Pergamon

Tetrahedron 55 (1999) 14829–14838

TETRAHEDRON

A Chiral Probe for the Asynchronous Transition State of Diels–Alder Reactions with Acetylenedicarboxylate

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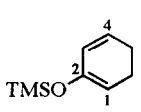
Received 30 September 1999; revised 2 November 1999; accepted 3 November 1999

Abstract: Diels–Alder reactions took place with modest diastereoselectivity between dimethylcyclohexadiene derivative **3a** and di-(-)-menthyl acetylenedicarboxylate, whereas the dimethylcyclohexadiene **2** showed no selectivity whatsoever. These results can be rationalized in terms of a complete lack of any *endo-exo* preference for the carboxylate groups and a more synchronous addition with **3a** than with **2**.

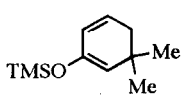
Keywords: Diels–Alder reactions; diastereoselection; alkynes

INTRODUCTION

A recent study from our laboratory[1] compared the rates of the Diels–Alder reactions of dienes **1**, **2**, and **3a**. Reaction rates for **2** and **3a** are similar when a symmetrical ethylenic dienophile such as *para*-benzoquinone, maleic anhydride or *N*-phenylmaleimide is employed. Both **2** and **3a** react more slowly than does diene **1**. These observations are evidence supporting a transition state geometry that is sufficiently synchronous that the extent of steric hindrance by a methyl on the diene is very similar in reactions with **2** and with **3a**. In contrast, addition of diethyl acetylenedicarboxylate to **2** is significantly faster than to **3a**. This suggests an unsymmetrical transition state geometry. A computationally-derived transition state geometry for acetylenedicarboxylic acid with cyclopentadiene is unsymmetrical with incipient σ-bonds of 2.030 Å and 2.712 Å.[2] This geometry places the carboxylate group nearer the longer incipient σ-bond parallel-planar with the π-system of the diene and *endo* with respect to the diene's π-system. The carboxylate nearer the shorter incipient σ-bond is far from parallel-planar with the π-system of the diene.



1



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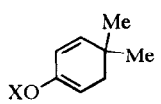

3a X = TMS
3b X = TBS

Whereas Diels–Alder reactions of dienophiles such as acrylates[3] and fumarates[4,5] with chiral auxiliaries can be very diastereoselective, little diastereoselectivity is seen in the reactions of acetylenedicarboxylates derived from chiral alcohols.[6] The same is true for chiral acetylenic imides,[7] and catalysis of the reaction of cyclopenta-

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0040-4020/99/$ - see front matter
PII: S0040-4020(99)00982-5

diene and methyl propiolate with a chiral Lewis acid catalyst gave the adduct with an ee of only 55%.[8] A lack of selectivity is obviously a synthetically infelicitous situation, but a situation in which competing reaction pathways are very similar in activation energy is well suited for a study involving subtle manipulation of the substrate because small changes in activation energies can result in easily measurable (by NMR) changes in the product ratio. We have exploited this idea in an attempt to probe experimentally the transition state geometry of the Diels–Alder reaction of acetylenedicarboxylate with diene **1** and its *gem*-dimethyl analogues **2** and **3a**.

RESULTS AND DISCUSSION

It can be hypothesized that, at the transition state of the Diels–Alder reaction between dienes **1–3a** and acetylenedicarboxylate (Figure 1), the carboxylate closer to the longer incipient σ-bond (bond *b*) is the one that activates the dienophile toward addition. This carboxylate group must be roughly parallel-planar with the diene moiety. This might mean that a chiral auxiliary on the parallel-planar carboxylate should provide better stereochemical discrimination, by means of steric interactions, than should the carboxylate closer to the shorter incipient σ-bond (bond *a*). The carboxylate near bond *a*, which may do little to activate the dienophile at the transition state, could simply rotate to minimize steric interactions and, in turn, minimize stereochemical discrimination. Thus, if the geometry of the transition states with **1–3a** were as hypothesized, **3a** should show better diastereoselectivity with a chiral acetylenedicarboxylate than should **1** or **2** when the reaction proceeds with the activating carbonyl *endo* with respect to the diene, as shown in Figure 1.

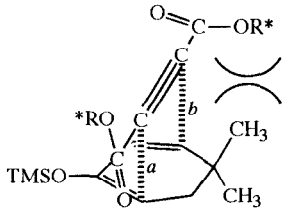
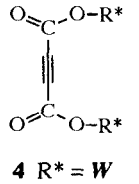
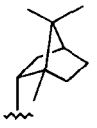


Figure 1. Hypothesized transition state for the Diels–Alder addition of acetylenedicarboxylate with diene **3a**. The incipient σ-bonds are indicated by hatched lines; $a < b$.

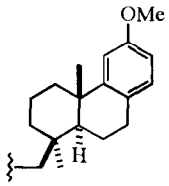
The preparation of the dienophiles used in this study was accomplished by transesterification of diethyl acetylenedicarboxylate with an excess of the chiral alcohol. Dienophile **4** was derived from [(1*S*)-*endo*]-(-)-borneol. Diels–Alder reactions of dienes **1**, **2**, and **3a** with **4** proceeded over a period of three to five days in benzene under reflux. The adducts, **5a/b**, **6a/b**, and **7a/b**, were very sensitive to moisture, so it was convenient



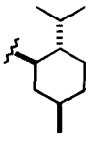
4 R* = ***W***
12 R* = ***X***
15 R* = ***Y***
23 R* = ***Z***



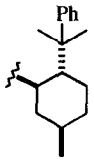
W



X



Y

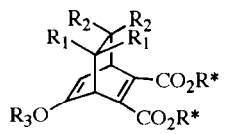


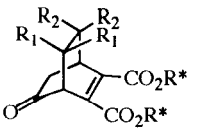
Z

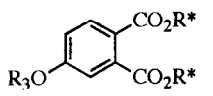
to hydrolyze the silyl enol ethers to the corresponding ketones **8a/b**, **9a/b**, and **10a/b** before NMR analysis. The product of each reaction proved to be a diastereomeric mixture in a ratio extremely close to 1:1. Higher temperatures during the Diels–Alder reaction resulted in an increased production of the phthalate **11**, presumably via *retro*-Diels–Alder ejection of the ethano bridge. Dienophile **12** incorporated a larger auxiliary but the reaction of **12** with the hardier diene **3b**, which was expected to provide more diastereoselectivity than **1** or **2**, neverthe-

less showed no diastereoselectivity whatsoever in the formation of **13a/b**. A significant amount of an aromatic by-product **14** (19%) was noted in the hot benzene solution.

