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OXIDATION OF VANILLINS WITH THALLIUM(III) NITRATE. AN EXERCISE IN NMR SPECTROSCOPY AND PHOTOCHEMISTRY

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Abstract—Oxidation of isovanillin, vanillin and *o*-vanillin with $Tl(NO_3)_3$ in MeOH gave the dimethyl acetals of 6,6-dimethoxy-2,4-cyclohexadien-1-one aldehydes (**4–6**) which dimerized spontaneously to give a single product each (**7–9**) the structure of which was elucidated by ^1H and ^{13}C NMR, photocyclization to the cage compounds **12–14** and of **7** and **9** by X-ray diffraction as well.

In a recent paper[1] we demonstrated that phenols *para* substituted by electron releasing groups can be smoothly oxidized in alcoholic media by thallium(III) nitrate trihydrate (TTN) to 4,4 - dialkoxy - 2,5 - cyclohexadien - 1 - ones. It was of interest to examine in this respect the three isomeric vanillins, since vanillin (**2**) itself could give rise either to a 2,5- or to a 2,4-cyclohexadien-1-one, whereas isovanillin (**1**) and *o*-vanillin (**3**) was expected to yield a 2,4-diene only.

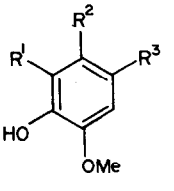
In fact all three phenolic aldehydes exclusively gave 2,4-cyclohexadien-1-ones (**4–6**) with TTN in methanol, with concomitant acetalization of the aldehyde function. Though the NMR spectra of **4** and **5** could be recorded, all three dienones dimerized rapidly at room temperature as did many analogous dienones derived from *o*-alkyl phenols.[2] Each of the monomers led to a single dimer; no isomers could be isolated or observed when the dimerization was conducted in an NMR sample tube.

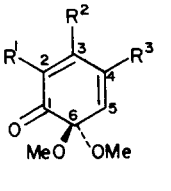
The constitution of the dimers (**7–9**) and their transformation products (**10** and **11**) was elucidated by NMR spectroscopy. Stereochemistry of the addition (*exo* or *endo*) was established by photocyclization of **7**, **11** and **9** to the cage compounds **12–14**; that of **7** and **9** also by an X-ray analysis.

The work on **7** will now be followed through in some detail. The constitution of **8**, **9**, **10** and **11** has been elucidated along similar lines, hence it will be discussed only briefly.

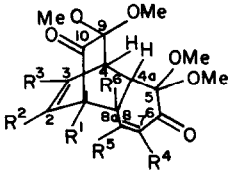
The double bond of the dienophile involved in addition was established first by counting the olefinic protons. The presence of but two of such protons indicated addition onto the 4,5-double bond; addition onto the 2,3-bond would have required three olefinic protons.

"Head-to-head" and "head-to-tail" approach of diene and dienophile (C_2–C_5, C_5–C_4 vs C_2–C_4, C_5–C_5 bond formation) gives rise to dimers of different constitution (e.g. **7*** and **15**). Distinction between the two possibilities required complete assignment of the ^1H NMR signals and determination of the ^1H–^1H coupling constants. The latter was accomplished by homonuclear double resonance experiments performed mainly on partially deuteriated derivatives prepared by oxidation of **1** in CD_3OD. Since there is no detectable preference for any of the diatereotopic faces of the trideuteriomethoxy monomer (**16**) the product is a mixture of four dias-

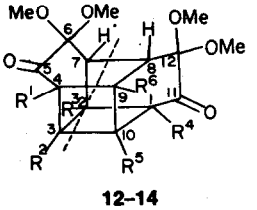




1: $R^1 = R^3 = H$, $R^2 = CHO$ **4**: $R^1 = R^3 = H$, $R^2 = CH(OMe)_2$
2: $R^1 = R^2 = H$, $R^3 = CHO$ **5**: $R^1 = R^2 = H$, $R^3 = CH(OMe)_2$
3: $R^1 = CHO$, $R^2 = R^3 = H$ **6**: $R^1 = CH(OMe)_2$, $R^2 = R^3 = H$

