Pergamon

Tetrahedron Vol. 51, No. 6, pp. 1809-1816, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)01058-7

Application of Microwave Heating Technique for Rapid Synthesis of γ,δ-Unsaturated Esters

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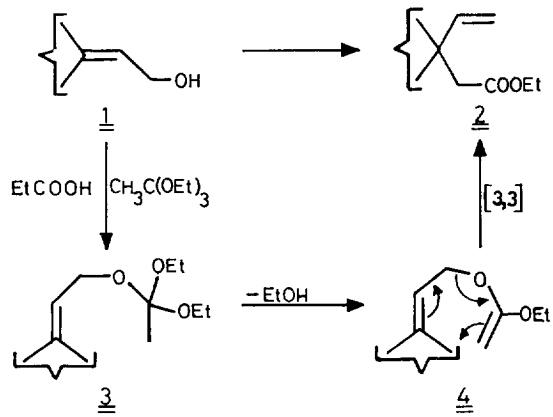
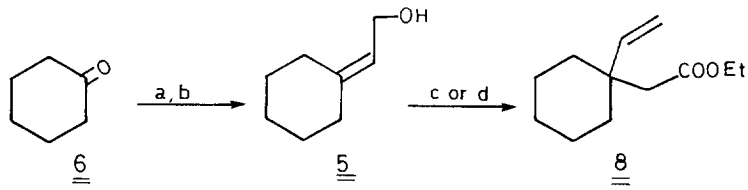
Abstract: *The use of microwave heating technique for the acceleration of ortho ester Claisen rearrangement (a three step transformation) is described. Irradiation of a DMF solution of the allyl alcohol* **5**, *triethyl orthoacetate and propionic acid (catalytic) in an Erlenmeyer flask for 10 minutes in a microwave oven generated the ester* **8** *in 83% yield. Analogously, ortho ester Claisen rearrangement of a variety of allyl and propargyl alcohols (***9**, **12**-**22***) were achieved. The formation of the diester* **10** *from 2-butyne-1,4-diol (***9***) via the ortho ester Claisen rearrangement of two allyl alcohol moieties (involving six steps) in 15 minutes, demonstrates the versatility of the microwave heating technique.*

The use of microwave energy ($\mu\nu$)[1] in organic synthesis probably originated when Vanderhoff *et al.* first observed dramatic rate enhancement in the aqueous emulsion polymerisation of butyl acrylate, acrylic acid and methacrylic acid using pulsed electromagnetic radiation. Since then the microwave heating has been used for a wide variety of purposes such as moisture analysis, acid decomposition of botanical or biological samples, dissolution of geological materials, rapid hydrolysis of peptides and proteins etc.[2] Apart from these, recently the use of microwave heating has attracted the attention of the organic chemists for its use in organic synthesis.[3] Remarkable decrease in the time necessary to carry out reactions (up to three orders of magnitude) and in some cases cleaner reactions with easier work-up when compared to conventional methods have been observed with microwave heating. Herein we describe the application of microwave heating technique for rapid generation of γ,δ-unsaturated esters by acceleration of the ortho ester Claisen rearrangement (three step transformation).[4]

In 1970, Johnson *et al.* reported[5] a variant of the original Claisen rearrangement. Instead of the conventional method[6] of generating a γ,δ-unsaturated aldehyde from allyl alcohols *via* the corresponding allyl vinyl ethers, Johnson and co-workers developed a one pot procedure for generating γ,δ-unsaturated esters from allyl alcohols. In this method, heating an allyl alcohol **1** in an excess of triethyl orthoacetate in the presence of a trace amount of a weak (*e.g.* propionic) acid furnishes the γ,δ-unsaturated esters **2**, and now commonly referred to as ortho ester Claisen rearrangement. Evidently in this variation of the Claisen rearrangement, first the allyl alcohol **1** forms a mixed ortho ester **3**, which subsequently looses a molecule of ethanol to generate the allyl ethyl keteneacetal **4**, a species well endowed to undergo a thermal



[3,3]-sigmatropic rearrangement to furnish the ene ester **2**. The ability to form a γ,δ-unsaturated ester as well as the ease with which a quaternary centre is created in one pot reaction from β,β-disubstituted allyl alcohol makes the ortho ester Claisen rearrangement a very useful and dependable reaction in organic synthesis. For investigating the applicability of microwave heating technique in accelerating the three step ortho ester Claisen rearrangement, the allyl alcohol **5** was chosen as a model substrate, which was prepared from cyclohexanone (**6**). Thus, Wittig-Horner-Emmons reaction of cyclohexanone (**6**) with triethyl phosphonoacetate using sodium hydride as base in dry THF followed by reduction of the resultant ester **7** with LAH in ether at -70°C furnished the allyl alcohol **5**[7] in over 70% yield.



