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Chiral Butadienes, 10[1]

# Barriers to Enantiomerization of 1,2,3,4-Tetramethyl-1,3-butadienes

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Diastereoisomers of the 1,3-dienes R – CMe = CMe – CMe = CMe – R (**2**, R = $CO_2CH_3$; **7**, R = $CH_2OCH_3$) have been prepared. The configurations at the C = C bonds (Schemes 2 and 3) and the conformations of these chiral dienes were investigated by several spectroscopic methods. The barriers to partial rotation about the central C – C single bond in (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-**2** were determined by dynamic $^1$H NMR in the presence of the optically active lanthanide complex (+)-Eu(hfbc)$_3$. The $\Delta G^{\neq}$-values (Table 6) allow conclusions to be drawn about the structure of the *s-trans* transition state of rotation.

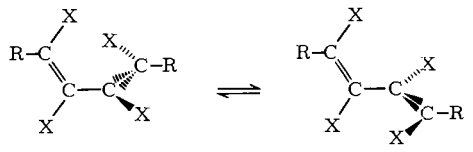
**Chirale Butadiene, 10**[1]

**Enantiomerisierungs-Schwellen von 1,2,3,4-Tetramethyl-1,3-butadienen**

Diastereomere der 1,3-Diene R – CMe = CMe – CMe = CMe – R (**2**, R = $CO_2CH_3$; **7**, R = $CH_2OCH_3$) wurden dargestellt. Die Konfigurationen an den C = C-Bindungen (Schemes 2 und 3) und die Konformationen dieser chiralen Diene wurden mit mehreren spektroskopischen Methoden untersucht. Die Schwellen der Teilrotation um die zentrale C – C-Einfachbindung in (*E,E*)-, (*E,Z*)- und (*Z,Z*)-**2** wurden durch dynamische $^1$H-NMR-Spektroskopie in Gegenwart des optisch aktiven Lanthaniden-Komplexes (+)-Eu(hfbc)$_3$ bestimmt. Die $\Delta G^{\neq}$-Werte (Table 6) lassen Schlüsse auf die jeweilige Struktur des *s-trans*-Übergangszustands der Rotation zu.

Highly substituted 1,3-butadienes adopt nonplanar conformations and are thus chiral[1,3] (Scheme 1). The barriers to enantiomerization of various chiral dienes have been determined by dynamic NMR measurements[3,4]. The barriers are of particular interest if the groups X in Scheme 1 show rotational symmetry (e. g. Cl, Br) or effective rotational symmetry (e. g. Me). In these cases a more detailed understanding of the process of interconversion by means of molecular-mechanics calculations can be

Scheme 1

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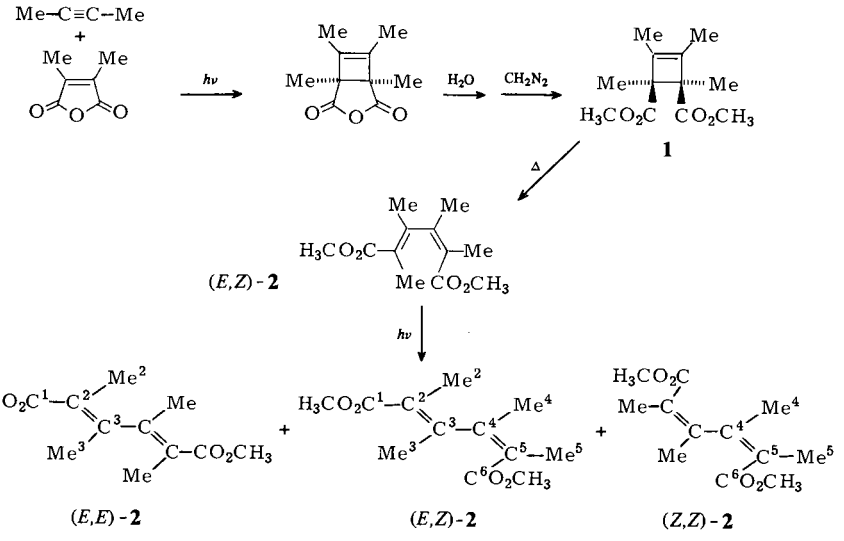
expected. Therefore, the objective of this work was to synthesize 1,2,3,4-tetramethyl-substituted butadienes (X = Me in Scheme 1) and to determine the barriers to internal rotation around the central single bond.

## Syntheses

*cis*-Dimethyl 1,2,3,4-tetramethyl-3-cyclobutene-1,2-dicarboxylate (**1**) was synthesized according to *Criegee* et al.[5] (Scheme 2).

