Unsaturated macrocyclic lactone synthesis *via* catalytic ring-closing metathesis[1]

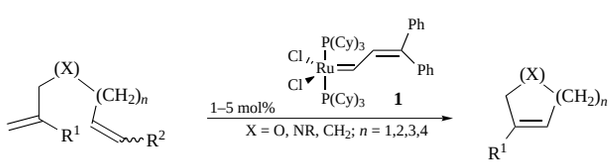
Konstantinos E. Litinas* and Basil E. Salteris

Laboratory of Organic Chemistry, Aristotle University of Thessaloniki, 54006, Thessaloniki, Greece

Ring-closing metathesis (RCM) of the terminal diene esters 2a,b with the Ru catalyst 1 results in the formation of the 20-, 21-membered macrolactones 3a,b in high yields. RCM of the diene oleate esters 4a,b with 1 gives the 19-, 20-membered macrolactones 5a,b in good yields, while an analogous reaction of the diene β,γ-unsaturated ester 6a gives the 13-membered lactone 7a in low yield.

Macrocyclic lactones are important components of naturally occurring compounds,[2,3] many of them insects pheromones.[4] They possess a range of significant biological activity,[5] (*e.g.* antibiotic,[3e,6] antifungal,[5c] antitumour, cytostatic,[7] oestrogenic and anabolic[2a,5c]) as well as being used as fragrances.[8] There are several multi-step syntheses of these compounds in moderate to high yields,[5] which include the following: ring enlargement of smaller rings,[9] lactonization of ω-hydroxycarboxylic acids[10] with different reagents, C–C bond formation by intramolecular addition of enolate ion with Pd^0 catalyst,[11a] intramolecular diacetylene ester coupling,[11b] by intramolecular Wittig[11c] or Horner–Emmons[11d] reactions and by olefin metathesis using WCl_6–Me_4Sn[12a] or WCl_6–Cp_2TiMe_2[12b,c] or $WOCl_4$–Cp_2TiMe_2[12c] as catalysts.

Recent progress in the development of well-defined metathesis catalysts with a single component has extended the use of olefin metathesis[13] in polymer chemistry through ring-opening metathesis polymerization (ROMP),[14] in organic synthesis[15,16] and in natural products synthesis.[17] Ring-closing metathesis (RCM) of dienes,[15] especially with the very efficient Ru catalyst **1**,[13b,18] is a general method for the construction of unsaturated carbocycles and heterocycles (Scheme 1).



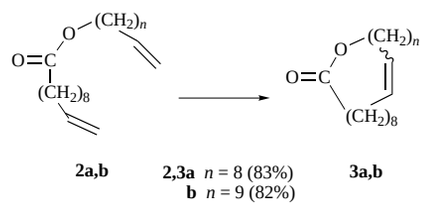
Scheme 1

In continuation of our efforts[19] to synthesize 6- and 7-membered unsaturated lactones, we report here our results for the preparation of 19-, 20-, 21-, 13- and 14-membered macrolactones from RCM of acyclic diene esters with the Ru catalyst **1** (Schemes 2–4). All diene esters were prepared from commercially available materials (Scheme 5) by simple esterification.

Dec-9-enyl undec-10-enoate **2a**, prepared in 78% yield by esterification of dec-9-enol with undec-10-enoic acid in the presence of conc. H_2SO_4 as catalyst in refluxing benzene for 5 h in a Dean–Stark trap, was heated with a benzene solution of the catalyst **1** (1.7 mol%) at 60 °C for 24 h under an argon atmosphere. Purification of the crude product by column chromatography gave the 20-membered macrolactone **3a** (83%) together with the first-eluted unchanged ester **2a** (13%). Compound **3a**, extracted in two fractions, was a mixture of *Z*- and *E*-isomers (ratio 57:43 as indicated by GC analysis). The first fraction [*Z*/*E* (80:20) by GC] showed in the IR spectrum more intense absorption for *cis*- (720 cm^{-1}) than for *trans*- (965 cm^{-1}) isomer in comparison to the IR spectrum of the second fraction [*Z*/*E* (40:60) by GC].