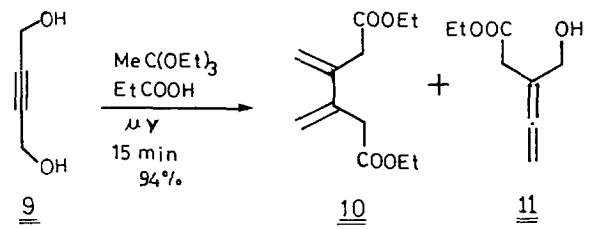
a) $(OEt)_2P(O)CH_2COOEt$, NaH, THF, 16 hr; b) $LiAlH_4$, Et_2O, -70°C, 2 hr; c) $MeC(OEt)_3$, EtCOOH, 180°C, 48 hr; d) $MeC(OEt)_3$, EtCOOH, DMF, $\mu\nu$, 10 min.

First a conventional method of ortho ester Claisen rearrangement was carried out. Thus thermal activation of a solution of the allyl alcohol **5**, triethyl orthoacetate and a catalytic amount of propionic acid in a sealed tube at 180°C for 48 hrs furnished[7] the ene ester **8** in 83% yield. To carry out the ortho ester Claisen rearrangement using microwave heating technique, a domestic microwave oven (operating at 650 W and generating a microwave frequency of 2450 MHz) was employed. After brief experiments using various solvents and conditions (no solvent, methanol, chloroform, hexane, DMF; in sealed tubes and in open vessels) DMF was chosen as the solvent for its high dielectric constant and boiling point, and reactions were carried out in open vessels. Microwave irradiation of a solution of the allyl alcohol **5**, triethyl orthoacetate and a catalytic amount of propionic acid (*ca.* 5 μl) in dry DMF in a clean Erlenmeyer flask furnished the ene ester **8**. Quite expectedly the yield of the ester **8** varied with the duration of the irradiation. The results are depicted in the table 1.

