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Diazadiene-stabilized palladacyclopent-2-enes and the catalytic addition of various allylic systems to dimethyl acetylenedicarboxylate

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Abstract

With diazadiene (dad = RN=CR′–CR′=NR) as co-ligand the palladacyclopent-2-enes **3** formed by direct coupling of a 1-alkene and an acetylenedicarboxylic acid ester can be trapped. With activated 1-alkenes such as allylic alcohols the reaction becomes catalytic, yielding linear addition-products **4–11** from two molecules of the alkene and one molecule of the alkyne; no simple reductive elimination occurs, but instead elimination of one mole of water takes place. Allylic esters react analogously but a cyclic 1 : 2-addition-product **15** (also formed by loss of the leaving group) is the main product. The elimination of the leaving group is probably the driving force of the reaction, since only β-H-transfers that make elimination possible are observed.

Introduction

From the diazadiene (dad = RN=CR′–CR′=NR) stabilized palladacyclopentadienes **1** a (dad)Pd^0 fragment capable of initiating various catalytic reactions is set free upon addition of an unsaturated substrate. We previously described the use of catalyst precursors **1** in the co-cyclotrimerisation of several alkynes to form benzene derivatives with various substitution patterns and also a cyclooctatetraene derivative [1,2], and also the catalytic formation of naphthalene derivatives from allenes and an alkyne [3]. Cyclopentene and cyclooctadiene derivatives can be obtained catalytically from vinyl ethers and electron-deficient alkynes [4].

Diazadienes are chelating co-ligands with a small *trans*-effect and their ability to stabilize metallacycles is well documented [3,5]. We therefore decided to try to trap the intermediates in catalytic reactions by use of these ligands.

Using complexes containing triphenylphosphine and maleic anhydride as co-ligands Itoh et al. reported the palladium-catalyzed formation of linear addition-products **2** from two molecules of a 1-alkene and one molecule of dimethyl acetylenedicarboxylate (dmad) [6–8]. Cyclohexadiene derivatives were found as by-products, and palladacyclopent-2-enes and palladacyclohept-4-enes were sug-

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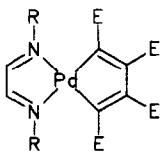
gested to be intermediates in the reaction. In this paper we describe the synthesis of stable palladacyclopent-2-enes and the catalytic formation of new 2:1 addition-products from various allylic systems and dmad.



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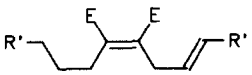


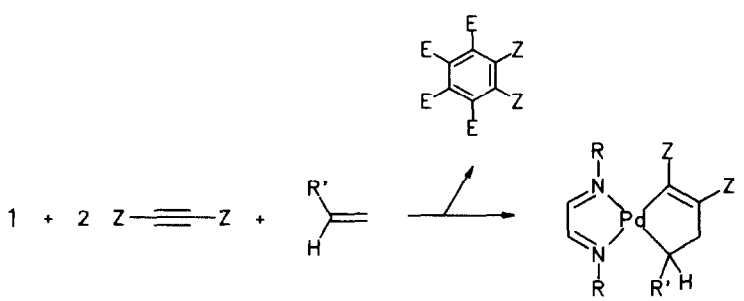
E = COOR"

2

Results and discussion

The palladacyclopent-2-enes **3** are formed very slowly at 40 °C from the palladacyclopentadienes **1** following addition of a 1-alkene and an acetylenedicarboxylic acid ester. When 1,4-hexadiene is the olefin used it reacts only as a 1-alkene and not at the internal double bond. Raising the temperature does not accelerate the reaction or lead to formation of any catalytic products.

Complexes **3** correspond with trapped intermediates from the Itoh-type catalysis since they are formed by direct coupling of the alkene and the alkyne. The question whether the alkyl group R′ is α or β to the metal could be answered by X-ray diffraction studies but single crystals could not be obtained from the powdery products. NMR spectra indicate that only one of the two possible isomers is formed. Comparison of the chemical shift of the methylene protons adjacent to the acetylenedicarboxylic acid ester moiety found in the catalytic products described