An analogous reaction (Scheme 2) of the diene ester **2b** (prepared in 94% yield, by esterification for 5 h of the corresponding alcohol and acid) with a benzene solution of **1** (4 mol%) gave after purification by PTLC unchanged ester **2b** (8%) and the 21-membered unsaturated lactone **3b** (82%). This lactone (eluted as two fractions) was also a mixture of *Z*- and *E*-isomers (IR absorptions 720 and 965 cm^{-1}, respectively) in a total ratio of 60:40 (by GC). In the first fraction the ratio was 73:27 (GC), and in the second 43:57. The ^1H NMR spectrum of the first fraction showed signals at δ 4.10 (t, 2 H, *J* 5.9, CO_2CH_2) and 5.31–5.36 (m, 2 H, CH=CH) for the *Z*-isomer whilst the second fraction showed two triplets at 4.10 (*J* 5.9, CO_2CH_2) and 4.11 (*J* 5.5, CO_2CH_2) for the *Z*- and *E*-isomers, respectively, and a multiplet at 5.30–5.38 (CH=CH) for both isomers. The ^{13}C NMR spectrum of the first fraction showed signals at 173.9 ppm (COO), 130.9 and 130.6 (CH=CH-), 64.0 ($COOCH_2$-) and 34.5 ppm (CH_2COO) for the *Z*- isomer as indicated from the more intense signals of the spectrum and that of the second spectrum showed similar signals together with others at 174.0, 130.1, 130.0, 64.2 and 34.8 ppm for the *E*-isomer. The lactone **3b** has previously been prepared[12c] by Tsuji and Hashigushi (12% yield) by olefin metathesis of the same ester **2b** with $WOCl_4$ (20 mol%)–Cp_2TiMe_2 (24 mol%).

An analogous reaction (Scheme 2) of the diene ester **2b** (pre-

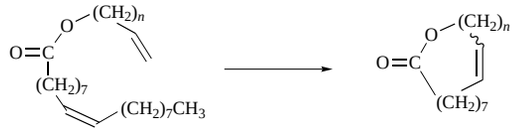


Scheme 2 *Reagents and conditions:* **1** (1.7, 4 mol%), C_6H_6, 60 °C, 24 h

Such macrolactonization gives, from commercially available materials, large-ring compounds in high yields by a simple two-step procedure.

RCM of dec-9-enyl oleate **4a** (prepared in 79% yield from esterification of dec-9-enol and oleic acid) with the catalyst **1** (0.8 mol%) (Scheme 3) gave after column chromatography the 19-membered unsaturated lactone **5a** (65%). The lactone **5a** was obtained as an inseparable (by GC) mixture of *Z*- and *E*-isomers (IR absorption at 720 and 965 cm^{-1}). This lactone was prepared[12c] earlier (18% yield) from RCM of dec-9-enyl oleate with WCl_6 (20 mol%)–Cp_2TiMe_2 (24 mol%).

The ester **4b** (prepared in 96% yield from undec-10-enol and oleic acid) with **1** (2 mol%; Scheme 3) gave the 20-membered ring lactone **5b** (63%) together with unchanged starting ester



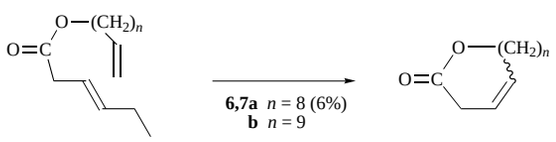
4a,b **4,5a** n = 8 (65%) **b** n = 9 (63%) **5a,b**

Scheme 3 *Reagents and conditions:* **1** (0.8, 2 mol%), C_6H_6, 60 °C, 24 h

(14%). This lactone, eluted in two fractions as a mixture of *Z*- and *E*-isomers in a total ratio of 61:39 (by GC). In the first fraction the ratio was 71:29 (GC), while in the second it was 42:58 (GC).