In the solid state, dienophile **15**, with (-)-menthol as the chiral auxiliary, has its ester groups orthogonal to each other,[9] i.e., its shape is approximately that of the computed transition state geometry for acetylenedicarboxylic acid.[2] The diastereomeric adduct mixtures **16a/b**, **17a/b**, and **18a/b** derived from **15** were hydrolyzed quantitatively to ketones **19a/b**, **20a/b**, and **21a/b**, which were not separable by flash chromatography. (Once again, some phthalate **22** was produced from the adducts under the Diels–Alder conditions.) NMR analysis of **19a/b** revealed a 1.22:1 ratio of products, but the ratio of **20a/b** was not significantly different from 1:1. Analysis of products **21a/b** from diene **3a**, from which the most diastereoselectivity was expected, showed a 1.45:1 ratio of diastereomers. This selectivity is modest, but it is similar to selectivities reported by Charlton[6] for thermal reactions with other dienes. (-)-8-Phenylmenthol was incorporated with difficulty into dienophile **23**, but, instead of leading to greater selectivity, the dienophile was merely recovered without any detectable amount of Diels–Alder adduct after heating **23** in benzene in the presence of 14 equivalents of **3a** for 10 days.



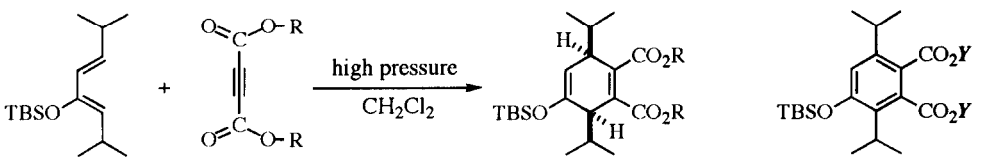




1:1 **5a/b** R* = ***W***, R_1 = H, R_2 = H, R_3 = TMS
1:1 **6a/b** R* = ***W***, R_1 = Me, R_2 = H, R_3 = TMS
1.03:1 **7a/b** R* = ***W***, R_1 = H, R_2 = Me, R_3 = TMS
1:1 **13a/b** R* = ***X***, R_1 = H, R_2 = Me, R_3 = TBS
1.22:1 **16a/b** R* = ***Y***, R_1 = H, R_2 = H, R_3 = TMS
1.02:1 **17a/b** R* = ***Y***, R_1 = Me, R_2 = H, R_3 = TMS
1.45:1 **18a/b** R* = ***Y***, R_1 = H, R_2 = Me, R_3 = TMS

8a/b R* = ***W***, R_1 = H, R_2 = H
9a/b R* = ***W***, R_1 = Me, R_2 = H
10a/b R* = ***W***, R_1 = H, R_2 = Me
19a/b R* = ***Y***, R_1 = H, R_2 = H
20a/b R* = ***Y***, R_1 = Me, R_2 = H
21a/b R* = ***Y***, R_1 = H, R_2 = Me

11 R* = ***W***, R_3 = H
14 R* = ***X***, R_3 = TBS
22 R* = ***Y***, R_3 = H



24 **15** R = ***Y*** **27** R = *t*-butyl

1.78:1 **25a/b** R = ***Y*** **28** R = *t*-butyl

26

As diene **1** had provided adducts **16a/b** with some diastereoselectivity, it showed that the silyloxy group at C-2 had a measurable influence on the stereochemical course of the reaction. In order to demonstrate the effect of a silyloxy group in a different diene system, dienophile **15** was then introduced to a solution of the acyclic diene **24**. No reaction was observed after 5 days under reflux in benzene, but under high pressure in CH_2Cl_2 these reacted to give a pair of diastereomers **25a/b** in a ratio of 1.78:1. (Aerial oxidation of **25a/b** was facile giving phthalate **26**.) Under the same conditions of high pressure, diene **24** with dienophile **27** afforded only one (racemic) adduct **28**. This confirmed that the formation of diastereomers was not the result of isomerization or stepwise addition to **24**, which might have yielded an isomeric 1,4-cyclohexadiene product with *trans* isopropyl groups. It should be noted that stereoselectivity in the reactions of both **1** and **24** must have resulted from proximity of a chiral auxiliary to the silyloxy group. As diene **2** showed no selectivity in its reaction with **15**, it appeared that the effect of the silyloxy group was balanced by a steric effect in the opposite direction by the *gem*-dimethyl moiety at C-6 of the diene. Thus, there cannot be much preference for the auxiliary to be placed in the *endo* or the *exo* region of the transition state. Diene **3a** showed greater selectivity than did **1**. This meant that

either the effect of the *gem*-dimethyl moiety at C-5 was small and simply added to the small effect of the silyloxy group, or the effect of the *gem*-dimethyl was larger but stereochemically opposite to that of the silyloxy group.

It seemed likely that the low diastereoselectivities with the chiral acetylenedicarboxylates were a consequence of no *endo-exo* bias for the carboxylate group(s) at the transition states with dienes **1**, **2**, and **3a**. However, Morokuma and co-workers[2] had published a computationally derived geometry for the addition of acetylenedicarboxylic acid with cyclopentadiene in which at least one carbonyl is *endo* with respect to the diene moiety. On the other hand, there is good evidence for a preferred *exo* geometry for the transition state of the enantioselective reaction of acetylenedicarboxaldehyde in the presence of a chiral catalyst.[10] We used AM1[11] to model the transition states for the additions of **27**, in four reasonable orientations, to analogues of dienes **1**, **2**, and **3a**, as shown in Figure 2. The results are summarized in Table 1.

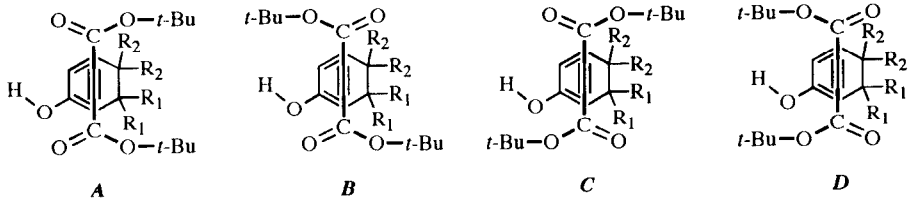


Figure 2. Four transition state geometries modeled by AM1 for the reactions of **27**.

Table 1. Incipient σ-bond[a] lengths (AM1) and energies for the four transition states shown in Figure 2.

transition state	R_1 = H, R_2 = H			R_1 = Me, R_2 = H			R_1 = H, R_2 = Me		
	bond *a* (Å)	bond *b* (Å)	Δ*H* (kcal/mol)	bond *a* (Å)	bond *b* (Å)	Δ*H* (kcal/mol)	bond *a* (Å)	bond *b* (Å)	Δ*H* (kcal/mol)
endo-endo (*A*)	2.041	2.241	−119.8	2.041	2.263	−125.1	2.082	2.209	−125.0
endo-exo (*B*)	2.045	2.239	−119.9	2.044	2.261	−125.1	2.074	2.217	−125.0
exo-endo (*C*)	2.043	2.245	−120.1	2.048	2.252	−125.5	2.084	2.216	−125.3
exo-exo (*D*)	2.045	2.245	−119.9	2.048	2.252	−125.3	2.076	2.222	−125.1

[a] Incipient σ-bonds, *a* and *b*, are defined in Figure 1.

