

Synthesis and Fluorescence of a Configurationally Locked Z-Hexatriene: 1,2-Divinylcyclopentene

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Abstract:

The syntheses of the configurationally locked Z-hexatriene, 1,2-divinylcyclopentene, and its terminally tetradeuterated isotopomer are described, and some photochemical and photophysical properties are reported. The trienes turn out to be photostable under oxygen-free conditions. In contrast to "unlocked" hexatrienes, both compounds fluoresce (room temperature, methanol). The fluorescence is structured and is the nearly perfect mirror image of the absorption band, with a small Stokes shift. Therefore the emission might originate in the 1^1B_1 state. This is the first observation of fluorescence of simple hexatrienes in solution. Apparently torsional motion around the central (originally double) bond in the excited singlet state is an important radiationless deactivation pathway in "unlocked" hexatrienes; if it is obstructed fluorescence becomes a passable deactivation pathway.

1. INTRODUCTION

Conjugated polyenes have been studied extensively, partly because they constitute a class of compounds of intrinsic chemical interest (especially for their fascinating photochemistry and spectroscopy), and partly because some of them are biologically important compounds (such as vitamin D, retinal and β -carotene). Conjugated trienes are good model systems, because they are the smallest polyenes with a central double bond. No fluorescence has been observed for trienes in solution so far, except for (iso)tachysterol¹ and some steroidal trienes². Therefore an important source of information on their lowest electronically excited singlet state is not available. The photochemistry of various alkyl substituted hexatrienes has been studied in detail^{3,4}; it was found that photoproduct formation occurs in agreement with the NEER (non-equilibration of excited rotamers) principle^{3a}. In general, the most important photochemical deactivation pathway is *cis/trans* isomerization around the central double bond⁴.

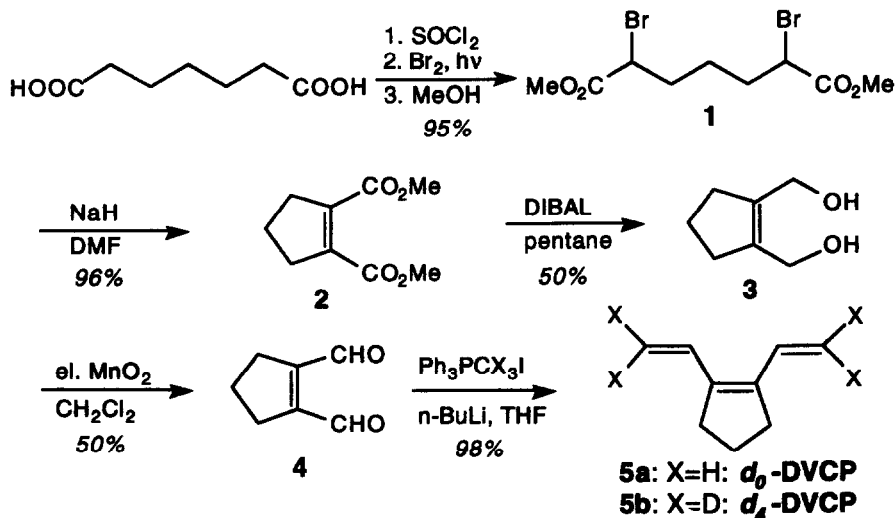
We thought it of interest to investigate the behaviour of an excited triene in which this torsional motion is prevented by "locking" the central double bond. This will not only block the usual photochemical deactivation route (*cis/trans* isomerization), but possibly also affect the efficiency of the nonradiative decay to the ground state, enabling fluorescence to become more competitive. We therefore synthesized 1,2-divinylcyclopentene (*d₀*-DVCP). For resonance Raman studies of the vinylic hydrogen vibrations of this "locked" Z-hexatriene in the lowest triplet state⁵, we also synthesized the terminally tetradeuterated isotopomer (*d₄*-DVCP).

In this paper we present the syntheses and the results of a study of conformation and photoreactivity of these trienes, as well as their fluorescence spectra.

