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The palladium-catalyzed addition of various vinyl compounds to dimethyl acetylenedicarboxylate

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Abstract

The catalyst precursor $L_2Pd(CE{=}CE{-}CE{=}CE)$ ($E = COOCH_3$) reacts with simple vinyl compounds and dimethyl acetylenedicarboxylate to give cyclic 1:2-, 2:1- and 2:2-addition products, namely substituted cyclohexadiene or benzene, cyclopentene and cyclooctadiene derivatives, which can be separated by column chromatography. Palladacyclopent-2-enes, palladacyclohepta-2,4-dienes and palladacyclohept-4-enes, which cannot be trapped, are suggested to be intermediates in the reaction. Different types of products are obtained depending on the nature of the vinyl compound: while α-methyl styrene gives only a cyclohexadiene species following 1:2-addition, vinyl ethers along with 1:2-addition undergo 2:1- and even 2:2-addition, and cyclopentene and 1,5-cyclooctadiene derivatives are formed. In the course of the reaction with vinyl ethers, alcohols are formed, probably in a reductive elimination step from Pd–H– intermediates in which an alkoxy group occupies a β-position and also in palladium-mediated aromatization of initially formed alkoxy cyclohexadiene and bisalkoxy cyclohexene products. Yields and product ratios can be influenced by changing the fixed ligand in the catalyst complex.

1. Introduction

The palladacyclopentadiene **1** which can be easily obtained from bis(dibenzylideneacetone)palladium by coupling of two molecules of dimethyl acetylenedicarboxylate (dmad) [1–4] is an effective catalyst precursor for the co-cyclization of various alkynes [5] and also promotes the cycloaddition of allenes to electron deficient alkynes to form 2,3,6,7-tetrasubstituted naphthalene derivatives [6–8]. Addition of dmad and a 1-alkene to a solution of **1** causes elimination of mellitic acid hexamethyl ester with subsequent coupling of the alkyne and the olefin to yield a palladacyclopent-2-ene **2**, and from various allylic systems and dmad, linear 2:1-addition products are formed catalytically [9]. The latter reaction, in particular which product is favoured, depends to some extent on the nature of the L_2 ligand system in the catalyst complex **1**, and so it is reasonable to assume that the ligand does not completely dissociate from the metal during the course of catalysis and that an L_2Pd^0 fragment can formally be regarded as the active catalyst. Furthermore, it should be possible to control to some extent the product selectivity by judicious choice of directing ligands. This paper presents the results of a study of the catalytic conversion of various vinyl systems and dmad into cyclic 1:2-, 2:1- and 2:2-addition products by various complexes of type **1** (see Fig. 1).

2. Results and discussion

When a solution of dmad in an excess of a vinyl compound is heated in the presence of a catalyst precursor **1**, the mixture becomes brown after a short induction period, and further heating affords various catalytic co-addition products depending on the nature of the vinyl compound. α-Methyl styrene, a non-activated olefin, gave only a cyclic 1:2-addition product **3**. (Some analogous 1,2,3,4-tetrakis(carbomethoxy)-cyclohexadienes were obtained previously by the same method by Itoh *et al.* [10–12].) With vinyl propionate, no cyclohexadiene was isolated but, instead, mellophanic acid tetramethyl ester **4** was obtained in good

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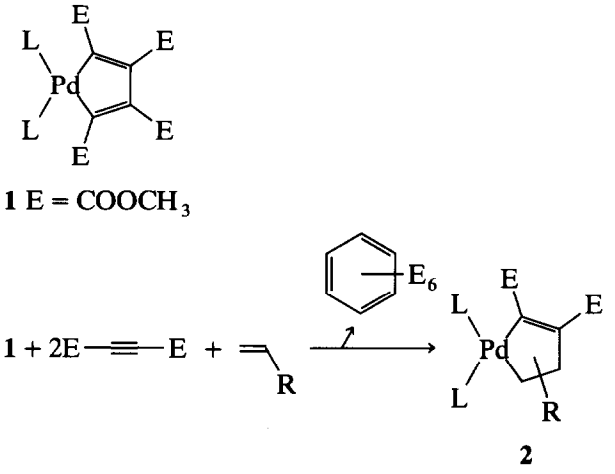