The modeling indicated that all four transition state geometries are energetically without significant difference, regardless of the presence or position of the *gem*-dimethyl moiety. Furthermore, the position of the methyl groups has no impact on the stability of the transition state. Clearly, reactions of **2** and **3a** must occur through many geometries, and it is therefore surprising that any diastereoselectivity could be seen with any of our dienophiles. The most important geometrical parameters are the lengths of incipient σ-bonds, *a* and *b*. These are not the same, with bond *b* being longer than bond *a*, although these transition states are less lop-sided than those with acetylenedicarboxylic acid. The incipient σ-bonds also show very little difference between the four orientations in Figure 2. What is important to note is that a comparison between incipient σ-bonds *a* and *b* for the analogues of **1** and **2** shows very little difference, whereas the incipient σ-bonds for the analogue of **3a** shows a somewhat longer bond *a* and a much shorter bond *b*. That the incipient σ-bonds are more different in length for **1** and **2** than for **3a** indicates that their reactions are less synchronous than with **3a**, even though the coefficients of the HOMO at C-1 and at C-4 for dienes **2** and **3a** are almost the same.[1] It has been reported that the reaction of **2** with an acetylenedicarboxylate is only slightly slower than that of **1**, whereas the rate of reaction with **3a** is about a twentieth the rate of **1**.[1] Thus, reaction rate seems to parallel the degree of asynchronicity in the transition state. The results are also consistent with the idea that the auxiliary near bond *b* is marginally more

important in determining diastereoselectivity since for **3a** the incipient σ-bond *b* is shorter and *a* is longer than for **2**, which shows no diastereoselectivity whatsoever with our chiral dienophiles.

In summary, **3a** is more diastereoselective than **2** because its Diels–Alder reactions are more synchronous than for **2**. This places a chiral auxiliary in **3a** somewhat closer to a sterically distinguishing element. However, diastereoselectivity is extremely low or nonexistent in most cases because the acetylenedicarboxylate has no *endo-exo* preference whatsoever, and reactions must proceed via a number of pathways. Bulkier auxiliaries such as in dienophile **12** need not show any more diastereoselectivity than smaller ones, and attempts to add more steric discrimination, as with **23**, may simply make the dienophile unreactive.

EXPERIMENTAL

Melting points (mp) were determined on a Fisher-Johns apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Mattson FT instrument as thin films unless otherwise indicated. Nuclear magnetic resonance (NMR) spectra were obtained on a General Electric GE 300-NB instrument as $CDCl_3$ solutions. In most instances, the ^{13}C NMR chemical shift (relative to δ 77.0 for $CDCl_3$) is followed in parentheses by the number of attached hydrogens, as determined by APT and/or heteronuclear correlation spectra. ^{13}C NMR shifts separated by "/" indicate corresponding pairs signals for diastereomeric mixtures. Mass spectral (MS) data were obtained with a V.G. Micromass 7070HS instrument. Flash chromatography ("chromatography") employed 230-400 mesh silica gel; elution was usually with hexanes containing an increasing proportion of ethyl acetate. Dienes **1–3a** were prepared as described previously.[1]

*5,5-Dimethyl-2-(*tert*-butyldimethylsilyloxy)-1,3-cyclohexadiene (**3b**).*

A solution of 4,4-dimethyl-2-cyclohexen-1-one (0.238 g, 1.92 mmol) in CH_2Cl_2 (10 mL) was cooled to 0 °C, and Et_3N (0.299 g, 0.412 mL, 2.95 mmol) was added dropwise. After 10 min, TBSOTf (0.730 g, 0.635 mL, 2.76 mmol) was added and this was stirred for 15 min. The ice-bath was removed, and stirring was continued for 45 min. The orange mixture was poured into Et_2O (100 mL), and the organic layer was washed with saturated $NaHCO_3$ (2 × 15 mL) and brine (15 mL). The solution was dried ($MgSO_4/K_2CO_3$) and then concentrated under vacuum. Chromatography gave **3b** (0.436 g, 95%) as a colorless oil: IR 2958, 1654, 1472, 1363, 1254, 1206, 891, 839, 782 cm^{-1}; ^1H NMR δ 5.56–5.54 (2H, m), 4.80–4.75 (1H, symmetrical m), 2.11 (2H, d, J = 4.6 Hz), 1.01 (6H, s), 0.93 (9H, s), 0.13 (6H, s); ^{13}C NMR δ 147.4 (0), 139.9 (1), 123.9 (1), 101.5 (1), 37.0 (2), 31.2 (0), 27.7 (2C, 3), 25.7 (3C, 3), 18.1 (0), 0.13 (2C, 3); MS 238 (17, M^+), 223 (31), 181 (45), 167 (9), 165 (11), 126 (37), 91 (14), 75 (100), 73 (59).

*Dibornyl acetylenedicarboxylate (**4**).*

A solution of diethyl acetylenedicarboxylate (1.0 g, 0.94 mL, 5.9 mmol), [(1*S*)-*endo*]-(-)-borneol (4.0 g, 26 mmol), and *p*TsOH•H_2O (0.12 g, 0.63 mmol) in benzene (25 mL) was heated at reflux for 7 days. The mixture was concentrated under vacuum. Chromatography of the oily residue gave **4** as colorless crystals (1.95 g, 86%): mp 87–88 °C; IR 2957, 2883, 1719, 1454, 1379, 1258 cm^{-1}; ^1H NMR δ 5.02 (2H, ddd, J = 2.1, 3.4, 9.9 Hz), 2.45–2.34 (2H, m), 2.02–1.89 (2H, m), 1.85–1.68 (4H, m), 1.41–1.23 (4H, m), 1.07 (2H, dd, J = 3.4, 14.0 Hz), 0.90 (6H, s), 0.89 (6H, s), 0.87 (6H, s); ^{13}C NMR δ 152.4 (0), 83.4 (1), 74.9 (0), 49.0 (0), 48.0 (0), 44.7 (1), 36.4 (2), 27.9 (2), 26.9 (2), 19.6 (3), 18.8 (3), 13.4 (3); MS 386 (4, M^+), 250 (0.5), 249 (0.9), 153 (4), 137 (45), 136 (82), 121 (31), 110 (44), 109 (15), 108 (12), 95 (100), 93 (39), 92 (11), 81 (48), 80 (15), 79 (8), 69 (20), 67 (13), 55 (17); HRMS calcd for $C_{24}H_{34}O_4$ 386.2455, found 386.2479.