2. RESULTS AND DISCUSSION

The trienes **5** are prepared according to Scheme 1. The dibromide **1** and the five-membered ring compound **2** are prepared as described in the literature^{6,7}. Then the ester groups are reduced to hydroxymethyl

groups with diisobutylaluminum hydride in *n*-pentane, leading to the diol **3**. This compound is oxidized to the dicarboxaldehyde **4** with electrolytic manganese dioxide⁸ in dichloromethane. Finally compounds **5** are obtained via a Wittig reaction with (trideutero)methyltriphenylphosphonium iodide⁹ and *n*-butyl lithium in tetrahydrofuran. The overall yield of this route is 22%. The purity of the trienes is 100% (GC) and the incorporation of deuterium in *d*₄-DVCP is 76% (EIMS).



Scheme 1

In principle for both compounds three conformations can be envisaged: the planar or almost planar *tZt* form and the probably non-planar *cZt* and *cZc* forms (Fig.1). These conformations may interconvert via rotation around the single bonds.

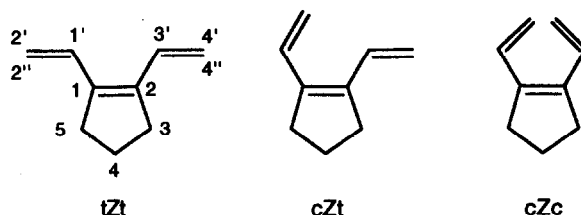


Figure 1

On the basis of studies on 3-alkyl substituted hexatrienes^{4f} the *tZt* conformation is expected to be the form with the lowest energy. This has been investigated with ¹H-NMR *Nuclear Overhauser Enhancement* spectroscopy. For *d*₀-DVCP in CDCl₃ two NOE effects are observed: one between H-2'' and H-5 (or H-4'' and H-3), and one between H-1' and H-2' (or H-3' and H-4'; Figs.1 and 2A). No NOE effects are observed for *d*₄-DVCP in CDCl₃ (Fig.2B). The NOE results for *d*₀-DVCP and the absence of an NOE effect between H-1' and H-5 (or H-3' and H-3) for *d*₄-DVCP indicate that both trienes exist exclusively in the *tZt* conformation.