Fig. 1.

yield and propionic acid was detected. Analogously, vinyl ethers also gave **4**, and in the case of phenyl vinyl ether some phenol was isolated. We have good reason to believe that **4** is formed by palladium-induced elimination of propionic acid and alcohol from initially formed substituted cyclohexadienes; an earlier investigation showed that at somewhat elevated temperatures, a palladium complex was able to liberate 2 mol of methanol from a bismethoxytetrahydronaphthalene obtained via cycloaddition between methoxyallene and dmad promoted by the same complex at 0°C [7]. With vinyl esters and ethers, however, no cyclohexadiene systems were observed even at low temperatures. Product **3** and the precursors of **4** might be formed either via palladacyclopent-2-enes analogous to **2** upon insertion of dmad or by incorporation of the vinyl compound into the palladacyclopentadiene **1**. Both pathways result in the formation of palladacycloheptadiene

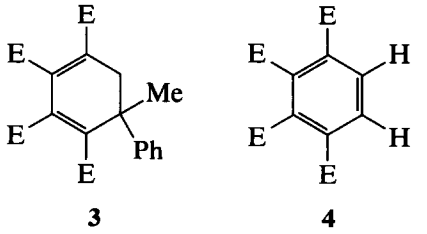


Fig. 2.

intermediates which release the cyclic 1:2-addition products (see Fig. 2).

Acid and alcohol can also be generated during the course of 2:1-addition. Consequently, vinyl propionate gives phthalic acid dimethyl ester **5** in moderate yield, probably by elimination of 2 mol of propionic acid from an initially formed cyclohexene derivative. Very small amounts of phthalic acid dimethyl ester are also obtained following 2:1-addition of vinyl ethers to dmad, along with the cyclopentenes **6** and **7** as the main products. Their formation can also be accounted for in terms of the intermediacy of a seven-membered palladacycle; insertion of the vinyl ether into the vinyl-palladium-bond of a palladacyclopent-2-ene could (by analogy with the reactions with allylic compounds [9]) yield a palladacyclohept-4-ene in which at least one ether group is in an equatorial β-position. Since there is no exocyclic β-hydrogen available, β-H-transfer of an axial methine hydrogen from the ring would then give a five coordinate Pd–H species in which the generated double bond is still coordinated to the metal. Such a complex could possibly rearrange to form a *trans*-annular bond between the α- and the β'-carbon atom, since this corresponds to the reaction step proposed for the isomerization of cyclooctadienes with a

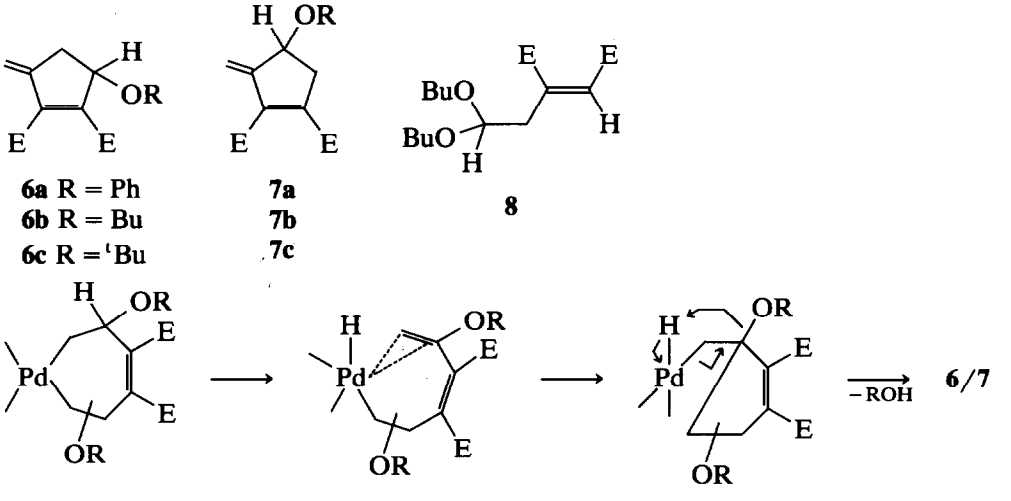
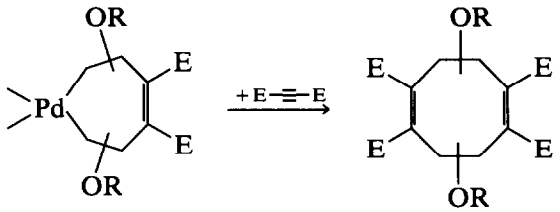