*Dibornyl 2-oxobicyclo[2.2.2]oct-5-ene-5,6-dicarboxylate (**8a/b**).*

A solution of **1** (0.124 g, 0.737 mmol) and **4** (0.819 g, 2.12 mmol) in benzene (25 mL) was heated at reflux for 3 days. Following concentration of the mixture under vacuum, methanol (10 mL) and 0.5 M HCl (0.5 mL) were added. This was stirred for 1 h then diluted with Et_2O (20 mL) and EtOAc (10 mL). The

organic solution was washed with brine (5 mL) and water (5 mL) and then dried over $MgSO_4$. Concentration under vacuum and chromatography of the residue gave **8a/b**, a 1:1 mixture of diastereomers, as a yellow solid (0.162 g, 46%) and **11** (0.037 g, 11%). For **8a/b**: mp 130–131 °C; IR 2955, 2879, 1730, 1715, 1639, 1454, 1258 cm^{-1}; ^1H NMR[12] δ 5.08–4.96 (2H, m), 3.63 (1H, m), 3.40 (1H, m), 2.46–2.31 (2H, symmetrical m), 2.23 (1H, m), 2.14 (1H, dd, J = 2.4, 18.6 Hz), 2.08–1.63 (10H, m), 1.37–1.21 (4H, m), 1.16–1.02 (2H, m), 0.92 (3H, s), 0.91 (3H, s), 0.884 (3H, s), 0.876 (3H, s), 0.87 (3H, s), 0.86 (1.5H, s), 0.85 (1.5H, s); ^{13}C NMR δ 209.2/209.1 (0), 165.8 (2C, 0), 164.3 (2C, 0), 143.4/143.3 (0), 134.1 (2C, 0), 81.44/81.40/81.34/81.27 (1), 49.82/49.78 (1), 49.02/48.97 (4C, 0), 47.93/47.89 (4C, 0), 44.8 (4C, 1), 39.1/39.0 (2), 36.6/36.4/36.3 (4C, 2), 35.24/35.20 (1), 28.0/27.94/27.90 (4C, 2), 27.2 (4C, 2), 24.1/24.0 (2), 22.8/22.7 (2), 19.4 (4C, 3), 18.8 (4C, 3), 13.60/13.56 (4C, 3); MS 483 (1, M^+ + 1), 482 (2, M^+), 346 (11), 211 (1), 210 (10), 153 (15), 138 (69), 137 (100), 136 (49), 135 (10), 121 (20), 109 (32), 95 (35), 93 (17), 81 (73), 69 (17); HRMS calcd for $C_{20}H_{26}O_5$ ($M^+ - C_{10}H_{16}$) 346.1779, found 346.1773.

For *dibornyl 4-hydroxyphthalate (11)*: mp 214–215 °C; IR 3371 (br), 3021 (w), 2957, 1709, 1605, 1580, 1453 cm^{-1}; ^1H NMR δ 7.70 (1H, d, J = 8.5 Hz), 7.57 (1H, br s, OH), 7.03 (1H, d, J = 2.5 Hz), 6.91 (1H, dd, J = 2.5, 8.5 Hz), 5.06 (2H, symmetrical m), 2.42 (2H, symmetrical m), 2.07–1.85 (2H, m), 1.85–1.65 (4H, m), 1.41–1.18 (5H, m), 1.13 (1H, dd, J = 3.4, 13.8 Hz), 0.92 (6H, s), 0.89 (3H, s), 0.88 (6H, s), 0.87 (3H, s); ^{13}C NMR δ 169.4 (0), 167.0 (0), 159.2 (0), 136.2 (0), 131.5 (1), 122.4 (0), 117.1 (1), 115.6 (1), 82.0 (1), 81.2 (1), 48.9 (2C, 0), 47.9 (2C, 0), 44.8 (2C, 1), 36.5 (2), 36.1 (2), 28.0 (2), 27.9 (2), 27.3 (2), 27.1 (2), 19.7 (2C, 3), 18.8 (2C, 3), 13.5 (2C, 3); MS 454 (3, M^+), 318 (0.1), 301 (2), 183 (2), 153 (1), 138 (12), 137 (100), 95 (12), 81 (50), 69 (12); HRMS calcd for $C_{28}H_{38}O_5$ 454.2717, found 454.2686.

Dibornyl 7,7-dimethyl-2-oxobicyclo[2.2.2]oct-5-ene-5,6-dicarboxylate (9a/b).

A solution of **2** (0.122 g, 0.619 mmol) and **4** (0.542 g, 1.40 mmol) in benzene (25 mL) was heated at reflux for 5 days. Treatment as for **8a/b** provided **9a/b**, a 1:1 mixture of diastereomers, as a yellow solid (0.208 g, 66 %) and **11** (0.077 g, 28%). For **9a/b**: mp 189–190 °C; IR 2957, 2875, 1732, 1713, 1640, 1265, 1234 cm^{-1}; ^1H NMR[12] δ 5.07–4.94 (2H, m), 3.32 (1H, m), 3.23 (~0.5H, s), 3.22 (~0.5H, s), 2.41–2.31 (2H, m), 2.20 (1H, m), 2.08 (1H, dd, J = 2.3, 18.5 Hz), 1.96–1.53 (8H, m), 1.38–1.06 (6H, m), 1.13 (3H, s), 1.05 (1.5H, s), 1.04 (1.5H, s), 0.92 (3H, s), 0.91 (3H, s), 0.882 (3H, s), 0.878 (3H, s), 0.87 (3H, s), 0.86 (1.5H, s), 0.84 (1.5H, s); ^{13}C NMR δ 209.0/208.9 (0), 165.8 (2C, 0), 164.5 (2C, 0), 142.8/142.6 (0), 134.4/134.1 (0), 81.25/81.20/81.1/81.0 (1), 62.4/62.3 (1), 48.92/48.89/48.83 (4C, 0), 47.81 (4C, 0), 44.71/44.66 (4C, 1), 39.8/39.7 (2), 37.4/37.3 (2), 36.6/36.22/36.17 (4C, 2), 35.6/35.52 (0), 35.48/35.3 (1), 30.4 (2C, 3), 29.7/29.6 (3), 27.927.8 (4C, 2), 27.1 (4C, 2), 19.6 (4C, 3), 18.7 (4C, 3), 13.50/13.46 (4C, 3); MS 510 (0.6, M^+), 374 (7), 238 (23), 153 (8), 138 (33), 137 (100), 136 (19), 109 (12), 95 (21), 81 (80), 69 (20); HRMS calcd for $C_{32}H_{46}O_5$ 510.3343, found 510.3325.

Dibornyl 8,8-dimethylbicyclo[2.2.2]oct-5-en-2-one-5,6-dicarboxylate (10a/b).