TABLE 1

TIME (MIN)	YIELD (%)
2	12
3	20
4	42
6	56
7[a]	72
8	74
10	83

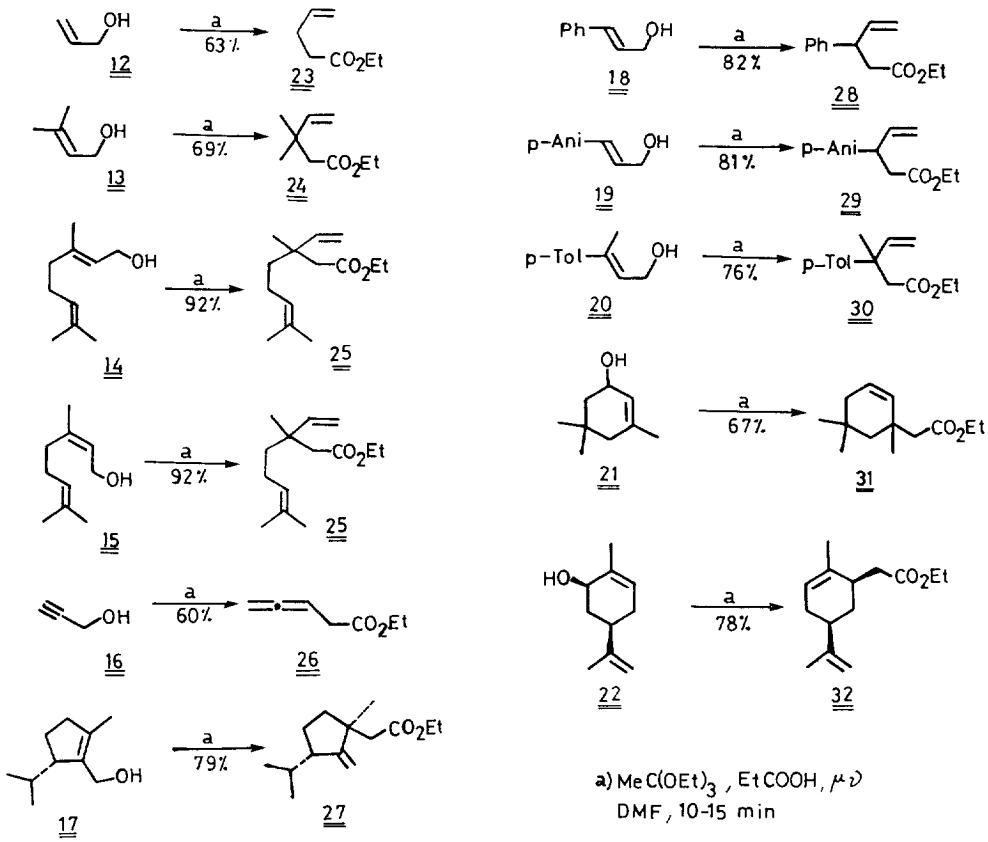
[a]In a sealed tube



9 10 11

After successfully demonstrating the use of microwave heating technique for the acceleration of the ortho ester Claisen rearrangement of the allyl alcohol **5**, the procedure has been extended to 2-butyne-1,4-diol (**9**), a molecule comprising of two allyl alcohol units. Microwave irradiation of a solution of the diol **9** with triethyl orthoacetate and propionic acid in DMF furnished the diene ester **10** *via* the double ortho ester Claisen rearrangement, as well as the allene alcohol **11**, the mono rearrangement product in 82 and 12% yields, respectively,[8] whose structures were derived from their spectral data. To extend the generality of this procedure, ortho ester Claisen rearrangement of a wide variety of allyl and propargyl alcohols **12**-**22** were carried out in a microwave oven. Microwave irradiation of the DMF solutions of the alcohols **12**-**22**, excess triethyl orthoacetate and a catalytic amount of propionic acid in clean Erlenmeyer flasks in a microwave oven for ten to fifteen minutes furnished[9] the esters **23**-**32** in good to excellent yields. The salient features are as follows. The presence of either scratches on the walls or solid particles in the flask results in rapid evaporation of the solvent and low yields of the products were realised. The reaction was found to be efficient with primary allyl alcohols, as in all the examples the reaction was complete in less than 15 minutes and the reactions were found to be cleaner when compared with the conventional method. Lower yields in some of the examples are probably due to the volatality of the starting alcohols and products. The catalytic amount (*ca.* 5 μl) of propionic acid seems to be appropriate, as considerable amount of by-products were formed with increased amount of the acid. The cinnamyl alcohol **20** and the secondary allyl alcohols **21** and **22** were found to be sluggish and the yields were on the lower side with the recovery of considerable amount of unreacted starting material.

In conclusion, a dramatic acceleration of the one pot, three step (trans ortho esterification, elimination of ethanol and 3,3-sigmatropic rearrangement) ortho ester Claisen rearrangement of allyl alcohols to the γ,δ-unsaturated esters has been achieved using the microwave heating technique, enhancing the synthetic potential of this important and useful synthetic transformation.[10] The double rearrangement of the alcohol **9** to the diester **10** in 15 minutes and the use of open vessels points to the versatility of this discovery. Incidentally, this is the first reaction,[11] wherein the microwave heating technique accelerated a three step (six steps in the case of the diol **9**) conversion.



EXPERIMENTAL SECTION

IR spectra (thin films) were recorded on a Perkin-Elmer 781 spectrophotometer. ^1H (60 and 90 MHz) and ^{13}C NMR (22.5 MHz) spectra in CCl_4 or $CDCl_3$ were recorded on Varian T-60 and JEOL FX-90Q spectrometers. The chemical shifts (δ) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane (for ^1H) or the central line (77.1 ppm) of $CDCl_3$ (for ^{13}C). The microwave accelerated reactions were carried out using Microwyn MX-1100 microwave oven operating at 650 W generating 2450 MHz frequency. DMF was dried by passing through an alumina column and storing over 4Å molecular sieves. Acme's silica gel (100-200 mesh) was used for column chromatography. The allyl alcohols were prepared as reported in the literature.