Fig. 3.



9a R = Ph
9b R = Bu
9c R = ^{t}Bu

Fig. 4.

hydrido nickel catalyst [13]. Elimination of alcohol is now possible, and **6** and **7** are set free.

In the case of butyl vinyl ether with triphenylphosphine as the controlling ligand, some of the eliminated 1-butanol seems to attack a 5-butoxy-palladacyclopent-2-ene intermediate and reductive elimination finally yields the acetal **8**, but most of the 1-butanol adds to the remaining butyl vinyl ether (present in excess) to give acetic aldehyde dibutyl acetal. With the other vinyl ethers examined, none of these side reactions were observed (see Fig. 3).

The reaction of vinyl ethers with dmad, besides 1:2- and 2:1-addition, results in 2:2-addition and gives the 1,5-cyclooctadienes **9**. Although there is no direct evidence, one can envisage that they might be formed via a palladacyclohept-4-ene upon incorporation of a second molecule of the very reactive dmad. Related palladacyclohept-4-enes that readily undergo β-H-transfer from a conformationally mobile side chain were suggested previously to be intermediates in other co-oligomerization reactions between 1-alkenes and dmad [9,14]. In the case of vinyl ethers, there is no exocyclic β-hydrogen, and the relative slowness of transfer of ring hydrogens could allow time for the complex to undergo a further insertion (see Fig. 4).

It can be seen from Table 1 that the product selectivities can in some cases depend on the L_2 ligand system as well as on the nature of the vinyl compound. The use of triphenylphosphine obviously increases the proportion of 2:1- and 2:2-addition products for every vinyl compound examined while use of diazadiene ligands (dad = RN=CR'–CR'=NR) gives rise to more mellophanic acid tetramethyl ester. The dad1-Pd-system shows a most remarkable effect: if dad1 is the fixed ligand in the catalyst complex, only one cyclopentene and two 3,8-bisalkoxy-cyclooctadienes are formed, indicating that the vinyl ether is incorporated both times in the same orientation. We think that electronic reasons (*e.g.* the basicity of the ligand) might account for this regioselectivity since, according to X-ray studies of some dad1-stabilized pallada- and platina-cycles [15], the steric demand of the diisopropylphenyl groups is only moderate, so that even large side chains can be in the α-position to the metal. The yields of 2:1- and 2:2-addition products are also determined by the nature of the vinyl system, and seem to be higher for electron rich vinyl ethers.

TABLE 1. Yields (%) of products arising from addition of vinyl compounds to dmad in the presence of catalyst precursors L_2Pd(CE=CE–CE=CE) [a]

Vinyl compound	Fixed ligand L_2	4	5	6	7	9	
CH_2=CHOCOC$_2$H$_5$	dad1 [b]	90	3	–	–	–	
	$(PPh_3)_2$	60	10	–	–	–	
CH_2=CHOPh	dad1 [b]	35	2	30	–	1	[d]
	dad2 [b]	50	1	4	6	1	
	$(PPh_3)_2$	10	4	20	30	18	
CH_2=CHOBu [c]	dad1 [b]	65	1	1	–	2	[d]
	$(PPh_3)_2$	50	1	2	1	3	
CH_2=CHO^{t}Bu	dad1 [b]	50	2	8	–	1	[d]
	$(PPh_3)_2$	40	2	15	15	5	
	dppe	40	1	8	8	3	

[a] Catalyst, dmad; vinyl compound = 1:50:5000; at 40°C for 3–5 days. [b] dad1 = glyoxalbis(2,6-diisopropylphenylimine); dad2 = biacetylbis(1-phenethylimine). [c] Additional product **8** in 5% yield. [d] Only 3,8-bisalkoxy derivatives.