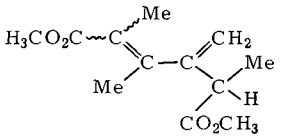
Scheme 2




Thermal ring opening leads to (*E,Z*)-**2**[6]. Stereoisomerization of (*E,Z*)-**2** was performed by photolysis. By gas liquid chromatography (Table 1) besides the three stereoisomers of **2** another major photoproduct is observed. IR and $^1$H NMR spectra suggest constitutions **3** or **4**. These products may result from a [1,3] hydrogen shift in the stereoisomers of **2**. After about 2 h, a photostationary equilibrium with (*Z,Z*)-**2** as the predominating isomer is obtained. Pure isomers were isolated by a combination of preparative liquid and gas chromatography. Reduction of the methoxycarbonyl groups of **1**, methylation, and thermal ring opening of **6** yielded (*E,Z*)-**7** (Scheme 3).

Table 1. Composition [%] of the product mixture obtained by photolysis of (*E,Z*)-**2** in *n*-hexane

| Photolysis time [h] | (*E,E*)-**2** | (*E,Z*)-**2** | (*Z,Z*)-**2** | Other products |
|---|---|---|---|---|
| 0 | – | 100 | – | – |
| 0.5 | 5 | 70 | 22 | 3 |
| 1 | 8 | 55 | 32 | 5 |
| 2 | 9 | 37 | 46 | 8 |
| 3 | 10 | 33 | 46 | 11 |



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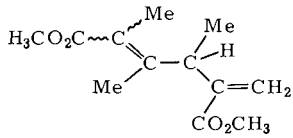

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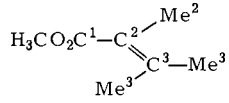

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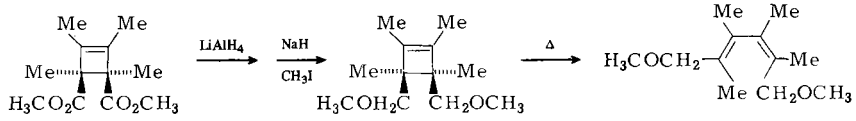
Scheme 3



1 6 (*E,Z*)-7

## Spectroscopic data of (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-2

The configurations of the three muconates were assigned by means of the homoallylic coupling constants $^5J_{HH}$ (Table 2).

Table 2. $^1$H NMR data of stereoisomeric muconates at +34°C[a)]

| | | $^5J_{HH}$ [Hz] | δ($C_6D_6$) | δ($CCl_4$) − δ($C_6D_6$) |
|---|---|---|---|---|
| (*E,E*)-2 | $Me^2$ | 1.5 | 1.72 | 0.00 |
| | $Me^3$ | 1.5 | 2.04 | +0.01 |
| (*E,Z*)-2 | $Me^2$ | 1.5 | 1.80[b)] | −0.17 |
| | $Me^3$ | 1.5 | 2.30[b)] | −0.25 |
| | $Me^4$ | 1.0 | 1.51[b,c)] | +0.36 |
| | $Me^5$ | 1.0 | 1.77[b,c)] | +0.10 |
| (*Z,Z*)-2 | $Me^4$ | 0.9 | 1.83 | 0.00 |
| | $Me^5$ | 0.9 | 1.89 | −0.06 |

a) For numbering of Me groups see Scheme 2. − b) Assignment corresponding to ref.[7]. − c) Assignment according to δ($CCl_4$) − δ($C_6D_6$); cf. ref.[8].

We have confirmed the validity of the rule[7] $^5J_{HH}(E) > {}^5J_{HH}(Z)$ by analysis of the $^{13}$C satellites of the $CH_3$ signals for dimethyl (*E*)-2,3-dimethyl-2-butenedioate ($^5J_{HH}$ = 1.57 Hz) and dimethyl (*Z*)-2,3-dimethyl-2-butenedioate ($^5J_{HH}$ = 1.17 Hz). An unusual aromatic solvent-induced shift δ($CCl_4$) − δ($C_6H_6$) is observed for the $^1$H NMR signals of $Me^2$ and $Me^3$ in (*E,Z*)-2 (Table 2). In contrast to the findings for several enones[7], these signals are shifted *down*field by benzene.

UV and $^{13}$C NMR spectra (Tables 3 and 4) indicate that there is little or no π interaction between the two C=C units. Methyl 2,3-dimethyl-2-butenoate (**5**) has been used as a model compound. The positions of the main UV absorption bands are the same for the dienes and the mono-alkene **5**. The $^{13}$C spectrum of (*E,Z*)-2 seems to be a mere superposition of the (*E,E*)- and (*Z,Z*)-2 spectra (Table 4). This is in agreement with a low π interaction between the two C=C units. The greatest difference (Δδ = 2.4) between (*E,E*)- and (*Z,Z*)-2 was found for $C^3/C^4$ which are connected by the formal single bond. However, the origin of this difference is not understood.