***Ethyl 3,3-pentamethylenepent-4-enoate* (8)**

Method A: A solution of the allyl alcohol **5** (190 mg, 1.5 mmols), triethyl orthoacetate (1.5 ml, 8.2 mmols) and a catalytic amount (*ca* 5μl) of propionic acid was placed in a Carius tube and heated at 180°C for 48 hrs in an oil bath. The reaction mixture was cooled, diluted with ether (20 ml), washed with 0.5

N HCl followed by saturated $NaHCO_3$ and brine and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel (2 gms) column using ethyl acetate-hexane (1:40) as eluent furnished the ester **8** (243 mg, 83%) as an oil.[7]

Method B (general procedure): A solution of the allyl alcohol **5** (190 mg, 1.5 mmol), triethyl orthoacetate (1.5 ml, 8.2 mmols) and propionic acid (catalytic) in dry DMF (5 ml) in a clean Erlenmeyer flask (25 ml capacity without any boiling chips) was placed in a microwave oven (650 W, 2450 MHz, using 100% power) and irradiated for 10 minutes. After completion of the irradiation, the reaction mixture was cooled, taken in ether (20 ml), washed with 0.5 N HCl followed by brine, and dried (Na_2SO_4). Evaporation of the solvent and purification as above furnished the ester **8** (245 mg, 83%). IR: ν_{max} 1737 (O-C=O), 1641 (C=C), 1452, 1371, 1338, 1230, 1155, 1131, 1035, 915 (C=CH_2) cm^{-1}. ^1H NMR: δ 5.78 (1 H, dd, $J_{4,5trans}$ 17, $J_{4,5cis}$ 11, C<u>H</u>=CH_2), 5.10 (1 H, dd, $J_{4,5trans}$ 11, J_{gem} 1.5) and 4.95 (1 H, dd, $J_{5,4trans}$ 17, J_{gem} 1.5) (C=C<u>H</u>$_2$), 4.08 (2 H, q, *J* 7.2, O-C<u>H</u>$_2$CH$_3$), 2.32 (2 H, s, CH_2-C=O), 1.10-1.90 (10 H, m, 5 x ring CH_2), 1.24 (3 H, t, *J* 7.2, O-CH_2C<u>H</u>$_3$). ^{13}C NMR: δ 170.7 (s, O-C=O), 144.6 (d, <u>C</u>H=CH_2), 112.6 (t, CH=<u>C</u>H$_2$), 59.3 (t, O-CH_2), 45.4 (t, <u>C</u>H$_2$-C=O), 38.9 (s, C-3), 35.2 (2 C, t, ring C-2' and 6'), 26.2 (2 C, t, ring C-3' and 5'), 22.0 (t, ring C-4'), 13.9 (q, O-CH_2<u>C</u>H$_3$).

Diethyl 3,4-bismethyleneadipate (10) and Ethyl 3-hydroxymethylpenta-3,4-dienoate (11): The ortho ester Claisen rearrangement of 2-butyn-1,4-diol (**9**, 250 mg, 2.9 mmols) with triethyl orthoacetate (5 ml, 27 mmols) and propionic acid (catalytic) in dry DMF (5 ml) for 15 minutes using a microwave oven as described for the alcohol **5** followed by purification of the product over a silica gel (4 gms) column using ethyl acetate-hexane (1:40) as eluent furnished the diester **10** (538 mg, 82%) as a liquid.[8] IR: ν_{max} 1740 (O-C=O), 1635 (C=C), 1605, 1449, 1392, 1368, 1323, 1263, 1170, 1032, 903 (C=CH_2) cm^{-1}. ^1H NMR: δ 5.30 (2 H, s) and 5.16 (2 H, s) (2 x C=CH_2), 4.16 (4 H, q, *J* 7.2, 2 x O-C<u>H</u>$_2$CH$_3$), 3.32 (4 H, s, 2 x CH_2-CO), 1.26 (6 H, t, *J* 7.2, 2 x O-CH_2C<u>H</u>$_3$).

Further elution of the column using CH_2Cl_2 as eluent furnished the allene ester **11** (54 mg, 12%) as a liquid.[8] IR: ν_{max} 3424 (OH), 1962 (C=C=CH_2), 1737 (O-C=O), 1446, 1410, 1371, 1332, 1179, 1026 cm^{-1}. ^1H NMR: δ 4.88 (2 H, quintet, $J_{2,5}$,$J_{5,1'}$ 3, C=CH_2), 4.16 (4 H, m, O-C<u>H</u>$_2$CH$_3$ and C<u>H</u>$_2$OH), 3.12 (2 H, t, *J* 3, CH_2-C=O), 2.40 (1 H, br s, CH_2-O<u>H</u>), 1.28 (3 H, t, *J* 7.2, O-CH_2C<u>H</u>$_3$).

