 157 (100), 77 (74), 59 (81). Anal. Calcd. for $C_{14}H_{16}O_2$ (216): C, 77.77; H, 7.40. Found: C, 77.81; H, 7.46%.

5-Ethyl-6-phenylhexa-3,5-dien-2-one 1c. IR (neat): 16.74 cm^{-1}; ^1H NMR: δ 1.03 (t, 3H, *J* 7.3, CH_2CH_3), 2.20 (q, 2H, *J* 7.3, CH_2CH$_3$), 2.24 (s, 3H, COCH_3), 5.90 (d, 1H, *J* 15.2, H-3), 6.33 (s, 1H, H-6), 6.44 (d, 1H, *J* 15.2, H-4), 7.21–7.43 (m, 5H, Ar-H); ^{13}C NMR: δ 16.7, 29.0, 31.5, 129.4, 131.7, 133.8, 136.2, 136.8, 137.4, 139.7, 145.3, 193.7; MS (EI) *m*/*z* (%): 200 (M^+, 61), 157 (41), 77 (56), 43 (100). Anal. Calcd. for $C_{14}H_{16}O$ (200): C, 84.00; H, 8.0. Found: C, 84.10; H, 8.02%.

Methyl (*E*,*E*)-5-ethyl-6-phenylhexa-3,5-dienoate 2c. IR (neat): 1737 cm^{-1}; ^1H NMR: δ 1.02 (t, 3H, *J* 7.3, CH_3CH$_2$), 2.21 (q, 2H, *J* 7.3, CH_2CH$_3$), 3.10 (d, 2H, *J* 7.2, CH_2CO), 3.68 (s, 3H, OCH_3), 5.62 (m, 1H, H-3), 5.98 (d, 1H, *J* 15.2, H-4), 6.23 (s, 1H, H-6), 7.09–7.38 (m, 4H, Ar-H); ^{13}C NMR: δ 15.8, 29.9, 34.1, 51.7, 126.5, 129.1, 131.2, 134.6, 136.6, 139.6, 144.1, 173.1; MS (EI) *m*/*z* (%): 230 (M^+, 67), 171 (100), 77 (71), 59 (72). Anal. Calcd. for $C_{15}H_{18}O_2$ (230): C, 78.26; H, 7.82. Found: C, 78.31; H, 7.91%.

6-(4-Methylphenyl)hexa-3,5-dien-2-one 1d. IR (neat): 1677 cm^{-1}; ^1H NMR: δ 2.05 (s, 3H, Ar-CH_3), 2.28 (s, 3H, COCH_3), 5.96 (d, 1H, *J* 15.2, H-3), 6.30 (dd, 1H, *J* 15.2, 10.1, H-5), 6.36 (d, 1H, *J* 15.2, H-6), 6.49 (dd, 1H, *J* 15.2, 10.1, H-4), 7.18–7.51 (m, 4H, Ar-H); ^{13}C NMR: δ 25.4, 33.5, 127.8, 130.8, 134.6, 135.3, 136.9, 137.4, 144.5, 149.3, 194.1; MS (EI) *m*/*z* (%): 186 (M^+, 55), 123 (45), 91 (100), 43 (70). Anal. Calcd. for $C_{13}H_{14}O$ (186): C, 83.87; H, 7.52. Found: C, 83.84; H, 7.54%.

Methyl (*E*,*E*)-6-(4-methylphenyl)hexa-3,5-dienoate 2d. IR (neat): 1739 cm^{-1}; ^1H NMR: δ 2.08 (s, 3H, Ar-CH_3), 3.20 (d, 2H, *J* 7.2, CH_2CO), 3.69 (s, 3H, OCH_3), 5.88 (m, 1H, H-3), 6.30 (dd, 1H, *J* 15.2, 10.1, H-5), 6.35 (dd, 1H, *J* 15.2, 10.1, H-4), 6.45 (d, 1H, *J* 15.2, H-6), 7.11–7.45 (m, 4H, Ar-H); ^{13}C NMR: δ 26.8, 44.2, 51.4, 126.4, 129.3, 130.6, 136.4, 136.6, 137.4, 138.2, 147.2, 173.9; MS (EI) *m*/*z* (%): 216 (M^+, 47), 157 (81), 91 (100), 59 (67). Anal. Calcd. for $C_{14}H_{16}O_2$ (216): C, 77.77; H, 7.40. Found: C, 77.85; H, 7.50%.