3. Experimental details

All reactions were carried out under dinitrogen. Chromatographic work-up was carried out in air with commercial grade eluents. IR-spectra: Perkin-Elmer spectrograph 577; NMR-spectra: Bruker WP80 SYFT and AM360. Microanalyses were performed by the analytical service of our institute on a Carlo-Erba machine. Catalyst precursors L_2Pd(CE=CE–CE=CE) [1–4] were prepared by published methods. All other materials were purchased.

3.1. Addition of vinyl compounds to dmad

The catalyst precursor **1** (0.1 mmol) was dissolved in 500 mmol of the vinyl compound, 0.6 ml (5 mmol) of dmad was added and the mixture was stirred at 40°C for 3–5 days. When no more dmad was detected by TLC, the excess of the vinyl compound was evaporated off and the residue chromatographed on silica gel 60 with ether/hexane (1:1) as eluent. Compound **3** was crystallized from the residue by adding ether/hexane. Phenol was eluted first from the column in the case of phenyl vinyl ether, then the cyclopentene derivatives **6** and **7**, followed by phthalic acid dimethyl ester **5** and the cyclooctadienes **9**, and finally mellophanic acid tetramethyl ester **4**. Yields are given in Table 1.

3.1.1. 1,2,3,4-Tetrakis(carbomethoxy)-5-methyl-5-phenyl-cyclohexa-1,3-diene (3)

Yield 70%. ^{1}H NMR ($CDCl_3$): δ 7.32 (m, H_{arom}, 5H); 3.80, 3.76, 3.75, 3.73 (4s, $COOCH_3$, 12H); 3.13, 2.63 (2d, CH_2, 2H, $^2J = 17.5$ Hz); 1.67 (s, CH_3, 3H). IR (KBr): ν(C=O) 1730; ν(C–O) 1230 cm^{-1}.

3.1.2. Mellophanic acid tetramethyl ester (4)

^{1}H NMR ($CDCl_3$): δ 8.01 (s, H_{arom}, 2H); 3.91, 3.90 (2s, $COOCH_3$, 12H). ^{13}C-NMR ($CDCl_3$): δ 166.8, 165.3 (C=O); 133.4, 132.8 (C_q); 131.0 (CH); 53.0 (OCH_3).

3.1.3. 1,2-Bis(carbomethoxy)-3-methylen-5-phenoxy-cyclopent-1-ene (6a)

^{1}H NMR ($CDCl_3$): δ 7.28, 7.00, 6.89 (3m, H_{arom}, 5H); 5.59 (dd, CH, 1H, $^3J = 6.8$ Hz, $^3J' = 1.7$ Hz); 5.37 (t, $=CH_2$, 1H, $^4J = 2.3$ Hz); 5.28 (t, $=CH_2$, 1H, $^4J = 1.6$ Hz); 3.95, 3.80 (2s, $COOCH_3$, 6H); 3.12 (ddt, CH_2, 1H, $^2J = 17.2$ Hz); 2.75 (pseudo-dq, CH_2, 1H). ^{13}C NMR ($CDCl_3$): δ 165.2, 163.2 (C=O); 157.7 ($C_{q,Ph}$); 147.3, 146.2 (C_q–E); 137.4 (C_q); 129.5 (C_{meta}); 121.4 (C_{para}); 115.9 (C_{ortho}); 113.4 ($=CH_2$); 78.7 (CH); 52.5, 52.1 (OCH_3); 36.9 (CH_2). IR (KBr): ν (C=O) 1740, 1720; ν(C=C) 1630, 1600, 1590; ν(C–O) 1275, 1235 cm^{-1}. Anal. Found: C, 66.60; H, 5.60. $C_{16}H_{16}O_5$ (288.28) calcd.: C, 66.66; H, 5.59%; m.p. 93°C.