A solution of **3a** (0.122 g, 0.622 mmol) and **4** (1.35 g, 3.49 mmol) in benzene (25 mL) was heated at reflux for 6 days. Treatment as for **8a/b** provided **10a/b**, a 1.03:1 mixture of diastereomers, as a white solid (0.104 g, 33%) and **11** (0.050 g, 18%). For **10a/b**: mp 177–178 °C; IR 2957, 2875, 1731, 1712, 1639, 1454, 1267 cm^{-1}; ^1H NMR[12] δ 5.10–4.94 (2H, m), 3.51 (1H, m), 2.90 (~0.5H, t, J = 2.5 Hz), 2.88 (~0.5H, t, J = 2.6 Hz), 2.49 (1H, dd, J = 2.3, 19.0 Hz), 2.46–2.31 (2H, m), 2.12 (1H, dd, J = 2.7, 19.0 Hz), 1.92–1.61 (8H, m), 1.40–1.03 (6H, m), 1.18 (3H, s), 1.10 (1.5H, s), 1.09 (1.5H, s), 0.93 (3H, s), 0.91 (3H, s), 0.89 (3H, s), 0.88–0.86 (6H, m), 0.85 (3H, s); ^{13}C NMR δ 209.3/209.2 (0), 166.2 (2C, 0), 164.4 (2C, 0), 145.3/145.0 (0), 133.1/132.8 (0), 81.4/81.3/81.2/81.1 (1), 51.4/51.2 (1), 49.0/48.9 (4C, 0), 47.9/47.8 (4C, 0), 47.3/47.1 (1), 44.8 (4C, 1), 38.8/38.7 (2), 36.5/36.4/36.30/36.26 (2), 35.5/35.4 (2), 34.3 (2C, 0), 31.6/31.5 (3), 28.2 (2C, 3), 27.91/27.86 (4C, 2), 27.21/27.17 (4C, 2), 19.6 (4C, 3), 18.8 (4C, 3), 13.5 (4C,

3); MS 510 (0.3, M^+), 374 (6), 238 (20), 138 (24), 137 (100), 136 (13), 95 (23), 81 (76), 69 (24); HRMS calcd for $C_{22}H_{30}O_5$ ($M^+ - C_{10}H_{16}$) 374.2092, found 374.2084.

Bis(O-methylpodocarpinyl) acetylenedicarboxylate (12).

Following the same procedure as for **4**, diethyl acetylenedicarboxylate (0.276 g, 0.260 mL, 1.62 mmol), *O*-methylpodocarpol (2.02 g, 7.36 mmol) and *p*TsOH•H_2O (0.0236 g, 0.124 mmol) provided **12** as a colorless solid (0.905 g, 89%); mp 65–67 °C; IR 2930, 1720, 1610, 1574 (w), 1502, 1469, 1376 (w), 1248, 1044, 788 cm^{-1}; ^1H NMR δ 6.96 (2H, d, J = 8.4 Hz), 6.80 (2H, d, J = 2.6 Hz), 6.67 (2H, dd, J = 2.6, 8.4 Hz), 4.53 (2H, d, J = 11.0 Hz), 4.15 (2H, d, J = 11.4 Hz), 3.77 (6H, s), 2.95–2.71 (4H, m), 2.35–2.25 (2H, symmetrical m), 2.04–1.94 (2H, m), 1.88–1.39 (12H, m), 1.20 (6H, s), 1.18–1.05 (2H, m), 1.08 (6H, s); ^{13}C NMR δ 157.8 (0), 152.2 (0), 150.4 (0), 129.8 (1), 126.8 (0), 111.1 (1), 110.2 (1), 74.9 (0), 69.5 (2), 55.2 (3), 51.1 (1), 38.6 (2), 37.8 (0), 37.3 (0), 35.6 (2), 29.9 (2), 27.1 (3), 25.6 (3), 19.2 (2), 18.8 (3); MS 626 (27, M^+), 625 (65), 370 (2), 369 (3), 257 (6), 256 (11), 255 (8), 243 (4), 242 (9), 241 (38), 199 (12), 187 (18), 185 (24), 175 (14), 174 (18), 173 (39), 172 (15), 171 (27), 162 (14), 161 (100), 159 (23), 158 (11), 148 (7), 147 (53), 135 (13), 134 (12), 121 (34), 95 (12), 91 (9), 83 (11), 81 (15), 69 (11), 55 (27).

*Bis[O-methylpodocarpinyl] 7,7-dimethyl-5-(*tert*-butyldimethylsilyloxy)bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate (13a/b).*

A solution of **3b** (0.328 g, 1.38 mmol) and **12** (0.164 g, 0.262 mmol) in benzene (3.5 mL) was heated at reflux for 9 days. The solution was concentrated under vacuum, and chromatography, with elution by an increasing proportion of Et_2O in light petroleum ether, provided **13a/b** (0.127 g, 56%) as a colorless oil and **14** (0.040 g, 19%) as a viscous yellow oil. For **13a/b**: IR 2931, 1712, 1650, 1631, 1610, 1502, 1470, 1260, 1249 cm^{-1}; ^1H NMR[12] δ 6.95 (2H, d, J = 8.4 Hz), 6.80 (2H, d, J = 2.3 Hz), 6.66 (2H, dd, J = 2.5, 8.4 Hz), 5.16 (1H, symmetrical m), 4.50–4.40 (2H, m), 4.15–4.05 (2H, symmetrical m), 3.76 (6H, s), 3.52 (1H, m), 3.29 (~0.5H, d, J = 6.6 Hz), 3.26 (~0.5H, d, J = 6.6 Hz), 2.94–2.70 (4H, m), 2.34–2.24 (2H, m), 2.05–1.27 (16H, m), 1.22 (6H, s), 1.17 (3H, s), 1.08–0.82 (11H, m), 0.92 (4.5H, s), 0.91 (4.5H, s), 0.139 (3H, s), 0.136 (3H, s); ^{13}C NMR (*a* and *b* refer to signals of the same diastereomer, as determined from samples enriched in one isomer or the other) δ 166.7*a*/166.5*b* (0), 166.1*b*/166.0*a* (0), 158.8*a*/158.6*b* (0), 157.7 (4C, 0), 150.6 (4C, 0), 145.8*a*/145.5*b* (0), 140.4*b*/139.9*a* (0), 129.8 (4C, 1), 126.9 (4C, 0), 111.0 (4C, 1), 110.2/110.1 (4C, 1), 103.9*b*/103.8*a* (1), 67.5/67.3 (4C, 2), 55.2 (4C, 3), 51.2 (4C, 1), 51.2/51.1 (1), 46.4*b*/46.3*a* (1), 40.1 (2C, 2), 39.1 (2C, 0), 38.7 (4C, 2), 37.9 (4C, 0), 37.46*b*/37.41*a*/37.36 (4C, 0), 35.96*b*/35.90*a*/35.86*a*/35.8*b* (2), 30.8/30.6 (3), 30.06/30.02/29.97 (4C, 2), 27.7/27.34/27.30 (6C, 3), 25.6 (10C, 3), 19.34*b*/19.29*a*/19.25*a*/19.21*b* (2), 18.9 (4C, 2), 18.0 (2C, 0), -4.5 /-4.6 (4C, 3); MS 553 (0.9), 552 (2), 297 (5), 280 (3), 279 (16), 274 (3), 273 (4), 257 (33), 256 (87), 255 (20), 254 (8), 241 (16), 221 (8), 187 (9), 186 (8), 185 (27), 175 (15), 174 (21), 173 (23), 172 (10), 171 (11), 162 (12), 161 (100), 159 (10), 147 (25), 121 (13), 83 (9), 69 (8), 55 (19).