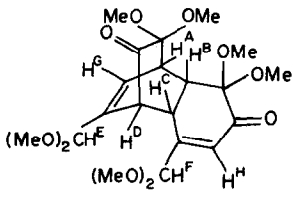


7–11

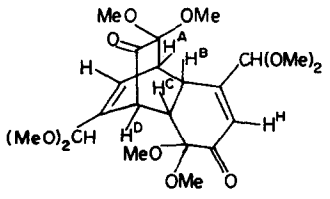


12–14

7, 12: $R^1 = R^3 = R^4 = R^6 = H$, $R^2 = R^5 = CH(OMe)_2$
8: $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = R^6 = CH(OMe)_2$
9, 14: $R^1 = R^4 = CH(OMe)_2$, $R^2 = R^3 = R^5 = R^6 = H$
10: $R^1 = R^3 = R^4 = R^6 = H$, $R^2 = CHO$, $R^5 = CH(OMe)_2$
11, 13: $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = CHO$, $R^6 = CH(OMe)_2$



7*



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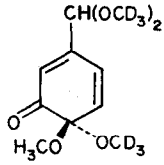

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tereomers differing in the orientation of the solitary ketalic OMe groups.

The assignment of the ^1H NMR signals (labelled downfield consecutively by capital letters A, B, etc.) as shown on formula **7*** was based on the following arguments (see also Tables 1 and 2):

Of the two olefinic signals (G and H) the one showing no vicinal coupling (H) corresponded to H-7. Consequently resonance G was produced by H-3. Collapse of the doublet F on irradiation of H-7 permitted assignment of both acetalic absorptions [F to C_8–$C\underline{H}(OMe)_2$ and E to C_2–$C\underline{H}(OMe)_2$]. On the basis of decoupling experiments, summarized in Table 2, it could be shown that signals G, A, B, C and D represented a contiguous chain of vicinal protons (H-3, 4, 4a, 8a and 1). Such an arrangement was compatible with both of the constitutions **7*** and **15**. In **7*** however it was signal C which was expected to show allylic coupling, whereas in **15** it was B. Double resonance has demonstrated coupling of C with both H-7 and C_8–$C\underline{H}(OMe)_2$ deciding in favour of constitution **7***.

For the dimer (**8**) prepared from vanillin (**2**) double resonance on a partially deuteriomethylated sample has shown that sceletal protons form three isolated vicinal pairs (H-1,2, H-4,4a, and H-7,8). This was in accord only with addition onto the 4,5-double bond of the dienophile

Table 1. ^1H and ^{13}C chemical shifts of the dimers **7**–**11** (ppm in C_6D_6 at 100 and 25.2 MHz resp. relative to internal TMS)

Assignment[d]	7		8		9		10		11	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
1	3.78	52.78	3.53	53.68		63.14	4.29 /	49.82	3.57	54.73
2		138.62	5.94	126.94[a]	5.92	130.15[a]		141.75	5.89	146.39[a]
3	6.19	129.14[a]		142.44	6.13	131.00[a]	6.62	148.66[a]		145.23
4	3.25	38.90[a]	3.41	41.73[a]	3.2	39.74[a]	b	42.56[a]	4.04	37.53[a]
4a	3.37	38.63[a]	3.49	42.12[a]	3.4	39.25[a]	3.36	39.30[a]	3.46	40.97[a]
5		95.32		94.77		95.67		95.73		94.50
6		192.69		192.13		193.23		193.25		191.59
7	6.45	127.66[a]	5.84	128.56[a]		136.61	6.38	128.10	5.7	129.17[a]
8		153.56	6.27	147.42	7.2	142.72		154.20	5.98	146.61
8a	3.57	40.32[a]		55.00	3.9	38.74[a]	3.64	39.46[a]		55.44
9		99.33		98.32		99.07		99.35		98.29
10		201.42		199.42		202.9		200.60		198.26
$C\underline{H}^E/OMe/_2$	4.42	102.74	4.94	101.69	4.71	105.71	8.93[c]	188.49[c]	9.12[c]	187.86[c]
$C\underline{H}^F/OMe/_2$	4.96	100.15	4.48	108.64	5.41	99.46	5.04	100.66	4.42	108.97
5-OMe	3.30	48.98	3.31	48.28	3.33	48.74	3.29	49.13	2.94	48.21
	3.04	49.31	3.27	48.39	3.02	49.07	2.88	49.76	3.1	49.09
9-OMe	2.90	49.54	3.01	49.68	3.10	49.86	3.07	50.06	3.18	49.92
	3.37	50.46	3.42	50.89	3.39	50.52	3.33	50.38	3.26	51.17
$CH^E/O\underline{Me}/_2$	3.00	53.37	3.24	53.93	3.19	58.02				
	3.02	52.78	3.16	50.89	3.47	58.62				
$CH^F/O\underline{Me}/_2$	3.14	54.02	3.27	56.50	3.24	53.45	3.14	54.16	3.26	57.35
	3.04	50.35	3.40	58.80	3.17	54.09	3.04	51.06	3.41	59.11

[a]Assignments based on selective heteronuclear decoupling. [b]Overlapped. [c]Free aldehyde group. [d]Relative assignment for groups of lines in braces are interchangable. Except for **11** ^{13}C and ^1H signals of the individual methoxy groups entered in the same line have been paired by selective decoupling experiments.