Methyl (*Z*,*E*)-6-(4-methylphenyl)hexa-3,5-dienoate 2d. IR (neat): 1740 cm^{-1}; ^1H NMR: δ 2.05 (s, 3H, Ar-CH_3), 3.18 (d, 2H, *J* 7.2, CH_2CO), 3.70 (s, 3H, OCH_3), 5.90 (m, 1H, H-3), 6.30 (dd, 1H, *J* 15.2, 10.1, H-5), 6.35 (dd, 1H, *J* 11.5, 10.1, H-4), 6.46 (d, 1H, *J* 15.2, H-6), 7.15–7.43 (m, 4H, Ar-H); ^{13}C NMR δ 25.8, 43.2, 52.1, 128.9, 129.3, 131.6, 135.9, 136.1, 136.9, 137.4, 147.8, 173.4; MS (EI) *m*/*z* (%): 216 (M^+, 31), 157 (57), 91 (100), 59 (69). Anal. Calcd. for $C_{14}H_{16}O_2$ (216): C, 77.77; H, 7.40. Found: C, 77.80; H, 7.45%.

5-Methyl-6-(4-methylphenyl)hexa-3,5-dien-2-one 1e. IR (neat): 1673 cm^{-1}; ^1H NMR: δ 1.93 (s, 3H, CH_3), 2.00 (s, 3H, Ar-CH_3), 2.23 (s, 3H, COCH_3), 5.93 (d, 1H, *J* 15.2, H-3), 6.34 (s, 1H, H-6), 6.46 (d, 1H, *J* 15.2, H-4), 7.20–7.45 (m, 4H, Ar-H); ^{13}C NMR: δ 22.0, 24.8, 30.7, 128.4, 131.8, 133.4, 135.6, 136.3, 138.3, 143.2, 147.4, 192.8; MS (EI) *m*/*z* (%): 200 (M^+, 58), 157 (47), 91 (100), 43 (74). Anal. Calcd. for $C_{14}H_{16}O$ (200): C, 84.0; H, 8.0. Found: C, 84.07; H, 8.06%.

Methyl (*E*,*E*)-5-methyl-6-(4-methylphenyl)hexa-3,5-dienoate 2e. IR (neat): 1738 cm^{-1}; ^1H NMR: δ 1.92 (s, 3H, CH_3), 1.98 (s, 3H, Ar-CH_3), 3.23 (d, 2H, *J* 7.2, CH_2CO), 3.68 (s, 3H, OCH_3), 5.84 (m, 1H, H-3), 6.25 (d, 1H, *J* 15.2, H-4), 6.48 (s, 1H, H-6), 7.21–7.50 (m, 4H, Ar-H); ^{13}C NMR: δ 20.8, 25.0, 45.2, 51.1, 129.1, 131.4, 135.2, 136.3, 138.2, 138.5, 148.4, 170.8; MS (EI) *m*/*z* (%): 230 (M^+, 61), 171 (71), 91 (100), 59 (60). Anal. Calcd for $C_{15}H_{18}O_2$ (230): C, 78.26; H, 7.82. Found: C, 78.31; H, 7.86%.