Thus, in RCM the oleate esters give lower yields than the undec-10-enoate esters probably because of steric hindrance by the non-9-enyl moiety in the former. This behaviour is in accord with previous observations that **1** is more effective with terminal dienes.[15b]

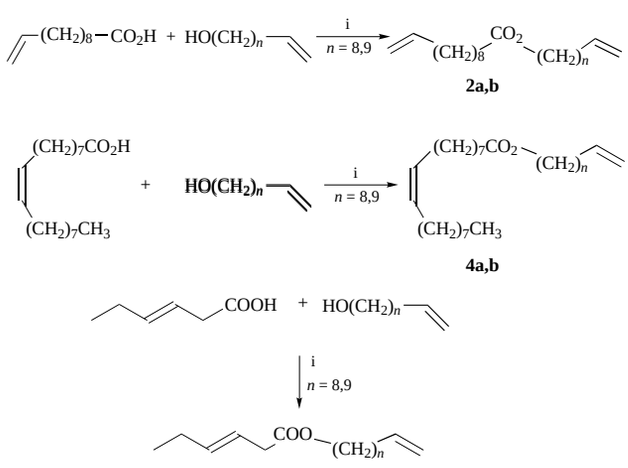
RCM of dec-9-enyl (*E*)-hex-3-enoate **6a** [prepared in 84% yield from esterification of dec-9-enol and (*E*)-hex-3-enoic acid] with a benzene solution of **1** (1.5 mol%) gave, after column chromatography, first unchanged **6a** (66%), followed by the



6a,b **6,7a** n = 8 (6%) **b** n = 9 **7a,b**

Scheme 4 *Reagents and conditions:* **1** (1.5 mol%), C_6H_6, 60 °C, 24 h

known[4c,f] 13-membered lactone **7a** (6%) and then a complex mixture. The lactone **7a** is an aggregation pheromone of the flat grain beetle, *Cryptolestes pusillus*.[4f] Attempted preparation of the 14-membered lactone **7b** from the diene ester **6b** [prepared in 95% yield from undec-10-enol and (*E*)-hex-3-enoic acid] and **1** (1.5 mol%) gave only a complex mixture eluted after unchanged **6b** (68%). The low yield in the preparation of the 13-membered lactone **7a** could be attributed to the possible



2a,b **4a,b** **6a,b**

Scheme 5 *Reagents and conditions:* i, C_6H_6, reflux (Dean–Stark trap), Cat. conc. H_2SO_4, 5 h, Yields 78–96%

unproductive complexation of Ru with the β,γ-double bond of the hex-3-enoate and the ester carbonyl and to steric hindrance of the propenyl ester moiety.

In conclusion, RCM of diene esters is an excellent method for macrolactone formation especially for terminal alkenes. The yield of this reaction is decreased with increasing steric hindrance and the possible complexation of the double bond, the Ru atom and the ester carbonyl.

Parallel work appeared very recently in the literature[20] in which the 21-membered lactone **3b** was synthesized (71% yield; 82% in our preparation), by using the catalyst **1** (4 mol%) and the ester **2b** in dichloromethane solution.

Experimental

IR spectra were run as films on a Perkin–Elmer 1310 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker 300 AM (300 MHz) spectrometer with $CDCl_3$ as a solvent with $SiMe_4$ as internal standard. *J* Values are given in Hz. ^{13}C NMR spectra were obtained at 75.5 MHz in $CDCl_3$ solutions with $SiMe_4$ as internal reference. Mass spectra were determined on a VG-250 spectrometer (70 eV). GC analyses were performed with a SS column packed with 20% Carbowax 20 M (3.78 g) on Chromosorb W, AW DMCS 60/80 mesh (10 ft × 1/8 in).

The acids and alcohols used were commercial products of Aldrich Chem. Co. Inc. The Ru catalyst **1** was prepared according to a published procedure.[18] Benzene was distilled under argon atmosphere with benzophenone ketyl and was degassed before use under anhydrous conditions. Catalyst and solvent transfers in the reaction flask were made under argon atmosphere by using a glove bag. All reactions were carried out under an argon atmosphere.