3

	R	R′	Z
3a	2,6-$Me_2C_6H_3$	n-butyl	$COOCH_3$
3b	2,6-$Me_2C_6H_3$	n-butyl	$COOCH_2CH_3$
3c	2,6-(^{i}Pr)$_2C_6H_3$	n-butyl	$COOCH_3$
3d	2,6-(^{i}Pr)$_2C_6H_3$	n-butyl	$COOCH_2CH_3$
3e	2,6-$Me_2C_6H_3$	$CH_2CH{=}CHCH_3$	$COOCH_3$
3f	2,6-(^{i}Pr)$_2C_6H_3$	$CH_2CH{=}CHCH_3$	$COOCH_3$
3g	2,6-(^{i}Pr)$_2C_6H_3$	$CH_2CH{=}CHCH_3$	$COOCH_2CH_3$

Scheme 1

Table 1

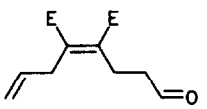
Yields (%) of linear 2:1-addition-products from allyl alcohol and dmad with catalyst precursors $L_2Pd(CE{=}CE{-}CE{=}CE)$ [a]

Fixed ligand L_2	4	5	6
dad			
(R = 2,6-(^{i}Pr)$_2$C$_6$H$_3$)	50	15	traces
tmeda	45	15	20
bipy	60	5	5
$(PPh_3)_2$	70	traces	5

[a] Catalyst : dmad : allyl alcohol = 1 : 50 : 500 in toluene; at 70 °C for 2 days (dad and PPh_3); at 100 °C for 1 week (tmeda); at 100 °C for 2 weeks (bipy).

later with the observed chemical shift of the methylene protons in the complexes **3** indicates that the α-position of the alkyl group is very likely.

Complexes **3** are stable in the presence of a normal alkene and dmad but the reaction becomes catalytic when 1-alkenes such as allylic alcohols and related species are used. Allyl alcohol itself and dmad give rise to three linear 2:1-addition-products **4**, **5** and **6**. During the reaction water is eliminated, giving a dienal as the main product along with two trienols. The product ratios are somewhat different when L_2Pd-type catalysts with ligands other than diazadiene are employed. Table 1 shows the yields of products arising from catalysis by various known $L_2Pd(CE{=}CE{-}CE{=}CE)$ complexes which were prepared as previously described [9].



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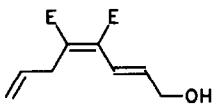

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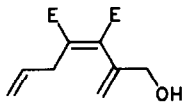

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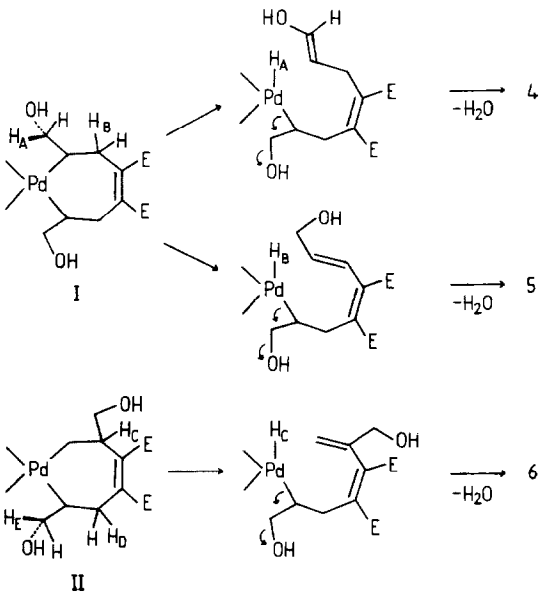
The reaction proceeds, as postulated by Itoh, via a palladacyclopent-2-ene analogous to **3** which undergoes insertion of a second molecule of allylic alcohol into the vinyl-palladium bond to yield a palladacyclohept-4-ene. Two possible orientations of the incoming allylic alcohol molecule give rise to two isomers I and II. In palladacyclohept-4-ene I there are two hydrogen atoms, H_A and H_B, β to the metal that can be transferred, to yield products **4** and **5**, respectively, by water elimination. β-H-transfer from the side chain is strongly favoured, as indicated by yields given in Table 1. This is in agreement with Itoh's observation that there was no β-H-transfer from the ring when triphenylphosphine was used as the fixed ligand, the ligand that also gives the highest yield of **4**. During the reaction leading to **5**, since the palladacyclohept-4-ene is in a chair conformation, only the axial H_B is available for β-H-transfer to the metal and, thus, the situation at the generated double bond is strictly *trans*.