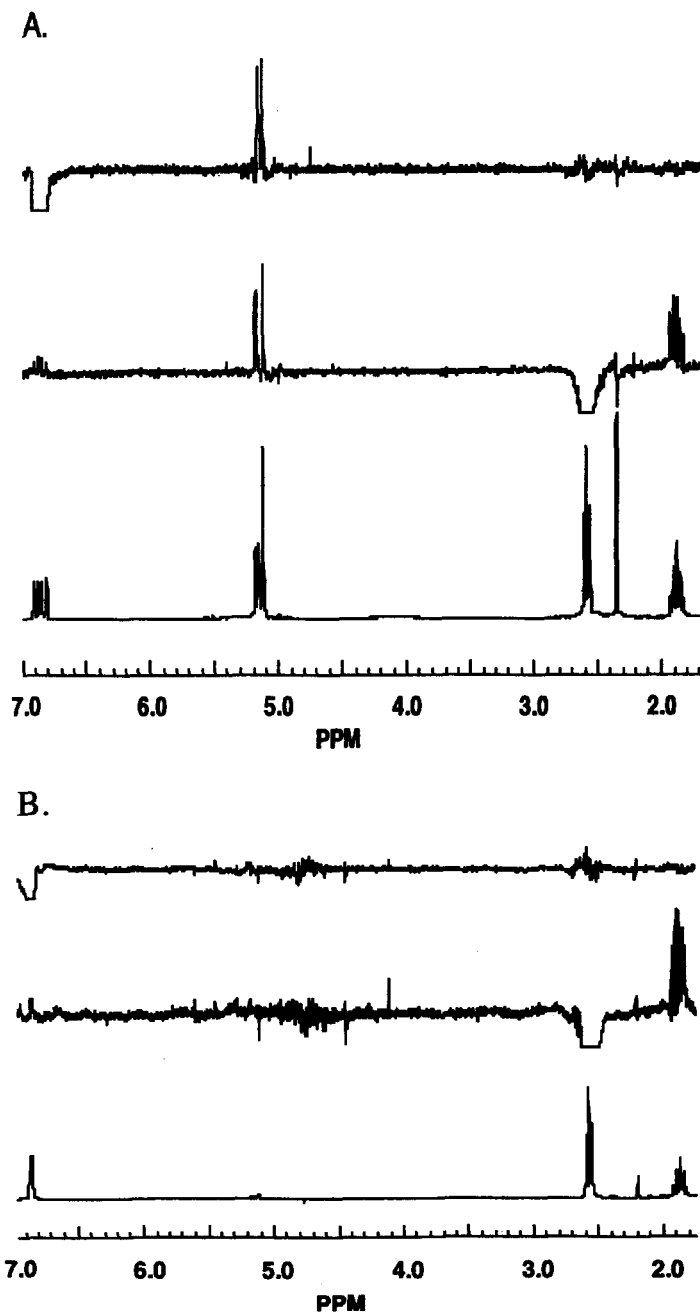


Figure 2: $^1\text{H-NMR}$ *Nuclear Overhauser Enhancement* spectra of the trienes in CDCl_3 ; A. d_0 -DVCP; B. d_4 -DVCP

The UV absorption spectra of d_0 - and d_4 -DVCP (Fig.3 and Table 1) show maxima at about 280 nm, 270 nm and 260 nm, and a shoulder at *circa* 250 nm. Although the spectra are very similar, there are small differences. In methanol the absorption of the deuterated triene is blue-shifted by about 1 nm compared to the undeuterated triene. In view of the NOE data the difference in UV absorption cannot be due to a different rotameric composition of the ground-state conformational equilibrium. The absorption spectra of both compounds confirm that the *tZt* rotamer dominates; both show the fine structure characteristic of (nearly) planar *tZt* trienes⁴. The difference in UV absorption may be related to a small difference in the twist angles around the bonds 1-1' and 2-3' in the ground state of the isotomers.

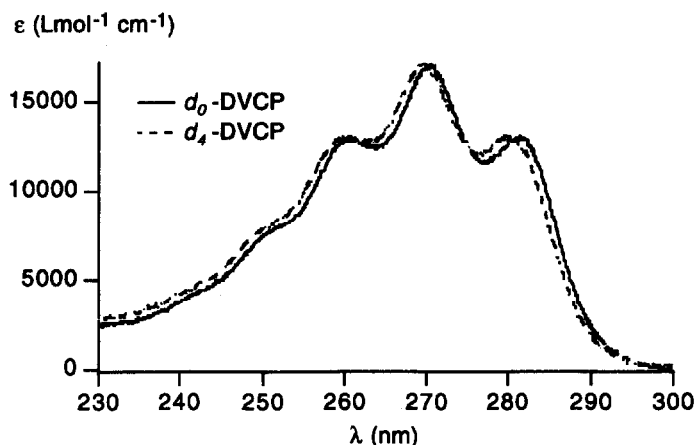


Figure 3: UV absorption spectra in methanol at room temperature

Table 1: UV Absorption and Fluorescence Maxima in Methanol at Room Temperature

compound	abs. max. (nm)	ϵ ($M^{-1} \text{ cm}^{-1}$)	fluor. max. (nm)
d_0 -DVCP	281.6	13200	316
	270.6	17600	305
	260.6	13400	293
	250 (sh)	7600	
d_4 -DVCP	280.1	13600	316
	269.6	17600	305
	260.0	13500	293
	249 (sh)	7600	

The photoreactivity of an almost planar and "locked" tZt hexatriene is expected to be low. The only conceivable photoreaction is bicyclobutane formation, but this photoproduct would thermally revert rapidly to the starting triene. Because of the "locked" central bond the tZt trienes cannot give the characteristic *cis/trans* photoisomerization product (tEt)⁴. We have investigated the photoreactivity of DVCP in solution (10^{-3} M in *n*-pentane) by irradiating at 254 nm and at 300 nm, and monitoring by GC analysis and UV absorption measurements. On condition that oxygen is rigorously excluded both d_0 - and d_4 -DVCP turn out to be photostable, even after very long irradiation times. If any oxygen is present, the trienes are photo-oxidized to unsaturated ketones¹⁰.