Table 2. ^{1}H coupling constants of the dimers 7–11 in Hz

	7	8	9	10	11
$^3J_{1,2}$	-	6.5	-	-	6.5
$^4J_{1,3}$	1.8	-	-	1.8	-
$^3J_{1,8a}$	2.8	-	-	2.8	-
$^4J_{1,F}$	-	br.	-	-	o
$^3J_{2,3}$	-	-	8.5	-	-
$^4J_{2,4}$	-	2	1.7–1.8	-	2
$^5J_{2,4a}$	-	o	o	-	o
$^4J_{2'E}$	-	1.5	o	-	-
$^3J_{3,4}$	7	-	6.5	7	-
$^4J_{3,4a}$	0.5	-	~0.5	~0.5	-
$^4J_{3,E}$	1	-	o	o	-
$^3J_{4,4a}$	1.5	1.8–2.0	1.3	~1.5	1.5
$^5J_{4,8}$	-	o	~0.5	-	o
$^4J_{4a,8}$	-	0.8–1.0	~0.5	-	1.1
$^3J_{4a,8a}$	8.0–8.5	-	8.0–8.5	8.0–8.5	-
$^3J_{7,8}$	-	10.2	-	-	10.2
$^4J_{7,8a}$	1	-	-	~1	-
$^4J_{7,F}$	1.5	br.	-	~1.8	o
$^3J_{8,8a}$	-	-	4	-	-
$^4J_{8,F}$	-	o	0.8–1	-	o
$^4J_{8a,F}$	~0.5	-	-	~0.5	-
$^5J_{8a,F}$	-	-	0.8	-	-
$^4J_{2,8a}$	-	-	~0.5	-	-
Protons irradiated	4,F,3,7, 1	4,2,8,F, E	3,8,4a, 8a,E	3,7	1,2,4

in a head-to-tail orientation. Any other combination would have produced a 3:2:1 distribution of adjacent protons.

Olefinic proton count (three) indicated that addition to the diene derived from *o*-vanillin (**3**) also involved the 4,5-double bond. The fact that the proton (H-8a) adjacent to the solitary olefinic proton (H-8) showed only one further vicinal coupling proved that again head-to-tail dimerization had taken place and the product had constitution **9**.

The dimer prepared from vanillin (**8**) turned out to be extremely sensitive to hydrolysis by which it gave a monoaldehyde. By contrast the hydrolytic decomposition of the dimer obtained from isovanillin (**7**) required treatment with aqueous hydrochloric acid in methanol. With the assigned spectra of the parent compounds in hand interpretation of those of the hydrolysis products was straightforward and showed that they had constitutions **11** and **10** respectively (Table 2).

We attempted to gain information about the relative stereochemistry of the dimers from the chemical shifts and ^{1}H relaxation times (T_1) of the OMe signals and by comparing the corresponding values for the parent dimers and the monoaldehydes. This required at least a partial assignment of the OMe signals. Since the partially deuteriomethylated compounds had only ketalic OMe functions, a division into ketalic and acetalic OMe signals was feasible. Distinction between pairs of acetalic OMe signals in **7** and **8** was enabled by comparison with the corresponding monoaldehydes. Cross correlation between ^{13}C and ^{1}H OMe signals was established by heteronuclear selective decoupling. In the ^{13}C spectrum only the signal of the ^{13}C nucleus attached directly to the protons irradiated appeared as a sharp singlet.

Since no ^{13}C NMR data seem to have been published on systems similar to those reported here, we present in Table 1 a nearly complete assignment of the corresponding spectra. Most of the lines could be assigned using standard ^{13}C NMR techniques including off-resonance, and for those marked with superscript "a" in Table 1, also by selective ^{13}C-{^{1}H} decoupling. Quaternary carbons could be distinguished by known correlations and by comparison with data on 2- and 3-cyclohexenone[3] (C-6 and 10, further C-5 and 9).