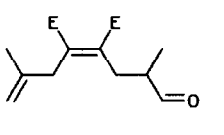
The regioisomer II has three hydrogen atoms, H_C, H_D and H_E, β to the metal, but only after transfer of H_C is subsequent water elimination possible, and this gives product **6**. Although transfer of H_E from the conformationally mobile side chain should be greatly favoured, as found by Oppolzer and Gaudin for a similar system [10], the corresponding catalytic product was never detected.



Scheme 2

Under the same conditions, when the diazadiene palladium catalyst is used, the substituted allylic alcohols 2-methyl-2-propene-1-ol and 3-butene-2-ol give linear products **7** and **8**, respectively, both of which are formed via exocyclic β-H-transfer. The yields are only moderate, the trimerisation of dmad to form mellitic acid hexamethyl ester **9** being the favoured reaction [1].

With 2-methyl-3-butene-2-ol and 2-phenyl-3-butene-2-ol no exocyclic β-H-transfer is possible since no H_A (see Scheme 2) is available. The system is forced to undergo transfer of H_B from the ring and products **10** and **11** are obtained. Again,



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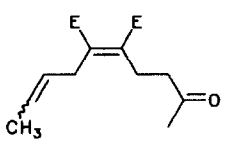

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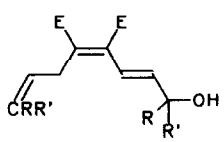
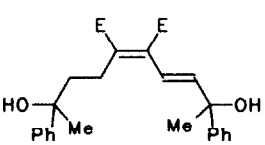


10 R, R' = Me
11 R = Me; R'= Ph



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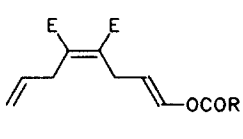
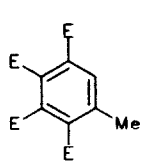


13 R = H
14 R = Me



15

yields are low, and **9** is the main product. With 2-phenyl-3-buten-2-ol a by-product, **12**, is also formed without elimination of water.

Allylic esters and dmad give **13** and **14** via exocyclic β-H-transfer and elimination of formic acid and acetic acid, respectively. A cyclic 1 : 2-addition-product **15** which is formed by elimination of the acid from an Itoh-type cyclohexadiene and subsequent 1,3-H-shift is the main product. This product, as well as Itoh's cyclohexadienes, might be formed either via the palladacyclopent-2-ene upon insertion of dmad [11] or by insertion of the alkene into the palladacyclopentadiene [7].

In the case of allylic chloride elimination of HCl occurs, and this converts any palladium species into inactive (dad)$PdCl_2$ and the reaction stops immediately. With 1-dimethylamino-2-propene the reaction is thought to be catalytic but the possible linear product is too unstable and quickly decomposes. The elimination product dimethylamine attacks the triple bond of the dmad non-catalytically to yield dimethylamino maleic acid dimethyl ester [12], which can be isolated from the mixture, indicating that a reaction has taken place.

Conclusions

With diazadiene as a co-ligand very stable palladacyclopent-2-enes that are not catalytically active are obtained from normal 1-alkenes and dmad. To get a catalytic reaction it is necessary to use activated olefinic compounds, especially those with potential leaving groups. The elimination of the leaving group is probably the driving force for the reaction, since in the case of palladacycloheptene II a very disfavoured β-H-transfer from the ring, which makes elimination possible, is the only observed reaction.

Experimental

All reactions were carried out under nitrogen. Chromatography was carried out in air with commerical grade eluents. IR spectra: Pye Unicam SP 1100; NMR spectra: Bruker WP80 SYFT and AM 360; mass spectra: Varian CH7. Microanalyses were performed by the analytical service of our institute on a Carlo Erba machine. $L_2\overline{Pd(CE{=}CE{-}CE{=}CE)}$ complexes were prepared as previously described [1,9]. All other starting materials were purchased.

Synthesis of palladacyclopent-2-enes (3).

A mixture of 0.2 mmol of **1**, 5 mmol of acetylenedicarboxylic acid ester, and 50 mmol of 1-hexene or 1,4-hexadiene was stirred in 20 ml of toluene at 40 °C for 1–2 weeks. The reaction was monitored by TLC with ether/hexane 4 : 1 as eluent. A considerable amount of **1** was still present after 2 weeks. **3** was isolated in 10–30% yield by column chromatography on silica gel 60 with ether/hexane as eluent.