Ethyl pent-4-enoate (23): The ortho ester Claisen rearrangement of allyl alcohol (**12**, 200 mg, 3.4 mmols) with triethyl orthoacetate (3 ml, 16.4 mmols) and propionic acid (catalytic) in dry DMF (6 ml) for 12 minutes using a microwave oven as described for the alcohol **5** followed by purification of the product over a silica gel (3 gms) column using pentane as eluent furnished the ester **23** (279 mg, 63%) as a volatile liquid.[9a] IR: ν_{max} 1737 (O-C=O), 1641 (C=C), 1446, 1374, 1173, 1098, 1038, 918 (C=CH_2) cm^{-1}. ^1H NMR: δ 5.82 (1 H, dd with st, J_{trans} 16, J_{cis} 10.8, C<u>H</u>=CH_2), 5.02 (1 H, d with st, J_{trans} 16) and 4.98 (1 H, d with st, J_{cis} 10.8) (CH=C<u>H</u>$_2$), 4.14 (2 H, q, *J* 7.2, O-C<u>H</u>$_2$CH$_3$), 2.35-2.45 (4 H, m, H-2 and 3), 1.26 (3 H, t, *J* 7.2, O-CH_2C<u>H</u>$_3$).

Ethyl 3,3-dimethylpent-4-enoate (24): The ortho ester Claisen rearrangement of 3,3-dimethylallyl alcohol (**13**, 303 mg, 3.5 mmols) with triethyl orthoacetate (5 ml, 27 mmols) and propionic acid (catalytic) in dry DMF (5 ml) for 12 minutes using a microwave oven as described for the alcohol **5** followed by purification of the product over a silica gel (3 gms) column using pentane as eluent furnished the ester **24** (379 mg, 69%) as a liquid.[9b] IR: ν_{max} 1731 (O-C=O), 1641 (C=C), 1446, 1416, 1368, 1326, 1122, 1035, 915 (C=CH_2) cm^{-1}. ^1H NMR: δ 5.92 (1 H, dd, J_{trans} 16.2, J_{cis} 10.8, C<u>H</u>=CH_2), 4.98 (1 H, dd, J_{trans} 16.2, J_{gem} 1.5) and 4.94 (1 H, dd, J_{cis} 10.8 and J_{gem} 1.5) (CH=C<u>H</u>$_2$), 4.12 (2 H, q, *J* 7.2, O-C<u>H</u>$_2$CH$_3$), 2.30 (2 H, s, CH_2-C=O), 1.26 (3 H, t, *J* 7.2, O-CH_2C<u>H</u>$_3$), 1.16 (6 H, s, 2 x *tert*-CH_3). ^{13}C NMR: δ 171.7 (s,

O-C=O), 146.8 (d, C<u>H</u>=CH_2), 110.7 (t, CH=C<u>H_2</u>), 60.0 (t, O-CH_2), 46.8 (t, <u>CH_2</u>-C=O), 36.1 (s, C-3), 26.9 (2 C, q, 2 x *tert*-CH_3), 14.3 (q, O-CH_2<u>CH_3</u>).

Ethyl 3,7-dimethyl-3-vinyloct-6-enoate (25):

a) From geraniol (14): The ortho ester Claisen rearrangement of geraniol (**14**, 162 mg, 1.05 mmol) with triethyl orthoacetate (5 ml, 27 mmols) and propionic acid (catalytic) in dry DMF (5 ml) for 12 minutes using a microwave oven as described for the alcohol **5** followed by purification of the product over a silica gel (4 gms) column using ethyl acetate-hexane (1:40) as eluent furnished the ester **25** (205 mg, 92%).

b) From nerol (15): The ortho ester Claisen rearrangement of nerol (**15**, 168 mg, 1.09 mmol) with triethyl orthoacetate (5 ml, 27 mmols) and propionic acid (catalytic) in dry DMF (5 ml) for 12 minutes using a microwave oven as described for the alcohol **5** followed by purification as above furnished the ester **25** (213 mg, 92%) as an oil.[9e] IR: ν_{max} 1737 (O-C=O), 1641 (C=C), 1449, 1380, 1305, 1233, 1116, 1035, 912 (C=CH_2), 834 cm^{-1}. ^1H NMR: δ 5.82 (1 H, dd, J_{trans} 19, J_{cis} 10.8, <u>H</u>C=CH_2), 4.90-5.20 (1 H, m, olefinic H-6), 5.00 (1 H, dd, J_{cis} 10.8, J_{gem} 1.5) and 4.94 (1 H, dd, J_{trans} 19, J_{gem} 1.5) (CH=C<u>H_2</u>), 4.10 (2 H, q, *J* 7, O-C<u>H_2</u>CH_3), 2.30 (2 H, s, CH_2-C=O), 1.30-2.15 (4 H, m, H-4 and 5), 1.68 (3 H, s) and 1.58 (3 H, s) (2 x olefinic CH_3), 1.24 (3 H, t, *J* 7, O-CH_2C<u>H_3</u>), 1.14 (3 H, s, *tert*-CH_3).