General procedure for the synthesis of the diene esters 2a,b, 4a,b and 6a,b

The acid (0.02 mol) was added in a benzene (30 cm^3) solution of the alcohol (0.03 mol) followed by 5 drops of conc. H_2SO_4. After the mixture had been heated under reflux in a Dean–Stark trap for 5 h, most of the benzene was removed and the residue was poured onto Et_2O (25 cm^3) and washed with water (15 cm^3). The aqueous layer was separated and extracted with Et_2O (15 cm^3) and the combined organic layer and extracts were washed with 5% aqueous $NaHCO_3$ (20 cm^3) and with water (cm^3), dried (Na_2SO_4) and concentrated under reduced pressure. Column chromatography [silica gel No 60, Merck, hexane–dichloromethane (4:1)] of the residue gave at first the corresponding diene ester followed by a small amount of unchanged alcohol.

Dec-9-enyl undec-10-enoate 2a. This ester (78%) was a colourless oil; ν_{max}/cm^{-1} 3070, 2920, 2840, 1730, 1632, 1460, 1170, 990, 910, 740 and 720; δ_H 1.21–1.43 (m, 20H), 1.55–1.7 (m, 4H), 1.98–2.1 (m, 4H), 2.29 (t, *J* 7.5, 2H), 4.05 (t, *J* 6.7, 2H), 4.9–5.03 (m, 4H) and 5.76–5.88 (m, 2H); δ_C 25.0, 25.9, 28.6, 28.8, 28.9, 29.0, 29.05, 29.1, 29.15, 29.2, 29.25, 29.3, 29.4, 33.75, 34.4, 64.3, 114.1, 139.1 and 173.9; *m/z* (%) 322 (57), 304 (9), 184 (54), 166 (62), 138 (77), 110 (74), 96 (88), 83 (94) and 55 (100) (Found: C, 78.4; H, 11.8. $C_{21}H_{38}O_2$ requires C, 78.2; H, 11.9%).

Undec-10-enyl undec-10-enoate 2b. The title ester (94%) as a colourless oil;[12c] ν_{max}/cm^{-1} 3060, 2920, 2840, 1730, 1630, 1460, 1170, 990, 900 and 725; δ_H 1.22–1.45 (m, 22H), 1.56–1.69 (m, 4H), 1.98–2.08 (m, 4H), 2.29 (t, *J* 7.5, 2H), 4.05 (t, *J* 6.7, 2H), 4.88–5.05 (m, 4H) and 5.72–5.88 (m, 2H); δ_C 24.9, 25.8, 28.6, 28.65, 28.7, 28.8, 28.9, 28.95, 29.0, 29.1, 29.2, 29.25, 29.3, 29.5, 33.6, 34.2, 64.1, 114.0, 138.8 and 173.4; *m/z* (%) 336 (50), 318 (7), 184 (55), 166 (62), 152 (69), 124 (71), 110 (75), 96 (90), 82 (95) and 55 (100).

Dec-9-enyl oleate 4a. This ester (79%) was a colourless oil; ν_{max}/cm^{-1} 3060, 2980, 2920, 2840, 1730, 1635, 1460, 1170, 990, 910 and 725; δ_H 0.88 (t, *J* 6.6, 3H), 1.18–1.42 (m, 30H), 1.54–1.68 (m, 4H), 1.94–2.01 (m, 6H), 2.29 (t, *J* 7.5, 2H), 4.05 (t, *J* 6.7, 2H), 4.90–5.05 (m, 2H), 5.27–5.43 (m, 2H) and 5.73–5.87 (m, 1H); δ_C 14.0, 22.6, 25.0, 25.9, 27.1, 27.2, 28.6, 28.9, 28.95, 29.0, 29.1, 29.15, 29.2, 29.3, 29.4, 29.5, 29.55, 29.65, 29.7, 31.9, 33.7, 34.3, 64.3, 114.1, 129.7, 129.9, 139.0 and 173.8; *m/z* (%) 420 (53), 392 (12), 283 (33), 264 (67), 222 (35), 138 (84), 97 (86), 83 (93) and 55 (100) (Found: C, 79.8; H, 12.6. $C_{28}H_{52}O_2$ requires C, 79.9; H, 12.45%).