Both d_0 - and d_4 -DVCP show a structured fluorescence band in methanol (Fig. 4, Table 1), with identical positions on the wavenumber scale.

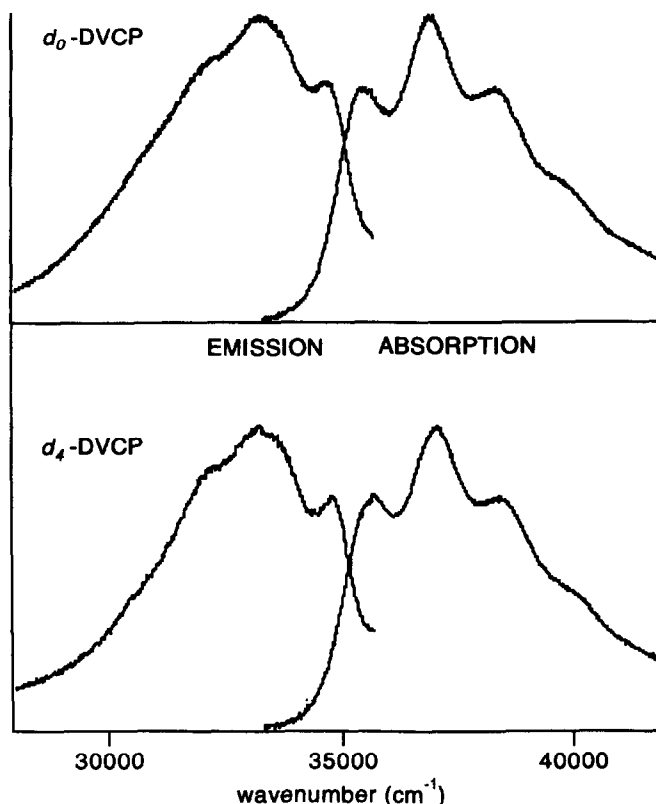


Figure 4: Fluorescence (left, λ_{exc} 250 nm) and UV absorption spectra (right) of the trienes in methanol (10^{-5} M) at room temperature

The fluorescence spectra show a nice mirror relationship to the absorption spectra (Fig. 4). Together with the small Stokes shift this suggests^{2a} that the emission process originates in the optically accessible lowest excited singlet state of B_1 symmetry (1^1B_1), and not in the proximate singlet state of A_1 symmetry (2^1A_1). The fluorescence quantum yield is 0.01 for both trienes. The fluorescence excitation spectra correspond to the high-energy part of the absorption spectra, with a maximum at 250 nm. Further investigations into the origin of the emission, including lifetime measurements and the effect of temperature and solvent on the fluorescence, are in progress.

3. CONCLUSIONS

The "locked" Z-hexatrienes 1,2-divinylcyclopentene and its terminally tetradeuterated isotopomer have been prepared from the known⁷ cyclopentene-1,2-dialdehyde *via* Wittig reactions. Their conformations have been studied with ¹H-NMR *Nuclear Overhauser Enhancement* spectroscopy; the tZt form turns out to be the exclusive rotamer. The trienes exhibit an absorption band around 270 nm; both compounds are photostable. They show an emission band around 305 nm, which may provisionally be ascribed to emission from the 1¹B₁ state. These are the first simple hexatrienes that show detectable fluorescence in solution. Apparently the rigidity of the central bond of the chromophore, imposed by its incorporation in the five-membered ring, not only closes the photochemical relaxation pathway (*cis/trans* isomerization), but also sufficiently affects the nonradiative decay channels back to the ground-state so as to bring about detectable fluorescence.