5-n-Butyl-2,3-bis(carbomethoxy)-glyoxalbis(2,6-dimethylphenylimine)palladacyclopent-2-ene (3a). ^{1}H-NMR ($CDCl_3$): δ 8.24, 8.14 (2s, 2 H_{glyox}, 2H); 7.15 (m, H_{arom}, 6H); 3.47, 2.88 (2s, 2 $COOCH_3$, 6H); 2.70, 2.38 (2dd, CH_{2ring}, 2H); 2.31, 2.27, 2.26, 2.20 (4s, 4 $CH_{3ligand}$, 12H); 1.65 (m, CH, 1H); 1.16 (m, 3 CH_2, 6H); 0.82 (t, CH_3, 3H). IR (KBr): $\nu = 1695$ (C=O); 1210 (C–O) cm^{-1}. Analysis. Found: C, 59.76; H, 6.50; N, 5.50. $C_{30}H_{38}N_2O_4Pd$ (596.99) calc.: C, 60.35; H, 6.42; N, 4.69%. Similar data for **3b**, **3c** and **3d**.

*5-(2-Butenyl)-2,3-bis(carbomethoxy)-glyoxalbis(2,6-dimethylphenylimine)palladacyclopent-2-ene (**3e**).* ^{1}H-NMR ($CDCl_3$): δ 8.22, 8.13 (2s, 2 H_{glyox}, 2H); 7.14 (m, H_{arom}, 6H); 5.24 (m, HC=CH, 2H); 3.47, 2.88 (2s, 2 $COOCH_3$, 6H); 2.62, 2.44 (2dd, CH_{2ring}, 2H); 2.31, 2.27, 2.20 (3s, 4 $CH_{3ligand}$, 12H); 2.00 (m, CH_2, 2H); 1.55 (dd, CH_3, 3H); 1.37 (m, CH, 1H). IR (KBr): ν = 1695 (C=O); 1220 (C–O) cm^{-1}. Analysis. Found: C, 60.18; H, 6.11; N, 4.03. $C_{30}H_{36}N_2O_4Pd$ (594.98) calc.: C, 60.56; H, 6.10; N, 4.71%. Similar data for **3f** and **3g**.

Catalytic 2 : 1-addition of allylic systems to dimethyl acetylenedicarboxylate (dmad)

A solution of 0.1 mmol of **1**, 0.6 ml (5 mmoles) of dmad, and an excess (50 mmol) of the allylic compound in 20 ml of toluene was stirred at 70 °C for 2–4 days. When tmeda or bipy was used as the fixed ligand, the low solubility of the corresponding complexes meant that the mixture had to be heated at 100 °C for 1–2 weeks. The reaction was monitored by TLC. When no more dmad was detected the solvent was evaporated and the residue chromatographed on silica gel 60 with ether/hexane 4 : 1 as eluent. The catalyst partly decomposed during the reaction. All the linear 2 : 1-addition-products are slightly yellow oils.

Addition of allylic alcohol to dmad

Yields are given in Table 1. Products were eluted from the column in the sequence **6**, **4**, **5**.

*(4Z)-4,5-Bis(carbomethoxy)-4,7-octadiene-1-al (**4**).* ^{1}H-NMR ($CDCl_3$): δ 9.76 (s, $H_{aldehyde}$, 1H); 5.8 (m, CH, 1H, ^3J = 5.5 Hz, $^3J'$ = 9.3 Hz, $^3J''$ = 15.5 Hz); 5.08 (m, $=CH_2$, 2H); 3.75, 3.74 (2s, 2 $COOCH_3$, 6H); 3.15 (pseudo-dt, CH_2, 2H, $^4J \simeq 1.1$ Hz, $^4J' \simeq 0.9$ Hz); 2.65 (s_{br}, 2 CH_2, 4H). ^{13}C-NMR ($CDCl_3$): δ 218.8 ($C_{aldehyde}$); 168.9, 168.3 (2 C=O); 138.9, 134.7 (2 C_q–E); 133.2 (CH); 116.9 ($=CH_2$); 52.0 (2 OCH_3); 33.3, 30.5, 24.7 (3 CH_2). IR (film): ν = 1740, 1715 (C=O); 1635 (C=C); 1270–1210 (C–O) cm^{-1}. Analysis. Found: C, 59.13; H, 6.72. $C_{12}H_{16}O_5$ (240.24) calc.: C, 59.99; H, 6.71%.