3.1.4. 1,2-Bis(carbomethoxy)-3-methylen-5-butoxy-cyclopent-1-ene (6b)

^{1}H-NMR ($CDCl_3$): δ 5.31 (t, $=CH_2$, 1H, $^4J = 2.2$ Hz); 5.25 (t, $=CH_2$, 1H, $^4J = 1.7$ Hz); 4.82 (dd, CH, 1H, $^3J = 6.8$ Hz, $^3J' = 2.2$ Hz); 3.90, 3.80 (2s, $COOCH_3$, 6H); 3.55, 3.48 (2dt, OCH_2, 2H); 2.94 (ddt, CH_{2ring}, 1H, $^2J = 17.0$ Hz); 2.59 (pseudo-dq, CH_{2ring}, 1H); 1.54, 1.41 (2m, CH_2, 4H); 0.96 (t, CH_3, 3H).

3.1.5. 1,2-Bis(carbomethoxy)-3-methylen-5-tert-butoxy-cyclopent-1-ene (6c)

^{1}H NMR ($CDCl_3$): δ 5.31 (t, $=CH_2$, 1H, $^4J = 2.4$ Hz); 5.18 (t, $=CH_2$, 1H, $^4J = 1.6$ Hz); 4.99 (dd, CH, 1H, $^3J = 7.0$ Hz, $^3J' = 2.2$ Hz); 3.80, 3.73 (2s, $COOCH_3$, 6H); 2.99 (ddt, CH_2, 1H, $^2J = 17.1$ Hz); 2.56 (pseudo-dq, CH_2, 1H); 1.31 (s, $C(CH_3)_3$, 9H).

3.1.6. 1,2-Bis(carbomethoxy)-3-methylen-4-phenoxy-cyclopent-1-ene (7a)

^{1}H-NMR ($CDCl_3$): δ 7.29, 6.98, 6.89 (3m, H_{arom}, 5H); 5.57 (m, $=CH_2$, 2H); 5.31 (m, CH, 1H, $^4J = 2.1$ Hz, $^4J' = 2.6$ Hz); 3.92, 3.78 (2s, $COOCH_3$, 6H); 3.22 (dd, CH_2, 1H, $^2J = 18.6$ Hz, $^3J = 7.0$ Hz); 2.83 (dd, CH_2, 1H, $^3J = 2.7$ Hz). ^{13}C NMR ($CDCl_3$): δ 165.1, 164.2 (C=O); 157.9 ($C_{q,Ph}$); 149.3, 142.4 (C_q–E); 136.6 (C_q); 129.7 (C_{meta}); 121.6 (C_{para}); 116.2 (C_{ortho}); 115.4 ($=CH_2$); 76.4 (CH); 52.4, 52.3 (OCH_3); 38.6 (CH_2).

3.1.7. 1,2-Bis(carbomethoxy)-3-methylen-4-butoxy-cyclopent-1-ene (7b)

^{1}H NMR ($CDCl_3$): δ 5.64 (m, $=CH_2$, 2H); 4.67 (m, CH, 1H); 3.88, 3.76 (2s, $COOCH_3$, 6H); 3.54, 3.46 (2dt, OCH_2, 2H); 2.98 (dd, CH_{2ring}, 1H, $^2J = 18.1$ Hz, $^3J = 7.1$ Hz); 2.72 (dd, CH_{2ring}, 1H, $^3J = 2.8$ Hz); 1.54, 1.41 (2m, CH_2, 4H); 0.96 (t, CH_3, 3H).