As expected, hydrolysis of one of the acetal functions in **7** and **8** to aldehyde resulted in characteristic changes of some of the shifts: in α-position +3.1 (**10**) and +2.8 ppm (**11**), in β-position 20 ppm at the sp^2 carbon in both **10** and **11** further −3.0 (**10**) and −4.2 (**11**) ppm at the sp^3 carbon.

Unfortunately NMR failed to provide unambiguous evidence for the relative configuration of the dimers.

Diels–Alder type dimers of cyclic dienes are known however to undergo [$^2\pi_s$, $^2\pi_s$] photocyclization to give cage compounds when of *endo* configuration, whereas with the *exo* dimers this reaction is sterically impossible.[4]

In fact, UV irradiation of compounds **7**, **11** and **9** in the presence of a triplet sensitizer gave the corresponding pentacyclic cage compounds **12**–**14** proving that the parent dimers were disposed *endo*. Note that **12** and **14** have a two-fold axis of symmetry (as indicated by the broken line). This makes their identification by NMR simple since the sceletal protons give only three signals. The spectrum of the monoaldehyde **13** is complicated but is in accordance with the proposed structure.

These results have been established concurrently by X-ray analyses carried out on **7** and **9**.[5]

DISCUSSION

The following comments can be made on the basis of the experiments described above.

No *para* oxidation of the vanillins has taken place. This was not unexpected since the OMe group certainly secures higher electron density at the adjacent C atom than does either an aldehyde or an acetal function.

In accordance with what has been recently reported by McKillop *et al.*[6] TTN is an efficient catalyst for acetalization. Acetalization preceded dimerization as indicated by the NMR spectra of the monomers (Experimental).

Dimerization was (within detection limits) completely stereospecific, regiospecific and specific as to the mutual orientation of the components. Stereochemistry of dimerization followed the *endo* rule.[7]

Dimerization involved irrespective of the position of the bulky aldehyde dimethylacetal moiety the 4,5- (i.e. the γ,δ) double bond. This regiospecificity in similar dimerizations had been discovered long ago[8] but has not been explained so far. Both the observed regiospecificity and the orientational specificity conform with an inter-

pretation put forward recently by Houk[9] invoking frontier orbital considerations and which predict addition onto the γ,δ-double bond and the observed "ortho" product. According to data presented by Houk in our type of dienes both HOMO and LUMO possess the highest coefficients at the terminal remote from the CO group and this promotes bond formation between these terminals.

It should be noted that of the three monomers the one derived from vanillin dimerizes appreciably slower than the other two. This fact and also the extreme sensitivity of the acetal moiety at C_3 in **8** may be ascribed to increased steric compression of this group.

Conclusions as to the mobility of the $CH(OMe)_2$ moieties can be drawn from chemical shift differences between the ^{13}C signals of the diastereotopic OMe groups associated with the C atom. These shifts are nearly averaged ($\Delta\delta \leq 0.6$ ppm) for that on C_2 in **7** and for both groups in **9** indicating fast rotation (low conformational contribution to anisochrony), whereas line separation for both acetalic functions in **8** and that on C_8 in **7** is substantial ($\Delta\delta$ 2.30–3.67) indicating hindered rotation. In addition ^1H-allylic coupling (^4J) involving the acetalic proton in the first group is 0.8–1.0 Hz, whereas in the second it amounts to 1.5 Hz, an indication that in the latter case this proton prefers to be oriented nearly orthogonal onto the plane of the double bond.

EXPERIMENTAL

M.ps were taken on a Kofler block and are not corrected. NMR spectra were recorded on a Varian XL 100 spectrometer and where indicated at 270 MHz on a Bruker Spectrospin instrument. MS were taken using gas ionization techniques (methylamine) on an A.E.I. MS 9 instrument and gave the expected molecular ions. Direct ionization gave invariably the M^+–CO peak. Since the fragmentation patterns had no direct relevance to our problems they were not reproduced here. Irradiations were carried out in a Pyrex immersion well apparatus at 16° under N_2 using a Philips HPK 125 W high pressure lamp.