Ethyl penta-3,4-dienoate (26): The ortho ester Claisen rearrangement of propargyl alcohol (**16**, 200 mg, 3.6 mmols) with triethyl orthoacetate (3 ml, 16.4 mmols) and propionic acid (catalytic) in dry DMF (3 ml) for 12 minutes using a microwave oven as described for the alcohol **5** followed by purification of the product over a silica gel (3 gms) column using pentane as eluent furnished the allene ester **26** (270 mg, 60%) as a volatile liquid.[9d] IR: ν_{max} 1959 (HC=C=CH_2), 1740 (O-C=O), 1641 (C=C), 1443, 1413, 1371, 1350, 1299, 1254, 1161, 1095, 1035, 852 cm^{-1}. ^1H NMR: δ 5.26 (1 H, t of t, $J_{2,3}$ 7.2, $J_{3,5}$ 7, <u>H</u>C=C=CH_2), 4.76 (2 H, t of d, $J_{3,5}$ 7 and $J_{2,5}$ 3.6, HC=C=C<u>H_2</u>), 4.12 (2 H, q, *J* 7.2, O-C<u>H_2</u>CH_3), 3.04 (2 H, t of d, $J_{2,3}$ 7.2, $J_{2,5}$ 3.6, H-2), 1.25 (3 H, t, *J* 7.2, O-CH_2C<u>H_3</u>).

(-)-(2S,5S)- Ethyl [(3-Isopropyl-1-methyl-2-methylene)-cyclopentane]-1-acetate (27): The ortho ester Claisen rearrangement of the allyl alcohol **17** (210 mg, 1.36 mmols) with triethyl orthoacetate (3 ml, 16.4 mmols) and propionic acid (catalytic) in dry DMF (3 ml) for 14 minutes using a microwave oven as described for the alcohol **5** followed by purification of the product over a silica gel (3 gms) column using ethyl acetate-hexane (1:40) as eluent furnished the ester **27** (242 mg, 79%) as a liquid.[9e] $[\alpha]_D$: -53.7° (c, 5.1; $CHCl_3$). IR: ν_{max} 3060 (=C-H), 1730 (O-C=O), 1640 (C=C), 1455, 1370, 1240, 1175, 1100, 1035, 880 (C=CH_2) cm^{-1}. ^1H NMR: δ 4.70-4.85 (2 H, m, C=CH_2), 4.10 (2 H, q, *J* 7, O-C<u>H_2</u>CH_3), 2.45-1.60 (8 H, m), 1.24 (3 H, t, *J* 7, O-CH_2C<u>H_3</u>), 1.08 (3 H, s, *tert*-CH_3), 0.98 (3 H, d, *J* 7) and 0.78 (3 H, d, *J* 7) (C<u>H_3</u>-CH-C<u>H_3</u>).

Ethyl 3-phenylpent-4-enoate (28): The ortho ester Claisen rearrangement of the cinnamyl alcohol (**18**, 149 mg, 1.11 mmols) with triethyl orthoacetate (5 ml, 27 mmols) and propionic acid (catalytic) in dry DMF (5 ml) for 12 minutes using a microwave oven as described for the alcohol **5** followed by purification of the product over a silica gel (3 gms) column using ethyl acetate-hexane (1:40) as eluent furnished the ester **28** (186 mg, 82%) as a liquid.[9f] IR: ν_{max} 1737 (O-C=O), 1641 (C=C), 1602, 1494, 1419, 1374, 1338, 1260, 1161, 1113, 1032, 918 (C=CH_2), 759, 699 cm^{-1}. ^1H NMR: δ 7.24 (5 H, br s, aromatic), 5.98 (1 H, ddd, $J_{4,5trans}$ 16.2, $J_{4,5cis}$ 9.3, $J_{3,4}$ 7.2, C<u>H</u>=CH_2), 5.06 (1 H, d with st., $J_{4,5trans}$ 16.2) and 5.05 (1 H, d with st., $J_{4,5cis}$ 9.3) (CH=C<u>H_2</u>), 4.06 (2 H, q, *J* 7.2, O-C<u>H_2</u>CH_3), 3.86 (1 H, q, $J_{2,3}$,$J_{3,4}$ 7.2, benzylic), 2.72 (2 H, d, *J* 7.2, CH_2-C=O), 1.18 (3 H, t, *J* 7.2, O-CH_2C<u>H_3</u>).