Methyl (*Z*,*E*)-5-methyl-6-(4-methylphenyl)hexa-3,5-dienoate 2e. IR (neat): 1739 cm^{-1}; ^1H NMR: δ 1.95 (s, 3H, CH_3), 2.00 (s, 3H, ArCH_3), 3.21 (m, 2H, *J* 7.2, CH_2CO), 3.71 (s, 3H, OCH_3), 5.87 (m, 1H, H-3), 6.28 (d, 1H, *J* 11.5, H-4), 6.48 (s, 1H, H-6), 7.10–7.44 (m, 4H, Ar-H); ^{13}C NMR: δ 21.7, 26.3, 44.3, 52.6, 128.7, 132.6, 135.4, 136.4, 137.3, 137.7, 138.1, 148.1, 171.0; MS (EI) *m*/*z* (%): 230 (M^+, 55), 171 (39), 91 (100), 59 (75). Anal. Calcd for $C_{15}H_{18}O_2$ (230): C, 78.26; H, 7.82. Found: C, 78.36; H, 7.90%.

5-Ethyl-6-(4-methylphenyl)hexa-3,5-dien-2-one 1f. IR (neat): 1674 cm^{-1}; ^1H NMR: δ 1.05 (s, 3H, *J* 7.3, CH_2CH_3), 1.94 (s, 3H, ArCH_3), 2.20 (q, 2H, *J* 7.3, CH_2CH$_3$), 2.22 (s, 3H, COCH_3), 5.91 (d, 1H, *J* 15.2, H-3), 6.35 (s, 1H, H-6), 6.45 (d, 1H, *J* 15.2, H-4), 7.23–7.43 (m, 4H, Ar-H); ^{13}C NMR: δ 18.3, 22.8, 28.7, 29.3, 130.0, 134.7, 135.6, 136.2, 137.8, 138.8, 144.2, 146.7, 191.9; MS (EI) *m*/*z* (%): 214 (M^+, 42), 171 (51), 91 (100), 43 (70). Anal. Calcd. for $C_{15}H_{18}O$ (214): C, 84.11; H, 8.41. Found: C, 84.07; H, 8.07%.

Methyl (*E*,*E*)-5-ethyl-6-(4-methylphenyl)hexa-3,5-dienoate 2f. IR (neat): 1735 cm^{-1}; ^1H NMR: δ 1.05 (t, 3H, *J* 7.3, CH_2CH_3), 1.90 (s, 3H, ArCH_3), 2.22 (s, 2H, *J* 7.3, CH_2CH$_3$), 2.24 (d, 2H, *J* 7.2, CH_2CO), 3.70 (s, 3H, OCH_3), 5.85 (m, 1H, H-3), 6.28 (d, 1H, *J* 15.2, H-4), 6.46 (s, 1H, H-6), 7.18–7.48 (m, 4H, Ar-H). ^{13}C NMR: δ 16.7, 21.1, 30.4, 46.3, 51.9, 128.3, 130.3, 134.1, 136.5, 138.1, 144.1, 148.6; MS (EI) *m*/*z* (%): 244 (M^+, 51), 213 (27), 185 (88), 91 (100), 59 (65). Anal. Calcd. for $C_{16}H_{20}O_2$ (244): C, 78.68; H, 7.82. Found: C, 78.74; H, 7.95%.

5-Methyl-6-(4-chlorophenyl)hexa-3,5-dien-2-one 1g. IR (neat): 1676 cm^{-1}; ^1H NMR: δ 1.95 (s, 3H, CH_3), 2.28 (s, 3H, COCH_3), 5.95 (d, 1H, *J* 15.2, H-3), 6.38 (s, 1H, H-6), 6.52 (d, 1H, *J* 15.2, H-4), 7.25–7.58 (m, 4H, Ar-H); ^{13}C NMR: δ 24.6, 34.0, 129.3, 132.7, 133.7, 135.4, 136.8, 141.3, 144.3, 146.7, 193.4; MS (EI) *m*/*z* (%): 220.5 (M^+, 48), 177.5 (39), 111.5 (91), 43 (100). Anal. Calcd. for $C_{13}H_{13}ClO$ (220.5): C, 70.74; H, 5.89. Found: C, 70.85; H, 5.94%.