3.1.8. 1,2-Bis(carbomethoxy)-3-methylen-4-tert-butoxy-cyclopent-1-ene (7c)

^{1}H NMR ($CDCl_3$): δ 5.74 (m, $=CH_2$, 2H); 4.75 (m, CH, 1H); 3.84, 3.77 (2s, $COOCH_3$, 6H); 2.89 (dd, CH_2, 1H, $^3J = 6.9$ Hz, $^2J = 18.0$ Hz); 2.66 (dd, CH_2, 1H, $^3J = 2.4$ Hz); 1.22 (s, $C(CH_3)_3$, 9H).

3.1.9. (Z)-3,4-Bis(carbomethoxy)-but-3-enyl-1-aldehyde-dibutylacetal (8)

^{1}H NMR ($CDCl_3$): δ 6.76 (s, =C(E)H, 1H); 4.63 (t, CH, 1H, $^3J = 5.8$ Hz); 3.80, 3.77 (2s, $COOCH_3$, 6H); 3.60, 3.39 (2dt, OCH_2, 4H, $^2J = 9.3$ Hz, ^{3}J = 6.5 Hz); 3.23 (d, $=C(E)CH_2$, 2H); 1.50, 1.33 (2m, 4 CH_2, 8H); 0.90 (t, 2 CH_3, 6H). Anal. Found: C, 16.22; H, 8.47. $C_{16}H_{28}O_6$ (316.39) calcd.: C, 60.74; H, 8.92%.

3.1.10. Tetrakis(carbomethoxy)-bisphenoxy-cis,cis-1,5-cyclooctadienes (9a); anti-3,7-bisphenoxy-, syn-3,7-bisphenoxy-, anti-3,8-bisphenoxy- and syn-3,8-bisphenoxy-isomer

IR (KBr): ν(C–H) 2950; ν(C=O) 1730; ν(C=C) 1600, 1590; ("scissoring"-C–H) 1493; 1456; 1435; ν(C–O) 1250–1170 cm^{-1}. **(A)** ^{1}H NMR ($CDCl_3$): δ 7.24, 6.93, 6.80 (3m, H_{arom}, 10H); 5.59 (dd, CH, 2H, $^3J = 6.9$ Hz, $^3J' = 2.2$ Hz); 3.86, 3.74 (2s, $COOCH_3$, 12H); 2.45 (dd, CH_2, 2H, $^2J = -12.9$ Hz); 1.77 (dd, CH_2, 2H). ^{13}C NMR ($CDCl_3$): δ 169.1, 162.2 (C=O); 157.7 ($C_{q,Ph}$); 135.6, 132.7 (C_q–E); 129.3 (C_{meta}); 121.3 (C_{para}); 116.4 (C_{ortho}); 85.9 (CH); 52.6, 52.1 (OCH_3); 39.5 (CH_2). **(B)** ^{1}H NMR ($CDCl_3$): δ 7.24, 6.93, 6.80 (3m, H_{arom}, 10H); 5.51 (dd, CH, 2H, $^2J = 6.9$ Hz, $^3J' = 2.2$ Hz); 3.88, 3.77 (2s, $COOCH_3$, 12H); 2.56 (m, CH_2, 2H, $^2J = -12.9$ Hz); 1.66 (dd, CH_2, 2H). ^{13}C NMR ($CDCl_3$): δ 168.7, 165.3 (C=O); 157.8 ($C_{q,Ph}$); 135.6, 132.7 (C_q–E); 129.3 (C_{meta}); 121.5 (C_{para}); 116.4 (C_{ortho}); 84.6 (CH); 52.3, 52.0 (OCH_3); 37.1 (CH_2). **(C)** ^{1}H NMR ($CDCl_3$): δ 7.24, 6.93, 6.80 (3m, H_{arom}, 10H); 4.64 (dd, CH, 2H, $^3J = 6.9$ Hz, $^3J' = 2.2$ Hz); 3.80, 3.60 (2s, $COOCH_3$, 12H); 2.79 (m, CH_2, 2H, $^2J = -12.9$ Hz); 2.13 (m, CH_2, 2H). ^{13}C NMR ($CDCl_3$): δ 171.2, 165.0 (C=O); 158.4 ($C_{q,Ph}$); 144.0, 135.0 (C_q–E); 129.3 (C_{meta}); 120.9 (C_{para}); 115.7 (C_{ortho}); 78.7 (CH); 52.4, 52.1 (OCH_3); 36.1 (CH_2). **(D)** ^{1}H NMR ($CDCl_3$): δ 7.24, 6.93, 6.80 (3m, H_{arom}, 10H); 5.22 (dd, CH, 2H, $^3J = 9.5$ Hz, $^3J' = 5.2$ Hz); 3.83, 3.49 (2s, $COOCH_3$, 12H); 2.78 (m, CH_2, 2H, $^2J = -12.9$ Hz); 2.19 (m, CH_2, 2H). ^{13}C NMR