Ethyl 3-(4-methoxyphenyl)-pent-4-enoate (29): The ortho ester Claisen rearrangement of the cinnamyl alcohol **19** (178 mg, 1 mmol) with triethyl orthoacetate (5 ml, 27 mmols), propionic acid (catalytic) in dry

DMF (5 ml) for 12 minutes using a microwave oven as described for the alcohol **5** followed by purification of the product over a silica gel (3 gms) column using ethyl acetate-hexane (1:40) as eluent furnished the ester **29** (205 mg, 81%) as a liquid. IR: ν_{max} 1737 (O-C=O), 1641 (C=C), 1614, 1587, 1515, 1464, 1446, 1374, 1344, 1305, 1251, 1179, 1110, 1035, 918 (C=CH_2), 831 cm^{-1}. ^1H NMR: δ 7.15 and 6.85 (4 H, A_2B_2 q, *J* 8, aromatic), 5.98 (1 H, ddd, $J_{4,5trans}$ 18, $J_{4,5cis}$ 10.8, $J_{3,4}$ 7.2, C**H**=CH_2), 5.07 (1 H, d with st, $J_{4,5trans}$ 18, $J_{allylic}$,J_{gem} 1.5) and 5.06 (1 H, d with st, $J_{4,5cis}$ 10.8, $J_{allylic}$,J_{gem} 1.5) (CH=C**H**$_2$), 4.08 (2 H, q, *J* 7.2, O-C**H**$_2$$CH_3$), 3.60-3.90 (1 H, m, benzylic), 3.80 (3 H, s, O-CH_3), 2.70 (2 H, d, $J_{2,3}$ 7.5, CH_2-C=O), 1.20 (3 H, t, *J* 7.2, O-CH_2C**H**$_3$). δ_C ($CDCl_3$) 171.4 (O-C=O), 158.1 (s, **C**-OCH_3), 140.5 (d, **C**H=CH_2), 134.2 (s, aromatic C-1'), 128.2 (2 C, d, aromatic C-2' and 6'), 113.9 (t, CH=C**H**$_2$), 113.6 (2 C, d, aromatic C-3' and 5'), 59.9 (t, O-CH_2), 54.7 (q, O-CH_3), 44.6 (d, C-3), 40.1 (t, **C**H_2-C=O), 13.8 (q, O-CH_2**C**H_3).

Ethyl 3-Methyl-3-(4-methylphenyl)-pent-4-enoate (30): The ortho ester Claisen rearrangement of the cinnamyl alcohol **20** (186 mg, 1 mmol) with triethyl orthoacetate (3 ml, 16.4 mmols) and propionic acid (catalytic) in dry DMF (5 ml) for 14 minutes using a microwave oven as described for the alcohol **5** followed by purification of the product over a silica gel (4 gms) column using ethyl acetate-hexane (1:40) as eluent furnished the ester **30** (156 mg, 59%, 76% based on starting material consumed) as a liquid. IR: ν_{max} 1740 (O-C=O), 1515 (aromatic), 1449, 1371, 1326, 1233, 1182, 1125, 1068, 1032, 915 (C=CH_2), 813 cm^{-1}. ^1H NMR: δ 7.22 (4 H, AB q, *J* 9, aromatic), 6.16 (1 H, dd, J_{trans} 18, J_{cis} 10.8, C**H**=CH_2), 5.14 (1 H, d, J_{cis} 10.8) and 5.06 (1 H, d, J_{trans} 18) (CH=C**H**$_2$), 4.02 (2 H, q, *J* 7.2, O-C**H**$_2$$CH_3$), 2.78 (2 H, s, CH_2-C=O), 2.34 (3 H, s, Ar-CH_3), 1.56 (3 H, s, *tert*-CH_3), 1.14 (3 H, t, *J* 7.2, O-CH_2C**H**$_3$). δ_C 171.0 (s, O-C=O), 145.9 (d, **C**H=CH_2), 143.0 (s, Ar-C_1), 135.5 (s, Ar-C_4), 129.0 (2 C, d, aromatic), 126.5 (2 C, d, aromatic), 112.0 (t, CH=**C**H_2), 60.0 (t, O-**C**$H_2$$CH_3$), 45.7 (t, **C**$H_2$-C=O), 43.2 (s, C-3), 25.5 (q, Ar-CH_3), 20.9 (q, *tert*-CH_3), 14.0 (q, O-CH_2**C**H_3). Further elution of the column using CH_2Cl_2 as eluent furnished the starting material (42 mg).