*For bis[O-methylpodocarpinyl] 4-(*tert*-butyldimethylsilyloxy)phthalate (14):* IR 2930, 1723, 1605, 1573, 1502, 1471, 1263 cm^{-1}; ^1H NMR δ 7.73 (1H, d, J = 8.5 Hz), 7.04 (1H, d, J = 2.4 Hz), 6.96 (2H, d, J = 8.4 Hz), 6.94 (1H, dd, J = 2.4, 8.5 Hz), 6.82 (2H, symmetrical m), 6.67 (2H, dd, J = 2.6, 8.4 Hz), 4.58 (1H, d, J = 10.8 Hz), 4.54 (1H, d, J = 10.7 Hz), 4.22 (1H, d, J =11.4 Hz), 4.18 (1H, d, J =11.2 Hz), 3.78 (6H, s), 2.96–2.71 (4H, m), 2.35–2.26 (2H, m), 2.07–1.38 (14H, m), 1.26 (3H, s), 1.24 (3H, s), 1.18–0.95 (2H, m), 1.11 (3H, s), 1.09 (3H, s), 0.99 (9H, s), 0.24 (6H, s); ^{13}C NMR δ 168.2 (0), 166.7 (0), 158.5 (0), 157.7 (2C, 0), 150.7 (2C, 0), 135.9 (0), 131.2 (1), 129.8 (2C, 1), 127.0 (2C, 0), 123.7 (0), 121.5 (1), 119.9 (1), 111.0 (2C, 1), 110.2 (2C, 1), 68.3 (2), 68.2 (2), 55.2 (2C, 3), 51.3 (2C, 1), 38.7 (2C, 2), 37.9 (2C, 0), 37.5 (0), 37.4 (0), 36.0 (2C, 2), 30.1 (2C, 2), 27.5 (3), 27.4 (3), 25.7 (2C, 3), 25.6 (3C, 3), 19.3 (2C, 2), 19.0 (2C, 2), 18.2 (0), -4.4 (2C, 3); MS 552 (1, M^+ – 256), 297 (4), 279 (16), 274 (6), 273 (4), 257 (31),

256 (85), 255 (20), 254 (8), 241 (18), 221 (15), 187 (10), 185 (25), 175 (14), 174 (20), 173 (24), 172 (10), 171 (11), 161 (100), 159 (11), 147 (26), 121 (16), 55 (19).

Dimenthyl acetylenedicarboxylate (15).

Following the same procedure as for **4**, diethyl acetylenedicarboxylate (2.45 g, 2.30 mL, 14.4 mmol), (1*R*,2*S*,5*R*)-(-)-menthol (10.0 g, 64.3 mmol) and *p*TsOH•H_2O (0.251 g, 1.32 mmol) gave **15** as a colorless solid (5.40 g, 96%): mp 135–136 °C; IR 2960, 2924, 1712, 1263 cm^{-1}; ^1H NMR δ 4.84 (2H, ddd, *J* = 4.5, 10.8, 11.0 Hz), 2.06–1.99 (2H, m), 1.98–1.82 (2H, doublet of septets, *J* = 2.7, 7.0 Hz), 1.75–1.64 (4H, m), 1.56–1.39 (4H, m), 1.14–0.97 (4H, m), 0.92 (6H, d, *J* = 6.6 Hz), 0.91–0.84 (2H, m), 0.91 (6H, d, *J* = 6.9 Hz), 0.76 (6H, d, *J* = 7.0 Hz); ^{13}C NMR δ 151.6 (0), 77.5 (1), 74.8 (0), 46.7 (1), 40.4 (2), 33.9 (2), 31.4 (1), 26.0 (1), 23.1 (2), 21.9 (3), 20.7 (3), 16.0 (3); MS no M^+, 155 (1), 139 (27), 138 (97), 137 (7), 124 (4), 123 (40), 97 (14), 96 (27), 95 (100), 83 (71), 82 (30), 81 (80), 69 (40), 67 (19), 57 (29), 55 (54). Anal. calcd for $C_{24}H_{38}O_4$ C 73.79, H 9.81; found C 73.87, H 9.75.

Dimenthyl 2-oxobicyclo[2.2.2]oct-5-ene-5,6-dicarboxylate (19a/b).

A solution of **1** (0.254 g, 1.51 mmol) and **15** (3.00 g, 7.68 mmol) in benzene (40 mL) was heated at reflux for 27 h. Evaporation of much of the solvent under vacuum followed by addition of a small amount of pentane precipitated some of the excess dienophile. Repeated chromatography gave the hydrolyzed adduct **19a/b**, a 1.22:1 mixture of diastereomers, as a pale yellow oil (0.461 g, 63%) and **22** (0.069 g, 10%). For **19a/b**: IR 2956, 2871, 1731, 1713, 1639, 1454, 1377, 1263 cm^{-1}; ^1H NMR[12] δ 4.87–4.74 (2H, m), 3.60 (1H, m), 3.37 (1H, m), 2.25–1.37 (18H, m), 1.17–0.81 (18H, m), 0.80 (1.5H, d, *J* = 7.1 Hz), 0.79 (1.5H, d, *J* = 7.1 Hz), 0.77 (3H, *J* = 7.1 Hz); ^{13}C NMR δ 209.12/209.07 (0), 165.2/165.1 (0), 163.7 (2C, 0), 143.3/143.1 (0), 134.0/133.7 (0), 75.60/75.56/75.5 (4C, 1), 49.6 (2C, 1), 46.8/46.74/46.70 (4C, 1), 40.6/40.5 (2), 39.0 (2C, 2), 35.10/35.06 (1), 34.1 (4C, 2), 31.3 (4C, 1), 26.13 /26.08/26.0/25.9 (1), 24.0/23.9 (2), 23.3/23.2 (4C, 2), 22.73/22.69 (2), 22.0 (4C, 3), 20.8/20.7 (4C, 3), 16.2/16.1 (4C, 3); MS no M^+, 348 (4), 211 (14), 210 (100), 192 (24), 151 (6), 139 (23), 138 (4), 123 (7), 97 (10), 95 (10), 85 (17), 83 (93), 81 (13), 69 (25), 57 (23), 55 (32); HRMS calcd for $C_{20}H_{28}O_5$ ($M^+ - C_{10}H_{18}$) 348.1935, found 348.1929.