2,8 - *Bis* - (*dimethoxymethyl*) - 5,5,9,9 - *tetramethoxy* - 1,4,4a,8a - *tetrahydro* - 1,4 - *ethanonaphtalene* - 6,10(4H) - *dione* (**7**). To isovanillin (5 mmol) in MeOH) a soln of TTN·3 H_2O (5.7 mmol) in MeOH (15 ml) was added at −20°. After warming to 0° the soln was filtered through basic alumina, the product eluted with CH_2Cl_2, the solvent evaporated and the residue crystallized from petroleum ether. Colorless crystals (0.38 g, 37%), m.p. 129–130°. (Found: C, 57.85; H, 7.03. Calc. for $C_{22}H_{32}O_{10}$: C, 57.88; H, 7.07%); IR (KBr): 1745, 1720 (CO), 1460, 1440 cm^{-1} (C=C).

The ^1H NMR spectrum of the crude product taken immediately after evaporation at 0° showed that it consisted mainly of the monomer, 6,6 - *dimethoxy* - 3 - *dimethoxymethyl* - 2,4 - *cyclohexydien* - 1 - *one* (**4**) but line positions could not be exactly evaluated due to overlap with dimer signals. Fast dimerization precluded the recording of the ^{13}C spectrum.

3,8a - *Bis* - (*dimethoxymethyl*) - 5,5,9,9 - *tetramethoxy* - 1,4 - 4a,8a - *tetrahydro* - 1,4 - *ethanonaphtalene* - 6,10(4H) - *dione* (**8**) was prepared from vanillin in 30% yield as **7** but with a rigorous exclusion of moisture during work up to prevent hydrolysis to **11**, m.p. 94–95° (Found: C, 58.18; H, 7.08. $C_{22}H_{32}O_{10}$ requires: C, 57.88; H, 7.07%); IR (KBr): 1740, 1720 (CO), 1610, 1460, 1440 cm^{-1} (C=C).

6,6 - *Dimethoxy* - 4 - *dimethoxymethyl* - 2,4 - *cyclohexadien* - 1 - *one* (**5**). δ^1H (C_6D_6) 3.00 [CH(OMe)$_2$], 3.31 [C^6(OMe)$_2$], 4.48 [CH(OMe)$_2$], 5.86 (H-2), 6.47 (H-5), 6.60 (H-3); $J_{2,3} = 10.0$, $J_{2,5} = 0.8$, $J_{3,5} = 2.2$, $J_{5,7} = 1.0$ Hz. $\delta^{13}C$ (in C_6D_6) 50.06 [C(OMe)$_2$], 52.54 [CH(OMe)$_2$], 93.0 (C-6), 102.02 [CH(OMe)$_2$], 126.94 (C-2), 134.34 (C-5), 135.21 (C-4), 138.50 (C-3) and 195.42 (CO).

1,7 - *Bis* - (*dimethoxymethyl*) - 5,5,9,9 - *tetramethoxy* - 1,4,4a,8a - *tetrahydro* - 1,4 - *ethanonaphtalene* - 6,10(4H) - *dione* (**9**) was prepared from *o*-vanillin in 34% yield as described for **7**, m.p. 135–136°. (Found: C, 57.63; H, 7.10. $C_{22}H_{32}O_{10}$ requires: C, 57.88; H, 7.07%); IR (KBr): 1725, 1700 (CO), 1605, 1460 and 1440 cm^{-1} (C=C).

8 - *Dimethoxymethyl* - 2 - *formyl* - 5,5,9,9 - *tetramethoxy* - 1,4,4a,8a - *tetrahydro* - 1,4 - *ethanonaphtalene* - 6,10(4H) - *dione* (**10**). Treatment of **7** (130 mg) with a mixture of MeOH (3 ml) and 10% HCl aq (0.3 ml) for 24 h at r.t. gave after evaporation and repeated crystallization from petroleum ether the monoaldehyde (14 mg, 12%), m.p. 151–153°. (Found: C, 58.51; H, 6.32. $C_{20}H_{26}O_9$ requires: C, 58.53; H, 6.39%); IR (KBr): 1740, 1700, 1680 (CO), 1450, 1440 cm^{-1} (C=C).

8a - *Dimethoxymethyl* - 2 - *formyl* - 5,5,9,9 - *tetramethoxy* - 1,4,4a,8a - *tetrahydro* - 1,4 - *ethanonaphtalene* - 6,10(4H) - *dione* (**11**) was obtained directly when crude **8** was recrystallized from benzene–petroleum ether, m.p. 175–176°. (Found: C, 58.72; H, 6.44. $C_{20}H_{26}O_9$ requires: C, 58.53; H, 6.39%); IR (KBr): 1735, 1690, 1670 cm^{-1} (CO).