Undec-10-enyl oleate 4b. The title ester (96%) was a colourless oil; ν_{max}/cm^{-1} 3060, 2985, 2910, 2840, 1730, 1635, 1460, 1170, 990, 910 and 725; δ_H 0.88 (t, *J* 6.6, 3H), 1.20–1.40 (m,

32H), 1.55–1.68 (m, 4H), 1.95–2.09 (m, 6H), 2.29 (t, *J* 7.5, 2H), 4.05 (t, *J* 6.7, 2H), 4.90–5.05 (m, 2H), 5.30–5.42 (m, 2H) and 5.75–5.88 (m, 1H); δ_C 14.0, 22.6, 25.0, 25.9, 27.1, 27.2, 28.6, 28.9, 28.95, 29.0, 29.1, 29.2, 29.25, 29.3, 29.35, 29.4, 29.5, 29.6, 29.65, 29.7, 31.9, 33.75, 34.3, 64.3, 114.1, 129.7, 129.9, 139.05 and 173.8; *m/z* (%) 434 (46), 406 (10), 283 (28), 264 (66), 222 (37), 152 (77), 97 (88), 83 (91) and 55 (100) (Found: C, 79.9; H, 12.2. $C_{29}H_{54}O_2$ requires C, 80.1; H, 12.5%).

Dec-9-enyl (*E*)-hex-3-enoate 6a. This ester (84%) was a colourless oil; ν_{max}/cm^{-1} 3060, 3020, 2920, 2840, 1730, 1630, 1460, 1160, 990, 965 and 910; δ_H 0.96 (t, *J* 7.5, 3H), 1.22–1.42 (m, 10H), 1.55–1.67 (m, 2H), 1.98–2.10 (m, 4H), 2.99 (d, *J* 6.2, 2H), 4.04 (t, *J* 6.7, 2H), 4.87–5.03 (m, 2H), 5.43–5.63 (m, 2H) and 5.72–5.86 (m, 1H); δ_C 13.5, 25.5, 26.0, 28.7, 29.0, 29.1, 29.3, 29.4, 33.9, 38.2, 64.7, 114.2, 120.9, 136.2, 139.1 and 172.5; *m/z* (%) 252 (46), 251 (32), 224 (6), 138 (70), 114 (79), 97 (83), 83 (85) and 55 (100) (Found: C, 76.4; H, 11.0. $C_{16}H_{28}O_2$ requires C, 76.1; H, 11.2%).

Undec-10-enyl (*E*)-hex-3-enoate 6b. The title ester (95%) was a colourless oil; ν_{max}/cm^{-1} 3060, 3020, 2915, 2840, 1730, 1630, 1460, 1160, 990, 965 and 910; δ_H 0.98 (t, *J* 7.5, 3H), 1.20–1.44 (m, 12H), 1.55–1.68 (m, 2H), 1.98–2.11 (m, 4H), 3.02 (d, *J* 6.0, 2H), 4.07 (t, *J* 6.7, 2H), 4.90–5.03 (m, 2H), 5.45–5.66 (m, 2H) and 5.74–5.88 (m, 1H); δ_C 13.4, 25.5, 25.8, 28.5, 28.9, 29.0, 29.2, 29.3, 29.4, 33.7, 38.1, 64.5, 114.1, 120.7, 136.2, 139.2 and 172.3; *m/z* (%) 266 (60), 265 (48), 238 (11), 152 (76), 124 (61), 114 (94), 97 (94), 83 (100) and 55 (96) (Found: C, 76.7; H, 11.4. $C_{17}H_{30}O_2$ requires C, 76.6; H, 11.35%).