For dimenthyl 4-hydroxyphthalate (22): mp 175–176 °C; IR 3361 (br), 2956, 1710, 1603, 1580, 1455, 1277 (br), 1128 cm^{-1}; ^1H NMR δ 7.70 (1H, d, *J* = 8.5 Hz), 6.97 (1H, d, *J* = 2.6 Hz), 6.88 (1H, dd, *J* = 2.7, 8.5 Hz), 6.40 (1H, br m, OH), 4.91 (2H, apparent dq, *J* = 4.2, 11.1 Hz), 2.25 (1H, m), 2.12 (1H, m), 2.03–1.89 (2H, symmetrical m), 1.84–1.37 (8H, m), 1.20–0.85 (6H, m), 0.93 (3H, d, *J* = 6.4 Hz), 0.92 (3H, d, *J* = 6.7 Hz), 0.90 (3H, d, *J* = 7.1 Hz), 0.89 (3H, d, *J* = 7.3 Hz), 0.83 (3H, d, *J* = 6.9 Hz), 0.79 (3H, d, *J* = 7.0 Hz); ^{13}C NMR δ 168.4 (0), 165.9 (0), 158.7 (0), 136.6 (0), 131.6 (1), 122.7 (0), 116.8 (1), 115.3 (1), 76.0 (1), 75.2 (1), 47.1 (2C, 1), 40.7 (2), 40.3 (2), 34.3 (2C, 2), 31.5 (2C, 1), 26.2 (1), 26.0 (1), 23.4 (2), 23.3 (2), 22.1 (2C, 3), 20.9 (2C, 3), 16.4 (3), 16.2 (3); MS no M^+, 321 (3), 184 (9), 183 (100), 166 (9), 165 (63), 139 (18), 138 (38), 123 (15), 97 (12), 96 (11), 95 (47), 83 (30), 82 (14), 81 (34), 69 (33), 67 (11), 57 (23), 55 (42). Anal. calcd for $C_{28}H_{42}O_5$ C 73.31, H 9.24; found C 73.37, H 9.17.

Dimenthyl 7,7-dimethyl-2-oxobicyclo[2.2.2]oct-5-ene-5,6-dicarboxylate (20a/b).

A solution of **2** (0.228 g, 1.16 mmol) and **15** (3.17 g, 8.12 mmol) in benzene (40 mL) was heated at reflux for 30 h. Evaporation of much of the solvent under vacuum followed by addition of a small amount of pentane precipitated some of the excess dienophile. Chromatography on silica gel and then on Florisil gave **20a/b**, a 1.02:1 mixture of diastereomers, as a colorless oil (0.401 g, 67%) and **22** (0.034 g, 6%). For **21a/b**: IR 2956, 2871, 1736, 1713, 1657, 1265, 1238 cm^{-1}; ^1H NMR[12] δ 4.86–4.73 (2H, m), 3.27 (1H, m), 3.22 (0.5 H, s), 3.19 (0.5H, s), 2.23–1.99 (4H, m), 1.96–1.78 (2H, m), 1.75–1.36 (10H, m), 1.11–0.82 (18H, m), 1.11 (3H, s), 1.00 (1.5H, s), 0.99 (1.5H, s), 0.79 (3H, d, *J* = 6.9 Hz), 0.75 (3H, d, *J* = 6.9 Hz); ^{13}C NMR δ 209.2/209.1 (0), 165.5/165.4 (0), 163.83/163.78 (0), 142.9/142.8 (0), 133.8/133.4 (0), 75.44/75.41/75.3 (4C, 1), 62.2/61.9 (1), 46.8/46.74/46.72 (4C, 1), 40.5 (4C, 2), 39.7 (2C, 2), 37.44/37.37 (2), 35.6/

35.38 (1), 35.5/35.43 (0), 34.1 (4C, 2), 31.3 (4C, 1), 30.4 (2C, 3), 29.6/29.4 (3), 26.3/26.2/25.9/25.8 (1), 23.5/23.4/23.0 (4C, 2), 22.0 (4C, 3), 20.8/20.6 (4C, 3), 16.4/16.0 (4C, 3); MS 515 (0.3, $M^+ + 1$), 377 (4), 376 (15), 240 (8), 239 (57), 238 (100), 222 (4), 221 (19), 220 (98), 179 (12), 178 (19), 139 (56), 138 (15), 123 (8), 97 (27), 95 (29), 84 (13), 83 (100), 81 (33), 69 (69), 67 (11), 57 (60); HRMS calcd for $C_{22}H_{32}O_5$ ($M^+ - C_{10}H_{18}$) 376.2248, found 376.2221.

*Dimenthyl 8,8-dimethyl-2-oxobicyclo[2.2.2]oct-5-ene-5,6-dicarboxylate (**21a/b**).*

A solution of **3a** (0.155 g, 0.787 mmol) and **15** (2.22 g, 5.68 mmol) in benzene (40 mL) was heated at reflux for 5 days. Evaporation of much of the solvent under vacuum followed by addition of a small amount of pentane precipitated some of the excess dienophile. Repeated chromatography gave **21a/b**, a 1.45:1 mixture of diastereomers, as a colorless oil (0.145 g, 36%) and **22** (0.044 g, 12%). For **21a/b**: IR 2956, 2871, 1734, 1712, 1639, 1265, 1240 cm^{-1}; ^1H NMR[12] δ 4.88-4.74 (2H, m), 3.45 (1H, m), 2.90 (~0.4H, t, J = 2.7 Hz), 2.85 (~0.6H, t, J = 2.7 Hz), 2.47 (1H, dd, J = 2.7, 18.9 Hz), 2.16–2.03 (3H, m), 1.96–1.79 (2H, symmetrical m), 1.79–1.35 (10H, m), 1.16 (3H, s), 1.14–0.87 (18H, m), 1.06 (3H, s), 0.80–0.75 (6H, m); ^{13}C NMR δ 209.5/209.4 (0), 165.4/165.3 (0), 164.2/164.0 (0), 144.4/143.9 (0), 133.6/133.2 (0), 75.61/75.57/75.5/75.4 (1), 51.6/51.2 (1), 47.0/46.9/46.80/46.76/46.7 (6C, 1), 40.6/40.5/40.4 (4C, 2), 38.7 (2C, 1), 35.5/35.4 (2), 34.14 (4C, 2), 34.08 (2C, 0), 31.5/31.4/31.3 (6C), 28.2 (2C, 3), 26.3/26.0/25.9 (4C, 1), 23.6/23.3/23.2/23.1 (2), 22.0 (4C, 3), 20.8/20.6 (3), 16.5/16.3/16.1/16.0 (3); MS 515 (0.1, $M^+ + 1$), 377 (1), 376 (4), 239 (15), 238 (100), 221 (4), 220 (26), 179 (5), 139 (17), 138 (5), 123 (3), 97 (10), 95 (12), 83 (51), 81 (10), 69 (21), 57 (19), 55 (34); HRMS calcd for $C_{22}H_{32}O_5$ ($M^+ - C_{10}H_{18}$) 376.2248, found 376.2251.

*Bis(phenylmenthyl) acetylenedicarboxylate (**23**).*

A solution of diethyl acetylenedicarboxylate (93.5 mg, 0.550 mmol), (1*R*,2*S*,5*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexanol (44.8 mg, 1.93 mmol; prepared from (*R*)-pulegone as described by Ort[13]) and *p*TsOH•H_2O (18 mg, 0.095 mmol) in benzene (15 mL) was maintained at 70 °C for 14 days. Chromatography provided **23** as a yellow oil (11.1 mg, 4%): IR 2955, 1715, 1257, 1028 cm^{-1}; ^1H NMR δ 7.33–7.25 (8H, m), 7.15 (2H, m), 4.90 (2H, dt, J = 4.4, 10.7 Hz), 2.04–1.86 (4H, m), 1.66–1.32 (6H, m), 1.34 (6H, s), 1.27 (6H, s), 1.20–0.75 (6H, m), 0.88 (6H, d, J = 6.5 Hz); ^{13}C NMR δ 151.2 (0), 150.3 (0), 128.1 (1), 125.5 (1), 125.4 (1), 77.6 (1), 74.6 (0), 50.5 (1), 41.3 (2), 39.8 (0), 34.2 (2), 31.4 (1), 26.7 (3), 21.7 (3); MS 542 (1, M^+), 423 (1), 327 (1), 215 (14), 214 (27), 119 (100), 118 (47), 105 (47), 91 (33).