Methyl (*E*,*E*)-5-methyl-6-(4-chlorophenyl)hexa-3,5-dienoate 2g. IR (neat): 1739 cm^{-1}; ^1H NMR: δ 1.93 (s, 3H, CH_3), 3.21 (d, 2H, *J* 7.2, CH_2CO), 3.71 (s, 3H, OCH_3), 5.94 (m, 1H, H-3), 6.30 (d, 1H, *J* 15.2, H-4), 6.48 (s, 1H, H-6), 7.18–7.56 (m, 4H, Ar-H); ^{13}C NMR: δ 22.7, 40.2, 52.1, 128.4, 132.1, 134.9, 136.3, 137.0,

138.5, 146.3; MS (EI) *m*/*z* (%): 250.5 (M^+, 70), 219.5 (21), 191.5 (100), 111.5 (84), 59 (67). Anal. Calcd. for $C_{14}H_{15}O_2Cl$ (250.5): C, 67.06; H, 5.98. Found: C, 67.11; H, 6.03%.

5-Ethyl-6-(4-chlorophenyl)hexa-3,5-dien-2-one 1h. IR (neat): 1675 cm^{-1}; ^1H NMR: δ 1.06 (t, 3H, *J* 7.3, CH_2CH_3), 2.25 (q, 2H, *J* 7.3, CH_2CH_3), 2.27 (s, 3H, $COCH_3$), 5.94 (d, 1H, *J* 15.2, H-3), 6.33 (s, 1H, H-6), 6.48 (d, 1H, *J* 15.2, H-4), 7.24–7.55 (m, 4H, Ar-H); ^{13}C NMR: δ 18.8, 31.4, 33.1, 130.3, 132.6, 133.7, 135.8, 136.4, 138.4, 139.8, 148.3, 193.8; MS (EI) *m*/*z* (%): 234.5 (M^+, 61), 191.5 (41), 111.5 (81), 43 (100). Anal. Calcd. for $C_{14}H_{15}ClO$ (234.5): C, 71.64; H, 6.39. Found: C, 71.69; H, 6.48%.

Methyl (*E*,*E*)-5-ethyl-6-(4-chlorophenyl)hexa-3,5-dienoate 2h. IR (neat): 1738 cm^{-1}; ^1H NMR: δ 1.08 (t, 3H, *J* 7.3, CH_2CH_3), 2.25 (q, 2H, *J* 7.3, CH_2CH_3), 3.24 (d, 2H, *J* 7.2, CH_2CO), 3.70 (s, 3H, OCH_3), 5.91 (m, 1H, H-3), 6.32 (d, 1H, H-4), 6.48 (s, 1H, H-6), 7.20–7.54 (m, 4H, Ar-H); ^{13}C NMR: δ 17.0, 31.8, 44.3, 52.0, 130.2, 133.4, 134.0, 134.7, 136.8, 138.7, 139.4, 149.2, 174.3; MS (EI) *m*/*z* (%): 248.5 (M^+, 55), 217.5 (23), 189.5 (100), 111.5 (79), 59 (61). Anal. Calcd. for $C_{15}H_{17}O_2Cl$ (248.5): C, 68.05; H, 6.42. Found: C, 68.13; H, 6.51%.

5-Methyl-6-(4-methoxyphenyl)hexa-3,5-dien-2-one 1i. IR (neat): 1675 cm^{-1}; ^1H NMR: δ 1.98 (s, 3H, CH_3), 2.24 (s, 3H, $COCH_3$), 3.75 (s, 3H, OCH_3), 5.92 (d, 1H, *J* 15.2, H-3), 6.33 (s, 1H, H-6), 6.49 (d, 1H, *J* 15.2, H-4), 7.23–7.49 (m, 4H, Ar-H); ^{13}C NMR: δ 24.6, 31.5, 55.2, 129.1, 131.4, 133.3, 137.4, 140.0, 146.7, 150.2, 158.3, 192.8; MS (EI) *m*/*z* (%): 216 (M^+, 48), 173 (32), 107 (100), 43 (92). Anal. Calcd. for $C_{14}H_{16}O_2$ (216): C, 77.77; H, 7.40. Found: C, 77.82; H, 7.47%.