*(2E,4Z)-4,5-Bis(carbomethoxy)-2,4,7-octatrien-1-ol (**5**).* ^{1}H-NMR ($CDCl_3$): δ 6.74 (dt, HC=CH, 1H, ^3J = 15.9 Hz, ^4J = 1.3 Hz); 6.07 (dt, HC=CH, 1H, $^3J'$ = 4.8 Hz); 5.8 (m, CH, 1H, ^3J = 5.5 Hz, $^3J'$ = 9.2 Hz, $^3J''$ = 15.6 Hz); 5.07 (m, $=CH_2$, 2H); 4.30 (dd, CH_2OH, 2H); 3.83, 3.75 (2s, 2 $COOCH_3$, 6H); 3.23 (pseudo-dt, CH_2, 2H, $^4J \simeq 1.2$ Hz, $^4J' \simeq 0.9$ Hz); 1.22 (s_{br}, OH, 1H). IR (film): ν = 3450 (OH); 1720 (C=O); 1640 (C=C); 1270–1210 (C–O) cm^{-1}.

*(3Z)-3,4-Bis(carbomethoxy)-2-methyliden-3,6-heptadien-1-ol (**6**).* ^{1}H-NMR ($CDCl_3$): δ 5.87 (t, $=CH_2$(1), 2H, $^4J \simeq 1.0$ Hz); 5.8 (m, CH, 1H, ^3J = 6.0 Hz, $^3J'$ = 9.5 Hz, $^3J''$ = 15.6 Hz); 5.25 (pseudo-t, CH_2OH, 2H, $^4J \simeq 1.0$ Hz); 5.10 (m, $=CH_2$(7), 2H); 3.82, 3.73 (2s, 2 $COOCH_3$, 6H); 3.10 (ddd, CH_2(5), 2H, ^4J = 1.1 Hz, $^4J'$ = 1.5 Hz); 1.23 (s_{br}, OH, 1H). ^{13}C-NMR ($CDCl_3$): δ 168.4, 165.3 (2 C=O); 147.6 (C_q); 136.4, 133.0 (2 C_q–E); 132.0 (CH); 120.8, 118.2 (2 $=CH_2$); 51.9, 51.5 (2 OCH_3); 37.9, 37.8 (2 CH_2). IR (film): ν = 3450 (OH); 1730 (C=O); 1645 (C=C); 1270–1210 (C–O) cm^{-1}. MS (70 eV): m/z (%) = 193 ($M^+ - OCH_3 - CH_4$; 3); 153 (52); 152 ($M^+ - OCH_3 - CH_4$ – allyl; 100); 143 (35); 124 ($M^+ - COOCH_3 - CH_3$ – allyl; 39); 113 (22); 101 (24); 96 (32); 93 (23); 79 (28); 71 (25); 66 (24); 65 (34); 59 ($COOCH_3$; 78); 55 (44); 53 (21).

Double addition of 2-methyl-2-propen-1-ol to dmad and 3-buten-2-ol to dmad

7 was obtained in 40% yield, and **8** in 26% yield. Mellitic acid hexamethyl ester **9** was the main product.

(4Z)-4,5-Bis(carbomethoxy)-2,7-dimethyl-4,7-octadien-1-al (7). ^{1}H-NMR ($CDCl_3$): δ 9.64 (d, $H_{aldehyde}$, 1H, $^3J = 0.7$ Hz); 4.82, 4.70 (2m, $=CH_2$, 2H); 3.75, 3.71 (2s, 2 $COOCH_3$, 6H); 3.10 (m, $CH_2(6)$, 2H); 2.88, 2.43 (2dd, $CH_2(3)$, 2H); 1.73 (s_{br}, CH_3, 3H); 1.70 (m, CH, 1H); 1.13 (d, CH_3, 3H, $^3J = 7.0$ Hz). ^{13}C-NMR ($CDCl_3$): δ 202.7 ($C_{aldehyde}$); 168.7, 164.9 (2 C=O); 144.1, 141.2, 137.6 (3 C_q); 112.5 ($=CH_2$); 52.7, 52.2 (2 OCH_3); 45.1 (CH); 37.4, 30.3 (2 CH_2); 22.7, 13.4 (2 CH_3). IR (film): $\nu = 1740$, 1710 (C=O); 1620 (C=C); 1210 (C–O) cm^{-1}.