4,10 - *Bis* - (*dimethoxymethyl*) - 6,6,12,12 - *tetramethoxy* - *pentacyclo*[6.2.2.0^{2,7}.0^{4,9}]*dodecan* - 5,11 - *dione* (**12**). A soln of **7** (0.50 g) in acetophenone (65 ml) was irradiated for 30 min. Removal of acetophenone by vacuum distillation at 5×10^{-2} Torr gave a pale yellow residue which crystallized upon treatment with ether. Recrystallization from CH_2Cl_2 by addition of petroleum ether gave **12** (0.25 g, 50%), m.p. 146–148°. (Found: C, 57.90; H, 7.04. $C_{22}H_{32}O_{10}$ requires: C, 57.89; H, 7.07%); IR (KBr): 1735 cm^{-1} (CO); ^1H NMR (270 MHz, $CDCl_3$); $\delta = 2.85$ (q, $^3J_{1,2} = {}^3J_{4,9} = 3.75$, $^4J_{1,9} = {}^4J_{2,4} = 1.50$ Hz, H-1,4), 3.10 (m, $^3J_{2,7} = {}^3J_{8,9} = 7.50$, $^4J_{2,4} = {}^4J_{1,9} = 1.50$ Hz, H-2, 7, 8, 9), 3.25, 3.35, 3.43, 3.49 (s, 8 × OMe), 4.29 [s, CH(OMe)$_2$].

2 - *Formyl* - 9 - *methoxymethyl* - 6,6,12,12 - *tetramethoxypentacyclo*[6.2.2.0^{2,7}.0^{4,9}]*dodecan* - 5,11 - *dione* (**13**). Treatment of **11** (0.25 g) as described with **12** gave **13** (0.10 g, 40%), m.p. 165–167° from ether. (Found: C, 58.51; H, 6.40. $C_{20}H_{26}O_9$ requires: C, 58.53; H, 6.39%); IR (KBr): 1730, 1715 cm^{-1} (CO); ^1H NMR (270 MHz, $CDCl_3$: $\delta = 3.08$, 3.30, 3.36, 3.40 and 3.48 (s, 6 × OMe), 4.67 [s, CH(OMe)$_2$], 9.48 (s, CHO), 2.97 (1H), 3.12 (2H), 3.26 (1H) and 3.47 (2H) (broad singlets or poorly resolved multiplets, tentative assignment H-1, H-4, 10, H-8, and H-3, 7).

1,4 - *Bis* - (*dimethoxymethyl*) - 6,6,12,12 - *tetramethoxypentacyclo*[6.2.2.0^{2,7}.0^{4,9}]*dodecan* - 5,11 - *dione* (**14**). Treatment of **9** as described for **12** gave **14** (0.20 g, 40%), m.p. 188–190° (CH_2Cl_2–MeOH). (Found: C, 57.79; H, 6.99. $C_{22}H_{32}O_{10}$ requires: C, 57.89; H, 7.07%); IR (KBr): 1720 cm^{-1} (CO); ^1H NMR (270 MHz, $CDCl_3$): $\delta = 2.80$ (q, $^3J_{2,7} = {}^3J_{8,9} = 4.0$, $^4J_{3,7} = {}^4J_{8,10} = 2.0$ Hz, H-7, 8), 3.13 (m, 2H, H-2, 9), 3.25 (mc, 2H, H-3, 10), 3.23, 3.36, 3.55, 3.57 (s, 8 × OMe), 4.78 [s, CH(OMe)$_2$].

X-Ray analysis. Intensity data were collected on a Philips PW 1100 diffractometer with Cu*Kα* radiation (λ 1.5418 Å). Crystal data: $a = 16.332(2)$, $b = 6.836(2)$, $c = 10.660$ Å, $\alpha = 96.56(1)$, $\beta = 93.58(1)$ and $\gamma = 104.77(1)°$, space group $P\cdot\bar{1}$, $D_X = 1.33$ g cm^{-3} for $Z = 2 \cdot \mu(CuK\alpha) = 8.95$ cm^{-1}. No correction for absorption was applied. The structure was determined by the direct method and refined by full-matrix least-squares technique ($R = 0.039$) including anisotropic thermal parameters for the heavy atoms and fixed isotropic for the H atoms. The latter were found from a difference map from chemical reasoning.

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