Methyl (*E*,*E*)-5-methyl-6-(4-methoxyphenyl)hexa-3,5-dienoate 2i. IR (neat): 1739 cm^{-1}; ^1H NMR: δ 1.95 (s, 3H, CH_3), 3.20 (d, 2H, *J* 7.2, CH_2CO), 3.68 (s, 3H, $COOCH_3$), 3.74 (s, 3H, $ArOCH_3$), 5.90 (m, 1H, H-3), 6.25 (d, 1H, *J* 15.2, H-4), 6.47 (s, 1H, H-6), 7.15–7.49 (m, 4H, Ar-H); ^{13}C NMR: δ 22.3, 35.9, 51.6, 54.3, 129.7, 132.0, 135.4, 136.4, 138.9, 143.2, 146.5, 159.1, 173.5; MS (EI) *m*/*z* (%): 246 (M^+, 50), 187 (100), 107 (94), 59 (78). Anal. Calcd. for $C_{15}H_{18}O_3$ (246): C, 73.17; H, 7.31. Found: C, 73.26; H, 7.45%.

Methyl (*Z*,*E*)-5-methyl-6-(4-methoxyphenyl)hexa-3,5-dienoate 2i. IR (neat): 1741 cm^{-1}; ^1H NMR: δ 1.98 (s, 3H, CH_3), 3.18 (d, 2H, *J* 7.2, CH_2CO), 3.75 (s, 3H, $ArOCH_3$), 5.95 (m, 1H, H-3), 6.27 (d, 1H, *J* 11.5, H-4), 6.48 (s, 1H, H-6), 7.15–7.51 (m, 4H, Ar-H); ^{13}C NMR: δ 23.4, 34.2, 51.9, 54.5, 129.2, 133.2, 134.2, 138.4, 140.2, 144.1, 144.6, 158.4, 173.8; MS (EI) *m*/*z* (%): 246 (M^+, 46), 215 (17), 187 (100), 107 (94), 59 (78). Anal. Calcd. for $C_{15}H_{18}O_2$ (246): C, 73.17; H, 7.31. Found: C, 73.22; H, 7.39%.

5-Ethyl-6-(4-methoxyphenyl)hexa-3,5-dien-2-one 1j. IR (neat): 1674 cm^{-1}; ^1H NMR: δ 1.07 (t, 3H, *J* 7.3, CH_2CH_3), 2.22 (q, 2H, *J* 7.3, CH_2CH_3), 2.25 (s, 3H, $COCH_3$), 3.74 (s, 3H, $ArOCH_3$), 5.93 (d, 1H, *J* 15.2, H-3), 6.35 (s, 1H, H-6), 6.45 (d, 1H, *J* 15.2, H-4), 7.20–7.48 (m, 4H, Ar-H); ^{13}C NMR: δ 18.9, 30.6, 32.0, 54.6, 132.3, 133.6, 135.4, 136.4, 141.7, 142.7, 146.8, 156.7, 192.6; MS (EI) *m*/*z* (%): 230 (M^+, 61), 187 (34), 107 (100), 43 (76). Anal. Calcd. for $C_{15}H_{18}O_2$ (230): C, 78.26; H, 7.82. Found: C, 78.31; H, 7.89%.