4. EXPERIMENTAL

Chemicals

Pimelic acid (98%), diisobutylaluminum hydride (1M solution in hexane), iodomethane-*d*₃ (99+ atom % D) and triphenyl phosphine were obtained from Janssen Chimica, thionyl chloride (>99%) from Merck, bromine from J.T. Baker Chemicals, sodium hydride (80% in mineral oil) and *n*-butyl lithium from Fluka Chemie, electrolytic manganese dioxide (TKV or p-EMD)⁸ from Mitsui Mining & Smelting Co., Takehara Refinery (Japan), and iodomethane (99.5%) from Aldrich. Solvents were distilled before use, and all reactions were carried out in an atmosphere of dry nitrogen. For the fluorescence measurements distilled spectrophotometric grade methanol (99.9%) was used, which was obtained from Janssen Chimica.

Apparatus

NMR spectra were taken on a Jeol JNM-FX 200 Fourier Transform NMR spectrometer or on a Bruker WM-300 spectrometer, with CDCl₃ as the solvent and tetramethylsilane as internal reference. UV absorption spectra were recorded in *n*-pentane or methanol on a Cary 14 or Cary 219 spectrophotometer, or on a Varian DMS 200 UV/visible spectrophotometer. IR spectra were taken on a Pye Unicam SP3-200 Infrared spectrophotometer. GC analyses were done on a Chrompack 437A gas chromatograph, and high resolution electron impact mass spectra were taken on a V.G. Micromass ZAB-HFqQ mass spectrometer coupled to a V.G. 11/250 data system (resolving power 15,000; 10% valley definition). The samples were introduced *via* the direct insertion probe into the ion source.

For the photochemical and fluorescence studies degassed samples were prepared in Quartz Suprasil cuvettes obtained from Hellma, using the freeze-pump-thaw method (three cycles). The photochemistry was studied by irradiation at 254 nm or at 300 nm in a Rayonet Photochemical Reactor (RPR-200). Fluorescence spectra were measured using a Spex Fluorolog 2 Model 111C instrument in the right-angle mode, exciting at 250 nm, with a spectral bandwidth of 23 nm. Spectral resolution in the emission spectra was 4 nm.

Syntheses of *d*₀- and *d*₄-1,2-divinylcyclopentene

Dimethyl α,α'-dibromopimelate **1**⁶. The compound was prepared as described in the literature, starting with 80.1 g (0.5 mole) of pimelic acid. Yield: 164.1 g (95%).

¹H-NMR (CDCl₃): δ 4.25 (t,2H,α-H), 3.79 (s,6H,OCH₃), 2.08 (m,4H,β-H), 1.20 (m,2H,γ-H)

Dimethyl 1-cyclopentene-1,2-dicarboxylate **2**⁷. The dicarboxylate was synthesized as described in the literature, starting with 76.5 g (0.22 mole) of the crude dibromopimelate **1**. Total yield: 38.7 g (96%).

¹H-NMR (CDCl₃): δ 3.75 (s,6H,CO₂Me), 2.70 (t,4H,allylic H), 1.95 ppm (q,2H, nonallylic H); IR (pure): 1725 (CO₂Me), 1645 cm⁻¹ (C=C)

1,2-Bis(hydroxymethyl)-1-cyclopentene 3⁷. 18.4 g (0.1 mole) of dimethyl 1-cyclopentene-1,2-dicarboxylate **2** was dissolved in 1 l of *n*-pentane. Then 440 ml (0.44 mole) of a 1 M-solution of diisobutylaluminum hydride in hexane was transferred to an addition funnel via a double tipped flex-needle. The DIBAL solution was added to the pentane solution at 5 °C, after which the mixture was stirred at 5 °C for 1 hr. The excess reagent was decomposed by cautious addition of 50 ml of methanol. Then 200 ml of icewater and 500 ml of 2 N hydrochloric acid were added, after which the mixture was stirred for 1 hr. The aqueous layer was separated, saturated with sodium chloride, and extracted three times with ethyl acetate. The combined organic layers were dried with magnesium sulphate, and the solvent was removed under reduced pressure (water bath at 25-30 °C). The yield was 17.4 g, but according to ¹H-NMR it contained *circa* 50% of the desired diol **3**. The crude product was not purified before use because attempts to do so (distillation, column chromatography) resulted in considerable decomposition of the diol.