5,6-Bis(carbomethoxy)-5,8-decadien-2-one (8), (5Z, 8Z)/(5Z, 8E)-mixture. ^{1}H-NMR ($CDCl_3$): δ 5.4 (m, HC=CH, 2H); 3.74, 3.73 (2s, 2 $COOCH_3$, 6H); 3.15 (d, $CH_2(7)$, 2H, $^3J = 6.9$ Hz); 2.61 (s_{br}, 2 CH_2, 4H); 2.14 (s, $C(O)CH_3$, 3H); 1.65 (d, CH_3, 3H, $^3J = 6.0$ Hz). ^{13}C-NMR ($CDCl_3$): δ 206.0 (C=O); 168.6 (2 C=O); 137.6, 136.3 (2 C_q–E); 126.5, 124.9 (2 CH); 52.2 (2 OCH_3); 41.5 ($CH_2(7)$); 29.8 ($CH_3(1)$); 27.5, 23.5 (2 CH_2); 12.8 ($CH_3(10)$). IR (film): $\nu = 1745$, 1730 (C=O); 1630 (C=C); 1260–1210 (C–O) cm^{-1}. MS (70 eV): m/z (%) = 268 (M^+; 1); 236 (17); 177 (17); 162 (23); 105 (15); 91 (17); 59 ($COOCH_3$; 15); 43 (100).

Mellitic acid hexamethyl ester (9). ^{1}H-NMR ($CDCl_3$): δ 3.88 (s, 6 $COOCH_3$, 18H). ^{13}C-NMR ($CDCl_3$): δ 165.0 (C=O); 133.8 (C_q); 53.3 (OCH_3).

Double addition of 2-methyl-3-buten-2-ol to dmad and 2-phenyl-3-buten-2-ol to dmad

10 was obtained in 24%, **11** in 10% and **12** in 11% yield. Mellitic acid hexamethyl ester **9** was the main product.

(3E,5Z)-5,6-Bis(carbomethoxy)-2,9-dimethyl-3,5,8-decatrien-2-ol (10). ^{1}H-NMR ($CDCl_3$): δ 6.62, 6.04 (2d, HC=CH, 2H, $^3J = 16.0$ Hz); 5.02 (m, CH, 1H, $^3J = 7.1$ Hz, $^4J \simeq 1.4$ Hz, $^4J' \simeq 0.8$ Hz); 3.84, 3.74 (2s, 2 $COOCH_3$, 6H); 3.16 (d, CH_2, 2H); 1.88 (s_{br}, OH, 1H); 1.70, 1.68 (2d, 2 CH_3, 6H); 1.35 (s, 2 CH_3, 6H). IR (film): $\nu = 3450$ (OH); 1740 (C=O); 1630 (C=C); 1210 (C–O) cm^{-1}. MS (70 eV): m/z (%) = 281 ($M^+ - CH_3$; 0.5); 181 (2); 169 (4); 148 (28); 133 (34); 119 (74); 105 (54); 55 (52); 43 (100).

5,6-Bis(carbomethoxy)-2,9-diphenyl-3,5,8-decatrien-2-ol (11). (3*E*,5*Z*,8*Z*)-isomer: ^{1}H-NMR ($CDCl_3$): δ 7.3 (m, H_{arom}, 10H); 6.68, 6.23 (2d, HC=CH, 2H, $^3J = 16.2$ Hz); 5.61 (m, CH, 1H, $^3J = 7.1$ Hz, $^4J \simeq 1.3$ Hz); 3.80, 3.73 (2s, 2 $COOCH_3$, 6H); 3.34 (d, CH_2, 2H); 2.41 (s_{br}, OH, 1H); 2.06 (d, CH_3, 3H); 1.67 (s, CH_3, 3H). (3*E*,5*Z*,8*E*)-isomer: ^{1}H-NMR ($CDCl_3$): δ 7.3 (m, H_{arom}, 10H); 6.40, 6.11 (d, HC=CH, 2H, $^3J = 16.2$ Hz); 5.40 (m, CH, 1H, $^3J = 7.1$ Hz, $^4J \simeq 1.3$ Hz); 3.85, 3.70 (2s, 2 $COOCH_3$, 6H); 3.18 (d, CH_2, 2H); 2.51 (s_{br}, OH, 1H); 2.05 (d, CH_3, 3H); 1.67 (s, CH_3, 3H). IR (film): $\nu = 3450$ (OH); 1730 (C=O); 1620 (C=C); 1270 (C–O) cm^{-1}.