Methyl (*E*,*E*)-5-ethyl-6-(4-methoxyphenyl)hexa-3,5-dienoate 2j. IR (neat): 1738 cm^{-1}; ^1H NMR: δ 1.09 (t, 3H, *J* 7.3, CH_2CH_3), 2.21 (q, 3H, *J* 7.2, CH_2CH_3), 3.23 (d, 2H, *J* 7.3, CH_2CO), 3.69 (s, 3H, $COOCH_3$), 3.75 (s, 3H, $ArOCH_3$), 5.93 (m, 1H, H-3), 6.33 (d, 1H, *J* 15.2, H-4), 6.46 (s, 1H, H-6), 7.13–7.50 (m, 4H, Ar-H); ^{13}C NMR: δ 18.0, 28.8, 40.8, 51.6, 55.6, 132.2, 133.3, 136.4, 138.4, 139.6, 143.5, 148.4, 155.3, 173.0; MS (EI) *m*/*z* (%): 260 (M^+, 64), 201 (100), 107 (83), 59 (87). Anal. Calcd. for $C_{16}H_{20}O_3$ (260): C, 73.84; H, 7.69. Found: C, 73.94; H, 7.81%.

5-Methyl-6-(3,4-dimethoxyphenyl)hexa-3,5-dien-2-one 1k. IR (neat): 1675 cm^{-1}; ^1H NMR: δ 1.97 (s, 3H, CH_3), 2.26 (s, 3H, $COCH_3$), 3.74 (s, 3H, $ArOCH_3$), 3.75 (s, 3H, $ArOCH_3$), 5.93 (d, 1H, *J* 15.2, H-3), 6.38 (s, 1H, H-6), 6.48 (d, 1H, *J* 15.2, C-4), 7.24–7.53 (m, 3H, Ar-H); ^{13}C NMR: δ 26.3, 33.4, 54.8, 55.4, 131.5, 132.5, 136.4, 138.4, 139.8, 142.7, 149.1, 158.6, 159.4, 194.0; MS (EI) *m*/*z* (%): 246 (M^+, 41), 203 (45), 137 (72), 43 (100). Anal. Calcd. for $C_{15}H_{18}O_3$ (246): C, 73.17; H, 7.31. Found: C, 73.24; H, 7.38%.

Methyl (*E*,*E*)-5-methyl-6-(3,4-dimethoxyphenyl)hexa-3,5-dienoate 2k. IR (neat): 1740 cm^{-1}; ^1H NMR δ 1.96 (s, 3H, CH_3), 3.18 (d, 2H, *J* 7.2, CH_2CO), 3.70 (s, 3H, $COOCH_3$), 3.76 (s, 3H, $ArOCH_3$), 3.77 (s, 3H, $ArOCH_3$), 5.91 (m, 1H, H-3), 6.30 (d, 1H, *J* 15.2, H-6), 6.48 (s, 1H, H-4), 7.22–7.58 (m, 3H, Ar-H); ^{13}C NMR: δ 23.7, 34.7, 52.4, 54.3, 55.1, 132.7, 134.3, 136.4, 138.6, 139.7, 142.3, 144.1, 149.0, 158.4, 159.6, 173.8; MS (EI) *m*/*z* (%): 276 (M^+, 47), 245 (35), 217 (100), 59 (64). Anal. Calcd. for $C_{16}H_{20}O_4$ (276): C, 69.56; H, 7.24. Found: C, 69.63; H, 7.36%.

5-Ethyl-6-(3,4-dimethoxyphenyl)hexa-3,5-dien-2-one 1l. IR (neat): 1676 cm^{-1}; ^1H NMR: δ 1.06 (t, 3H, *J* 7.3, CH_2CH_3), 2.20 (q, 2H, *J* 7.3, CH_2CH_3), 2.25 (s, 3H, $COCH_3$), 3.75 (s, 3H, $ArOCH_3$), 3.76 (s, 3H, $ArOCH_3$), 5.91 (d, 1H, *J* 15.2, H-3), 6.30 (s, 1H, H-6), 6.50 (d, 1H, *J* 15.2, H-4), 7.23–7.51 (m, 3H, Ar-H); ^{13}C NMR: δ 17.8, 29.4, 32.1, 55.3, 55.9, 133.3, 134.4, 135.8, 136.8, 139.8, 142.3, 143.2, 151.0, 157.8, 159.0, 194.8; MS (EI) *m*/*z* (%): 260 (M^+, 41), 217 (20), 137 (72), 43 (100). Anal. Calcd. for $C_{16}H_{20}O_3$ (260): C, 73.84; H, 7.69. Found: C, 73.90; H, 7.74%.