Representative procedure for the synthesis of macrolactones

Nonadec-10-en-19-olide 3a. Ruthenium catalyst **1** (9.3 mg, 0.01 mmol) was dissolved in a three-necked flask in benzene (80 cm^3) in a glove bag at room temperature. The diene ester **2a** (191 mg, 0.593 mmol) was added to the resulting light orange–brown solution *via* a syringe under argon atmosphere and the mixture was then heated at 60 °C for 24 h. After cooling, the mixture was quenched by exposure to air and concentrated under reduced pressure. The residue was separated by column chromatography [silica gel No 60, Merck, hexane–dichloromethane (2:1 to 1:2)] to give after elution of unchanged **2a** (25 mg, 13%) the olide **3a** as a colourless oil in two fractions [first fraction 60 mg, *Z/E* (80:20 by GC); second fraction 85 mg, *Z/E* (40:60 by GC); total 145 mg, 83% yield, *Z/E* (57:43)]; ν_{max}/cm^{-1} 3050, 2920, 2840, 1730, 1460, 1165, 965 [w (weak) for first and m (medium) for second fraction], 735 and 720 (m for both fractions); δ_H 1.20–1.42 (m, 20H), 1.55–1.70 (m, 4H), 1.96–2.08 (m, 4H), 2.315 (t, *J* 6.9, CH_2CO_2) and 2.33 (t, *J* 6.6, CH_2CO_2), 4.10 (t, *J* 6.2, CO_2CH_2) and 4.12 (t, *J* 5.9, CO_2CH_2) and 5.26–5.41 (m, 2H); δ_C 24.9, 25.1, 26.0, 26.2, 26.4, 26.5, 27.3, 27.35, 27.5, 27.55, 28.1, 28.15, 28.4, 28.45, 28.5, 28.6, 28.65, 28.75, 28.8, 28.9, 29.0, 29.1, 29.2, 29.3, 29.4, 29.45, 31.7, 31.8, 34.1, 34.75, 64.2, 64.25, 130.0, 130.05, 130.6, 130.7, 174.0 and 174.05; *m/z* (%) 294 (20), 276 (10), 149 (46), 137 (47), 123 (84), 109 (95), 95 (99), 81 (99) and 55 (100) (Found: C, 77.4; H, 11.5. $C_{19}H_{34}O_2$ requires C, 77.5; H, 11.65%).

Eicos-10-en-20-olide 3b. Addition of the diene **2b** (130 mg, 0.387 mmol) to a benzene solution of the Ru catalyst **1** (15 mg, 0.016 mmol) according to the above described procedure gave after separation of the resulting mixture by PTLC [silica gel, hexane–CH_2Cl_2 (1:2)] unchanged **2b** (10 mg, 8%) and the olide **3b** as a colourless oil[12c] in two fractions [first fraction 55 mg, *Z/E* (73:27 by GC); second fraction 42 mg, *Z/E* (43:57 by GC); total 97 mg, 82% yield, *Z/E* (60:40)]; ν_{max}/cm^{-1} 3070, 2920, 2840, 1730, 1460, 1170, 965 (m for both fractions), 735sh and 720 (m for first and w for second fraction); δ_H(first fraction) 1.22–1.41 (m, 22H), 1.55–1.70 (m, 4H), 1.93–2.06 (m, 4H), 2.31 (t, *J* 6.7, 2H), 4.10 (t, *J* 5.9, 2H) and 5.31–5.36 (m, 2H); δ_H-(second fraction) 1.22–1.41 (m, 22H), 1.55–1.70 (m, 4H), 1.93–2.06 (m, 4H), 2.31 (t, *J* 6.7, 2H), 4.10 (t, *J* 5.9, CO_2CH_2) and 4.12 (t, *J* 5.5, CO_2CH_2) and 5.30–5.38 (m, 2H); δ_C 25.2, 25.75, 25.8, 26.0, 26.15, 26.5, 26.6, 27.7, 27.9, 27.95, 28.3, 28.4, 28.45, 28.5, 28.55, 28.65, 28.7, 28.8, 28.9, 29.0, 29.1, 29.15, 29.2, 29.35, 29.4, 29.45, 29.5, 29.55, 31.7, 31.95, 34.5, 34.8, 64.0, 64.2, 130.0, 130.1, 130.6, 130.9, 173.9 and 174.0; *m/z* (%) 308 (22), 290 (8), 110 (86), 96 (84), 82 (100), 55 (79) and 54 (85).