(3E,5Z)-5,6-Bis(carbomethoxy)-2,9-diphenyl-3,5-decadiene-2,9-diol (12). ^{1}H-NMR ($CDCl_3$): δ 7.3 (m, H_{arom}, 10H); 6.52 (d, CH, 1H, $^3J = 15.9$ Hz); 6.22 (dd, CH, 1H, $^4J = 2.7$ Hz); 3.79, 3.72 (2s, 2 $COOCH_3$, 6H); 2.49, 2.26 (2m, CH_2, 2H, $^2J = 12.8$ Hz, $^3J = 11.7$ Hz, $^3J' = 4.6$ Hz); 1.96 (m, CH_2, 2H, $^2J = 14.4$ Hz); 1.78 (s_{br}, OH, 1H); 1.62 (s, CH_3, 3H); 1.50 (d, CH_3, 3H, $^4J = 2.7$ Hz); 1.29 (s_{br}, OH, 1H). ^{13}C-NMR ($CDCl_3$): δ 165.1 (2 C=O); 145.2 (2 C_q–E); 139.9 (2 $C_{q,Ph}$); 133.9 (CH); 128.4, 128.3 (4 C_{ortho}); 127.4, 126.7 (2 C_{para}); 125.3, 124.7 (4 C_{meta}); 120.7 (CH);

74.6, 74.4 (2 C_q); 53.4 (2 OCH_3); 43.0 (CH_2); 30.6, 29.6 (2 CH_3); 23.0 (CH_2). IR (film): ν = 3450 (OH); 1740 (C=O); 1620 (C=C); 1280 (C–O) cm^{-1}.

Addition of allylic esters to dmad

From allyl formate **13** was obtained in 30% yield and **15** in 40% yield. From allyl acetate the yield of the linear product **14** was 17%, that of **15** 80%.

(1E,4Z)-4,5-Bis(carbomethoxy)-1,4,7-octatrienyl formate (13). ^{1}H-NMR ($CDCl_3$): δ 8.10 (s, OOCH, 1H); 6.58 (dt, CH, 1H, ^3J = 15.9 Hz, ^4J = 0.7 Hz); 6.04 (dt, CH, 1H, ^3J = 7.9 Hz); 5.8 (m, CH, 1H, ^3J = 15.2 Hz, $^3J'$ = 9.6 Hz, $^3J''$ = 5.7 Hz); 5.09 (m, $=CH_2$, 2H, ^4J = 1.0 Hz); 4.80 (dd, CH_2, 2H); 3.86, 3.76 (2s, 2 $COOCH_3$, 6H); 3.23 (pseudo-dt, CH_2, 2H). IR (film): ν = 1740 (C=O); 1640, 1600 (C=C); 1270–1200 (C–O) cm^{-1}.

(1E,4Z)-4,5-Bis(carbomethoxy)-1,4,7-octatrienyl acetate (14). ^{1}H-NMR ($CDCl_3$): δ 6.59 (dt, CH, 1H, ^3J = 15.6 Hz, ^4J = 0.6 Hz); 6.05 (dt, CH, 1H, ^3J = 7.9 Hz); 5.7 (m, CH, 1H, ^3J = 15.4 Hz, $^3J'$ = 9.5 Hz, $^3J''$ = 5.7 Hz); 5.08 (m, $=CH_2$, 2H, ^4J = 1.0 Hz); 4.68 (dd, CH_2, 2H); 3.83, 3.74 (2s, 2 $COOCH_3$, 6H); 3.23 (pseudo-dt, CH_2, 2H); 2.07 (s, CH_3, 3H). IR (film): ν = 1735 (C=O); 1640, 1600 (C=C); 1270–1200 (C–O) cm^{-1}.

2,3,4,5-Tetrakis(carbomethoxy)-toluene (15). ^{1}H-NMR ($CDCl_3$): δ 7.93 (d, H_{arom}, 1H, ^4J = 0.5 Hz); 3.90, 3.85 (2s, 4 $COOCH_3$, 12H); 2.43 (d, CH_3, 3H). IR (KBr): ν = 1740 (C=O); 1250–1200 (C–O) cm^{-1}. Analysis. Found: C, 55.27; H, 5.30. $C_{15}H_{16}O_8$ (324.28) calc.: C, 55.56; H, 4.97%.

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