Methyl (*E*,*E*)-5-ethyl-6-(3,4-dimethoxyphenyl)hexa-3,5-dienoate 2l. IR (neat): 1739 cm^{-1}; ^1H NMR: δ 1.05 (t, 3H, *J* 7.3, CH_2CH_3), 2.21 (q, 2H, *J* 7.3, CH_2CH_3), 3.21 (d, 2H, *J* 7.2, CH_2CO), 3.70 (s, 3H, $COOCH_3$), 3.75 (s, 3H, $ArOCH_3$), 3.76 (s, 3H, $ArOCH_3$), 5.91 (m, 1H, H-3), 6.31 (d, 1H, *J* 15.2, H-4), 6.51 (s, 1H, H-6), 7.15–7.54 (m, 3H, Ar-H); ^{13}C NMR: δ 21.6, 29.3, 38.6, 51.8, 54.7, 55.6, 132.6, 136.7, 136.9, 137.4, 139.1, 139.3, 143.5, 147.7, 158.9, 159.4, 174.6; MS (EI) *m*/*z* (%): 290 (M^+, 31), 259 (31), 231 (100), 137 (72), 59 (61). Anal. Calcd. for $C_{17}H_{22}O_4$ (290): C, 70.34; H, 7.58. Found: C, 70.50; H, 7.69%.

References

1 R. V. Stevens, R. E. Cherpeck, B. L. Harrison and R. Lapalme, *J. Am. Chem. Soc.*, 1976, **98**, 6317.
2 K. Tossell, *Tetrahedron Lett.*, 1974, **8**, 623.
3 G. P. Chiusoli, M. Costa, C. Gallo and G. Salerno, *J. Organomet. Chem.*, 1986, **317**, 373.
4 G. P. Chiusoli, G. Salerno and L. Pallini, *J. Organomet. Chem.*, 1981, **219**, C16.
5 G. P. Chiusoli and S. Merzoni, *Chem. Abstr.*, 1964, **61**, 14535a.
6 J. L. Herrmann and R. H. Schlessinger, *Tetrahedron Lett.*, 1973, 2433.
7 B. Myrboh, H. Ila and H. Junjappa, *Synthesis*, 1981, 126.
8 F. Mathew and B. Myrboh, *Tetrahedron Lett.*, 1990, **31**, 3757.
9 (*a*) F. M. Nongrum and B. Myrboh, *Synthesis*, 1987, 845; (*b*) F. Mathew and B. Myrboh, *Synth. Commun.*, 1996, **26**, 1097; (*c*) F. Mathew and B. Myrboh, *Molecules*, 1996, **1**, 79.
10 G. P. Chiusoli, F. Gigliotti and G. Salerno, *J. Organomet. Chem.*, 1986, **314**, 231.
11 *Vogel's Textbook of Practical Organic Chemistry*, ELBS, Longman Group Ltd.,England, 1978.
12 (*a*) J. Font and P. March, *Tetrahedron Lett.*, 1978, **38**, 3601; (*b*) H. Zak and U. Schmidt, *Chem Ber.*, 1973, **106**, 3652; (*c*) A. F. Kluge and C. P. Lillya, *J. Org. Chem.*, 1971, **36**, 1977; (*d*) M. Fujii, K. Nakamura, S. Yasui and A. Ohno, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 2423; (*e*) Y. Z. Huang, L. Shi and J. Yang, *Tetrahedron Lett.*, 1987, **28**, 2155.