($CDCl_3$): δ 169.6, 162.0 (C=O); 158.1 ($C_{q,Ph}$); 144.0, 135.0 (C_q–E); 129.3 (C_{meta}); 121.3 (C_{para}); 115.9 (C_{ortho}); 80.5 (CH); 52.1, 51.7 (OCH_3); 36.0 (CH_2).

3.1.11. Bisbutoxy analogues (9b)

MS (70 eV): m/z (%) = 484 (M^+; 14); 393 (M^+ – $COOCH_3$ – CH_3OH; 20); 380 (M^+ – OBu – OCH_3; 2); 351 (M^+ – $COOCH_3$ – BuOH; 3); 319 (M^+ – $COOCH_3$ – BuOH – CH_3OH; 4); 279 (M^+ – $COOCH_3$ – 2OBu; 28); 233 (10); 231 (22); 221 (7); 100 (24); 85 (16); 59 ($COOCH_3$; 16); 57 (100); 41 (79). **(A)** ^1H NMR ($CDCl_3$): δ 5.67 (dd, CH, 2H, ^3J = 6.5 Hz, $^3J'$ = 2.3 Hz); 3.75, 3.70 (2s, $COOCH_3$, 12H); 3.61, 3.55 (2ddd, OCH_2, 4H); 2.79 (dd, CH_2, 2H, ^2J = –13.2 Hz); 2.21 (dd, CH_2, 2H); 1.51, 1.36 (2m, CH_2, 8H); 0.90 (t, CH_3, 6H). **(B)** ^1H NMR ($CDCl_3$): δ 5.47 (dd, CH, 2H, ^3J = 4.9 Hz, $^3J'$ = 2.1 Hz); 3.73, 3.68 (2s, $COOCH_3$, 12H); 3.60, 3.33 (2ddd, OCH_2, 4H); 2.73 (dd, CH_2, 2H, ^2J = –13.2 Hz); 2.18 (dd, CH_2, 2H); 1.50, 1.36 (2m, CH_2, 8H); 0.90 (t, CH_3, 6H). **(C)** ^1H NMR ($CDCl_3$): δ 4.41 (dd, CH, 2H, ^3J = 7.6 Hz, $^3J'$ = 2.0 Hz); 3.73, 3.71 (2s, $COOCH_3$, 12H); 3.55, 3.29 (2ddd, OCH_2, 4H); 2.25 (dd, CH_2, 2H, ^2J = –13.2 Hz); 1.67 (dd, CH_2, 2H); 1.47, 1.34 (2m, CH_2, 8H); 0.89 (t, CH_3, 6H). **(D)** ^1H NMR ($CDCl_3$): δ 4.06 (dd, CH, 2H, ^3J = 7.9 Hz, $^3J'$ = 3.1 Hz); 3.71, 3.68 (2s, $COOCH_3$, 12H); 3.48, 3.30 (2ddd, OCH_2, 4H); 2.76 (dd, CH_2, 2H, ^2J = –13.2 Hz); 1.78 (dd, CH_2, 2H); 1.48, 1.35 (2m, CH_2, 8H); 0.87 (t, CH_3, 6H).

3.1.12. Bis(tertbutoxy) analogues (9c)

^1H NMR ($CDCl_3$): CH-signals at 6.09, 5.92, 5.07, 5.03 ppm; CH_2-signals around 2.8 and 1.7 ppm.

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