*Dimenthyl (cis)-4-(tert-butyldimethylsilyloxy)-3,6-diisopropylcyclohexa-1,4-diene-1,2-dicarboxylate (**25a/b**).*

A solution of diene **24** (0.0466 g, 0.174 mmol) and **15** (0.308 g, 0.789 mmol) in CH_2Cl_2 (2.0 mL) was maintained at 1.28 GPa for 3 days. The solvent was removed using a stream of N_2. Chromatography provided **25a/b**, a 1.78:1 mixture of isomers, as a colorless oil (0.0277 g, 24%): ^1H NMR[12] δ 4.81-4.69 (3H, m), 3.18 (1H, m), 3.09–3.04 (0.65H, dd, J = 2.5, 6.2 Hz), 3.03–2.99 (0.35H, dd, J = 2.2, 6.1 Hz), 2.28–1.81 (6H, m), 1.74–1.24 (8H, m), 1.16–0.80 (39H, m), 0.80–0.72 (6H, m), 0.20 (3H, s), 0.18 (3H, s); ^{13}C NMR δ 168.6/168.3 (0), 166.6/165.8 (0), 151.5/150.4 (0), 142.4/138.9 (0), 135.3/131.3 (0), 99.9/98.7 (1), 75.1/74.9/74.7 (4C, 1), 47.2/47.1/47.0 (4C, 1), 46.5/46.3 (1), 45.4/45.2 (1), 40.6/40.5/40.4 /40.3 (2), 34.3/34.2 (4C, 2), 33.3/32.3/31.4/31.2/30.5 (8C, 1), 26.03/25.96/25.86/25.7/25.5 (10C), 23.7/23.3/23.0/22.8 (6C), 22.1 (4C, 3), 21.4/21.2/21.0/20.9/20.8 (6C, 3), 19.4 (2C, 3), 18.8/18.5/18.3/18.2 (4C), 16.3/15.8/15.7 (4C, 3), -4.2/-4.3 (4C, 3).

Aerial oxidation of **25a/b** rapidly gave *dimenthyl 3,6-diisopropyl-4-(tert-butyldimethylsilyloxy)phthalate (**26**)*: IR 2957, 1720, 1591, 1463, 1326, 1263, 1192, 830 cm^{-1}; ^1H NMR δ 6.77 (1H, s), 4.88–4.78 (2H, symmetrical m), 3.18 (1H, septet, J = 6.7 Hz), 2.93 (1H, septet, J = 7.0 Hz), 2.37–2.00 (4H, m), 1.75–1.36 (8H, m), 1.33 (3H, d, J = 7.0 Hz), 1.32 (3H, d, J = 6.9 Hz), 1.21 (3H, d, J = 7.2 Hz), 1.18 (3H, d, J = 7.2 Hz), 1.15–0.80 (6H, m), 1.03 (9H, s), 0.95 (3H, d, J = 6.7 Hz), 0.94 (3H, d, J = 6.5 Hz), 0.89 (3H, d, J = 7.1 Hz), 0.88 (3H, d, J = 7.1 Hz), 0.81 (3H, d, J = 6.9 Hz), 0.80 (3H, d, J = 7.0 Hz), 0.33 (3H, s), 0.32

(3H, s); ^{13}C NMR δ 169.1 (0), 168.4 (0), 156.3 (0), 145.7 (0), 135.4 (0), 131.9 (0), 123.0 (0), 116.7 (1), 76.0 (1), 75.8 (1), 46.9 (1), 46.8 (1), 40.5 (2), 40.0 (2), 34.2 (2C, 2), 31.5 (2C, 1), 31.1 (1), 30.3 (1), 26.2 (3C, 3), 25.5 (1), 25.2 (1), 24.3 (2C, 3), 24.0 (2C, 3), 23.0 (2), 22.8 (2), 22.1 (2C, 3), 21.0 (2C, 3), 20.8 (2C, 3), 20.6 (2C, 3), 18.8 (0), 16.1 (2C, 1), 15.6 (2C, 3), -3.6 (2C, 3); MS no M^+, 517 (0.5), 380 (10), 363 (43), 362 (59), 361 (22), 334 (23), 305 (100), 95 (18), 84 (27), 83 (53), 73 (43), 69 (31), 55 (47).

*Di-*tert*-butyl 3,6-diisopropyl-4-(*tert*-butyldimethylsilyloxy)-1,4-cyclohexadiene-1,2-dioate (**28**).*

A solution of diene **24** (0.0764 g, 0.285 mmol) and dienophile **27** (0.287 g, 1.27 mmol) in CH_2Cl_2 (2.0 mL) was maintained at 1.28 GPa for 24 h. Chromatography gave **28** (0.0276 g, 20%) as a yellow oil: IR 2961, 1721, 1680, 1473, 1393, 1367, 1255, 1156, 845 cm^{-1}; ^{1}H NMR δ 4.76 (1H, d, J = 4.1 Hz), 3.10 (1H, dt, J = 4.2, 6.2 Hz), 3.02 (1H, dd, J = 3.0, 6.2 Hz), 2.08 (1H, br m), 2.00 (1H, dd, J = 3.0, 7.0 Hz), 1.49 (18H, s), 1.07 (3H, d, J = 7.1 Hz), 0.98 (3H, d, J = 6.7 Hz), 0.97–0.94 (3H, m), 0.94 (9H, s), 0.86 (3H, d, J = 6.7 Hz), 0.19 (3H, s), 0.18 (3H, s); ^{13}C NMR δ 168.3 (0), 166.6 (0), 151.0 (0), 140.0 (0), 133.7 (0), 99.5 (1), 81.2 (0), 81.1 (0), 46.1 (1), 45.4 (1), 32.4 (1), 31.1 (1), 28.0 (6C, 3), 25.9 (3C, 3), 22.5 (3), 21.4 (3), 19.7 (3), 18.6 (2C, 3),18.1 (0), -4.3 (2C, 3); MS no M^+, 409 (0.2), 365 (5), 339 (5), 321 (5), 297 (35), 279 (100), 86 (17), 84 (26), 73 (32), 57 (63).

ACKNOWLEDGEMENT

We thank Dr. Robert H. Burnell (Université Laval) for methyl *O*-methylpodocarpate and Dr. Michael A. Kerr (Acadia University) for running the high pressure reactions. Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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