¹H-NMR (CDCl₃): δ 4.20 (s,4H,CH₂O), 3.64 (bs,2H,OH), 2.47 (t,4H,allylic H), 1.85 (q,2H,nonallylic H) ppm; IR (pure): 3300 (OH), 1645 cm⁻¹ (C=C)

1-Cyclopentene-1,2-dicarboxaldehyde 4¹. 3.3 g (26 mmole) of the crude diol **3** was dissolved in 330 ml of dichloromethane and added over 1 hr from an addition funnel to 44.8 g (516 mmole) of electrolytic manganese dioxide⁸ type 1 or 2 (TKV or p-EMD, activated by drying in vacuo at 100 °C). The mixture was stirred for 2 hr, after which the manganese dioxide was filtered off through Celite. The filtrate was evaporated and 2.8 g of the crude **4** was obtained as an orange oil. Column chromatography with distilled *n*-pentane/ethyl acetate (2:1) gave 1.6 g (50%) of the pure dicarboxaldehyde **4** as a yellow oil.

¹H-NMR (CDCl₃): δ 10.41 (s,2H,CHO), 2.78 (t,4H,allylic H), 1.92 (q,2H,nonallylic H) ppm; UV (ether): λ_{max} 261 nm (ε 7100); IR (CCl₄): 2865 (-CO-H), 1720 (C=O), 1640 cm⁻¹ (C=C); HRMS (C₇H₈O₂): M⁺, m/z: calc. 124.0524, found 124.0525

d₀-1,2-Divinylcyclopentene 5a. To a cooled (-20 °C) and vigorously stirred suspension of 7.2 g (18 mmole) of finely powdered methyltriphenylphosphonium iodide⁹ in 25 ml of dry tetrahydrofuran (freshly distilled from LiAlH₄) in an atmosphere of dry nitrogen was added dropwise 11.5 ml (18 mmole) of a 1.6 M-solution of *n*-butyl lithium in hexane in about 30 min. The resulting orange-red mixture was then stirred at room temperature for 1 hr, and cooled again to -10 °C. To this cooled and well stirred reaction mixture a solution of 1.1 g (9 mmole) of dicarboxaldehyde **4** in 6 ml of dry tetrahydrofuran was added dropwise in an atmosphere of dry nitrogen in about 15 min. After the addition the mixture was warmed to room temperature and stirred for 1 hr, after which all dicarboxaldehyde had reacted (as evidenced by ¹H-NMR). The dark brown mixture was treated successively with 25 ml of aqueous methanol (1:1) and 25 ml of *n*-pentane, after which it was stirred at room temperature for 1 hr. Then the pentane layer was separated, and the aqueous layer was extracted three times with 25 ml of *n*-pentane. The combined pentane layers were washed three times with 15 ml of aqueous methanol (1:1) and dried over magnesium sulphate. The pentane was removed by slow evaporation under reduced pressure (200 mm Hg, bath temperature 25 °C). The residual red liquid (7.1 g) was redissolved in 5 ml of *n*-pentane and passed through a column of silica gel (Kiesel gel 60, 0.063-0.200 mm, 100 g, column height 30 cm) with 500 ml of distilled *n*-pentane. The colourless pentane solution was evaporated as above which gave 1.0 g (98%) of *d₀*-1,2-divinylcyclopentene **5a** as a colourless liquid.