Ethyl (1,5,5-trimethylcyclohex-2-ene)-1-acetate (31): The ortho ester Claisen rearrangement of the allyl alcohol **21** (300 mg, 2.1 mmols) with triethyl orthoacetate (5 ml, 27 mmols) and propionic acid (catalytic) in dry DMF (5 ml) for 12 minutes using a microwave oven as described for the alcohol **5** followed by purification of the product mixture on a silica gel (3 gms) column using CH_2Cl_2-pentane (1:9) as eluent furnished the ester **31** (248 mg, 55%, 67% based on starting material consumed) as a liquid. IR: ν_{max} 1731 (O-C=O), 1677 (C=C), 1458, 1368, 1350, 1185, 1080, 1032, 945 cm^{-1}. ^1H NMR: δ 5.53 (2 H, br s, olefinic), 4.06 (2 H, q, *J* 7, O-C**H**$_2$$CH_3$), 2.20 (2 H, s, CH_2-C=O), 1.40-1.90 (4 H, m, H-4 and 6), 1.20 (3 H, t, *J* 7, O-CH_2C**H**$_3$), 1.10 (3 H, s) and 0.96 (6 H, s) (3 x *tert*-CH_3). Furhter elution of the column using CH_2Cl_2 as eluent furnished the starting material (25 mg).

(1R,5R)-Ethyl [(2-methyl-5-isopropenyl)-cyclohex-2-ene]-1-acetate (32): The ortho ester Claisen rearrangement of carveol (**22**, 260 mg, 1.7 mmol) with triethyl orthoacetate (3 ml, 16.4 mmols) and propionic acid (catalytic) in dry DMF (3 ml) for 12 minutes using a microwave oven as described for the alcohol **5** followed by purification of the product over a silica gel (4 gms) column using ethyl acetate-hexane (1:20) as eluent furnished the ester **32** (164 mg, 43%, 78% based on starting material recovered) as a liquid. IR: ν_{max} 1737 (O-C=O), 1647 (C=C), 1452, 1374, 1239, 1167, 1140, 1023, 924, 888 (C=CH_2) cm^{-1}. ^1H NMR 5.28 (1 H, m, ring olefin), 4.55 (2 H, br s, C=C**H**$_2$), 3.96 (2 H, q, *J* 7.2, O-C**H**$_2$$CH_3$), 1.73-2.66 (4 H, m), 1.66 (3 H, s) and 1.58 (3 H, s) (2 x olefinic CH_3), 1.20 (3 H, t, *J* 7.2, O-CH_2C**H**$_3$). Further elution of the column with CH_2Cl_2 furnished the unreacted carveol (58 mg).

ACKNOWLEDGEMENTS: We thank Prof. G. Mehta for the generous gift of the allyl alcohol **17**. SN thanks the CSIR, New Delhi for the award of the research fellowship.

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10) Subsequent to the publication of our preliminary communication,[4] Jones and co-workers reported the ortho ester Claisen rearrangement of secondary allyl alcohols in DMF in sealed teflon tubes *via* the microwave heating technique using Montmorillonite-KSF as catalyst. Huber, R.S.; Jones, G.B. *J. Org. Chem.*, 1992, 57, 5778; Jones, G.B.; Huber, R.S.; Chan, S. *Tetrahedron*, 1993, 49, 369;

11) An example of Claisen rearrangement by adsorption on KSF-clay followed by microwave heating was reported by Villemin *et al.*,[3h] wherein probably transvinylation step took place much before the microwave heating. This is further supported by our observation that no Claisen rearrangement products were obtained using our methodology, which is probably due to the fast evaporation of ethyl vinyl ether.

(*Received in UK* 7 *September* 1994; *revised* 1 *December* 1994; *accepted* 2 *December* 1994)