Octadec-9-en-18-olide 5a. Reaction of the diene **4a** (244 mg, 0.581 mmol) with the catalyst **1** (4.25 mg, 0.0046 mmol) gave after purification by column chromatography and after the elution of the unchanged ester **4a** (64 mg, 26%) the olide **5a**, as a colourless oil[12c] (106 mg, 65%), not separated by GC; ν_{max}/cm^{-1} 3060, 2920, 2850, 1730, 1460, 1170, 965, 730sh and 720; δ_H 1.18–1.45 (m, 18H), 1.56–1.70 (m, 4H), 1.96–2.09 (m, 4H), 2.31 (t, *J* 6.8, 2H), 4.11 (t, *J* 5.4, 2H) and 5.25–5.40 (m, 2H); δ_C 25.3, 25.9, 26.1, 26.3, 26.35, 27.1, 27.2, 27.8, 27.9, 28.1, 28.6, 28.8, 28.85, 28.9, 28.95, 29.05, 29.1, 29.15, 29.2, 29.3, 29.4, 29.5, 29.6, 29.65, 32.0, 32.1, 34.9, 35.0, 64.2, 64.6, 130.1, 130.3, 130.6, 130.8, 174.0 and 174.1; *m/z* (%) 280 (62), 262 (28), 252 (12), 149 (30), 137 (48), 123 (6), 109 (68), 95 (78), 82 (88) and 55 (100).

Nonadec-9-en-19-olide 5b. Reaction of the diene **4b** (174 mg, 0.4 mmol) with the catalyst **1** (7.3 mg, 0.079 mmol) gave after elution of the unchanged **4b** (25 mg, 14%) the olide **5b**, as a colourless oil in two fractions [first fraction 48 mg, *Z/E* (71:29 by GC); second fraction 26 mg, *Z/E* (42:58 by GC); total 74 mg, 63% yield, *Z/E* (61:39)]; ν_{max}/cm^{-1} 3060, 2910, 2840, 1730, 1460, 1170, 965, 735sh and 720; δ_H 1.55–1.45 (m, 20H), 1.55–1.70 (m, 4H), 1.92–2.10 (m, 4H), 2.32 (t, *J* 6.7, 2H), 4.12 (t, *J* 6.1, 2H) and 5.25–5.40 (m, 2H); δ_C 24.9, 25.3, 25.4, 25.5, 25.9, 26.5, 27.0, 27.4, 27.9, 28.0, 28.05, 28.1, 28.2, 28.4, 28.5, 28.6, 28.7, 28.8, 28.9, 29.05, 29.1, 29.3, 29.4, 29.5, 29.55, 29.7, 31.6, 32.3, 34.6, 34.8, 63.8, 64.1, 129.9, 130.0, 130.6, 130.9, 173.85 and 173.9; *m/z* (%) 294 (13), 276 (6), 149 (62), 123 (60), 109 (91), 95 (98), 81 (100), 55 (99) (Found: C, 77.3; H, 11.6. $C_{19}H_{34}O_2$ requires C, 77.5; H, 11.65%).

Dodec-3-en-12-olide 7a. Reaction of the diene **6a** (167 mg, 0.663 mmol) with **1** (9 mg, 0.0097 mmol) gave after separation by column chromatography the unchanged ester **6a** (110 mg, 66%), followed by the olide **7a** as colourless oil[4c,f] (8 mg, 6%): δ_H 1.22–1.46 (m, 10H), 1.55–1.66 (m, 2H), 1.98–2.11 (m, 2H), 3.01 (d, *J* 6.1), 4.08 (t, *J* 5.0) and 5.52–5.95 (m, 2H); *m/z* (%) 196 (8), 149 (34), 137 (52), 123 (67), 110 (79), 96 (94), 82 (96) and 55 (100). Finally, a complex mixture (27 mg) was eluted.

Attempted preparation of tridec-3-en-13-olide 7b. Reaction of the diene **6b** (151 mg, 0.568 mmol) with **1** (8 mg, 0.0086 mmol) gave after separation by column chromatography unchanged **6b** (103 mg, 68%), followed by a complex mixture (25 mg).

Acknowledgements

We gratefully acknowledge the generous gift of the Ru catalyst **1** by Prof. R. H. Grubbs (California Institute of Technology).

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Paper 7/02353G
Received 7*th April* 1997
Accepted 29*th May* 1997