According to GC the purity was 100% (column: Chrompack CP-Sil-5CB, 25m×0.25mm ID, DF=0.40, 70 °C; injector 200 °C, detector 280 °C, τ=10.3 min.); 300 MHz ¹H-NMR (CDCl₃; cf. Fig. 1): δ 6.86 (dd,2H,H-1' and H-3', ³J_{1'2''}=³J_{3'4''}=16.92 Hz, ³J_{1'2'}=³J_{3'4'}=10.91 Hz), 5.15 (dd,2H,H-2'' and H-4'', ³J_{1'2''}=³J_{3'4''}=16.92 Hz, ²J_{2'2''}=²J_{4'4''}=1.61 Hz), 5.13 (dd,2H,H-2' and H-4', ³J_{1'2'}=³J_{3'4'}=10.91 Hz, ²J_{2'2''}=²J_{4'4''}=1.61 Hz), 2.59 (t,4H,H-3 and H-5, ³J₃₄=³J₄₅=7.42 Hz), 1.88 (m,2H,H-4, ³J₃₄=³J₄₅=7.42 Hz) ppm; NOE between H-2'' and H-5 (or H-4'' and H-3), and between H-1' and H-2' (or H-3' and H-4'); 75.5 MHz ¹³C-NMR (CDCl₃): δ 138.9 (s,2C,C-1 and C-2), 130.2 (s,2C,C-1' and C-3'), 114.7 (s,2C,C-2' and C-4'), 33.1 (s,2C,C-3 and C-5), 21.2 (s,1C,C-4) ppm; UV (10⁻⁵ M in methanol): λ_{max} 250 (sh, ε 7600), 260.6 (ε 13400), 270.6 (ε 17600), 281.6 (ε 13200) nm; IR (pure): 3100-3010 (w, C-H stretch, vinylic), 3000-2800 (s, C-H stretch, aliphatic), 1790 (w,

overtone CH₂ wag, vinylic), 1602 (m, C=C stretch, vinylic), 1450 (w, C-H def., aliphatic), 984 (m, C-H o.o.p., vinylic), 898 (s, C-H o.o.p., vinylic) cm⁻¹; HRMS (C₉H₁₂): M⁺, m/z: calc. 120.0939, found 120.0953

[2',2'',4',4''-²H₄]-1,2-Divinylcyclopentene **5b**. The tetradeuterated triene **5b** was prepared in the same way as the undeuterated compound (**5a**, see above), but with methyl-*d*₃-triphenylphosphonium iodide⁹ and with 1.0 g (8 mmole) of dialdehyde **4**. Yield of **5b**: 1.0 g (98%) of a colourless liquid. Purity according to GC (inj.200 °C, col.70 °C, det.280 °C, τ=10.1 min.): 100%, 100 atom-% D. UV (10⁻⁵ M in methanol): λ_{max} 249 (sh, ε 7600), 260.0 (ε 13500), 269.6 (ε 17600), 280.1 (ε 13600) nm; 300 MHz ¹H-NMR (CDCl₃, cf. Fig.1): δ 6.85 (s,2H,H-1' and H-3'), 2.59 (t,4H,H-3 and H-5,³J₃₄=³J₄₅=7.53 Hz), 1.88 (m,2H,H-4,³J₃₄=³J₄₅=7.53 Hz) ppm; no NOE effect; 75.5 MHz ¹³C-NMR (CDCl₃): δ 138.9 (s,2C,C-1 and C-2), 130.0 (s,2C,C-1' and C-3'), 114.1 (quintet,2C,C-2' and C-4',¹J_{CD}=23.7 Hz), 33.1 (s,2C,C-3 and C-5), 21.2 (s,1C,C-4) ppm; 46.1 MHz ²H-NMR (CCl₄): δ 5.16 (d,2D,D-2'' and D-4'',³J_{12''}=³J_{34''}=17.59 Hz), 5.14 (d,2D,D-2' and D-4',³J_{12'}=³J_{34'}=8.93 Hz) ppm; IR (pure): 3010 (w, C-H stretch, vinylic), 3000-2800 (s, C-H stretch, aliphatic), 2300 (w, C-D stretch, vinylic), 1560 (m, C=C stretch, vinylic), 1450 (m, C-H def., aliphatic), 932 (s, C-H o.o.p., vinylic), 720 (s, C-D o.o.p., vinylic) cm⁻¹; HRMS (C₉D₄H₈): M⁺, m/z: calc. 124.1190, found 124.1179, D-incorporation: 76±10%

The overall yields of the syntheses of *d*₀- and *d*₄-DVCP are 22%. The trienes are very volatile, polymerize easily and are easily photo-oxidized. Therefore they should be stored in a volatile, dry solvent (such as distilled *n*-pentane), in degassed capillaries in a freezer.

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