Table 3. UV data of stereoisomeric muconates **2** and of butenoate **5** in methanol

| | $\lambda_{max}$[nm] | ε |
|---|---|---|
| (*E*,*E*)-**2** | 223 | 15 500 |
| (*E*,*Z*)-**2** | 222 | 14 500 |
| (*Z*,*Z*)-**2** | 223 | 11 600 |
| **5** | 223 | 8100 |

Table 4. $^{13}C$ NMR δ-values of stereoisomeric muconates **2** and of butenoate **5** in $CDCl_3$ at +30°C[a]

| | $C^1$ | $C^6$ | $C^2$ | $C^5$ | $C^3$ | $C^4$ | $Me^2$ | $Me^3$ | $Me^4$ | $Me^5$ |
|---|---|---|---|---|---|---|---|---|---|---|
| (*E*,*E*)-**2** | 169.2 | | 122.0 | | 148.6 | | 15.9[b] | 18.8[b] | | |
| (*E*,*Z*)-**2**[c] | 169.2 | 168.4 | 122.8 | 120.0 | 148.0 | 151.1 | 16.2 | 18.7 | 19.8 | 14.7 |
| (*Z*,*Z*)-**2** | | 168.7 | | 120.4 | | 151.0 | | | 19.9[b] | 14.8[b] |
| **5** | 169.7 | | 122.5 | | 143.7 | | 15.6[b] | 22.5[b]<br>22.9 | | |

[a] For numbering of carbon atoms see Scheme 2 and formula **5**. – [b] Assignment is uncertain. – [c] Assignments within the different groups of carbons are tentative.

In the IR spectra of the three isomers of **2** the carbonyl stretching frequency is found at about 1723 $cm^{-1}$ (Table 5) which is characteristic for conjugated carboxylate groups[9]. The minor differences of wavenumbers might reflect variations in the conjugation between the C=O and the C=C bonds. The difference between the wavenumbers of the symmetrical and antisymmetrical stretching vibrations of the C=C bonds in 1,3-dienes has been used to estimate the torsion angle (Θ) of the double bonds[10]. $\tilde{\nu}_s - \tilde{\nu}_a$ is found to be +34 $cm^{-1}$ for 1,3-butadiene (Θ = 180°) and −32 $cm^{-1}$ for 1,3-cycloheptadiene (Θ = 0°). Both the symmetrical and antisymmetrical C=C stretching ($\tilde{\nu}_s$ and $\tilde{\nu}_a$) can be identified (Table 5). $\tilde{\nu}_s$ gives rise to a strong band in the Raman spectrum and appears at higher wavenumber than $\tilde{\nu}_a$. The differences $\tilde{\nu}_s - \tilde{\nu}_a$ are approximately +27 $cm^{-1}$ and indicate skewed conformations for all three isomers with torsion angles between 180 and 90°.

Table 5. IR and Raman wavenumbers $\tilde{\nu}$ [$cm^{-1}$] of 1,3-butadienes **2** and **7** as well as of butenoate **5**. s = strong, m = medium, w = weak

| | IR (capillary film) | | Raman (neat) | |
|---|---|---|---|---|
| | C=C | C=O | C=C | C=O |
| (*E*,*E*)-**2** | 1622 (m) | 1729 (s) | 1630 (m, shoulder)<br>1644 | 1716 (m) |
| (*E*,*Z*)-**2** | 1620 (w)<br>1646 (w) | 1716 (s) | 1625 (m)<br>1648 (s) | 1713 (m) |
| (*Z*,*Z*)-**2** | 1611 (w)<br>1640 (w) | 1723 (s) | 1613 (m)<br>1641 (s) | 1708 (m) |
| **5** | 1641 (m) | 1716 (s) | 1645 (s) | 1715 (m) |
| **7** | 1668 (m) | – | – | – |

## Barriers to Internal Rotation about the Central Single Bond

The isomeric muconates do not possess diastereotopic groups for the direct measurement of the barriers to internal rotation. However, it has been shown that addition of optically active auxiliary compounds may lead to formation of diastereomeric association complexes such that unequal spectra might appear for the enantiomers[4,11-13]. Figure 1 shows the NMR of the methyl protons of (*E,Z*)-**2** before and after addition of 0.4 equivalents of (+)-tris[3-(heptafluorobutyryl)-D-camphorato]europium(III), (+)-Eu(hfbc)$_3$.

The expected temperature dependence of the $OCH_3$ lineshapes at $\delta = 8.37$ and 7.81 resulted in $\Delta G^{\neq} = 65.2$ kJ mol$^{-1}$ at +13 °C for the partial rotation about the central single bond (Table 6). Lineshape parameters were calculated using a method developed by *Küspert*[12]. This procedure, called TAPIRS, is based on intensity ratios in one single spectrum without previous knowledge of other parameters. Similarly, $\Delta G^{\neq}$ was obtained for (*E,E*)-**2**. In the case of (*Z,Z*)-**2**, however, TAPIRS could not be applied

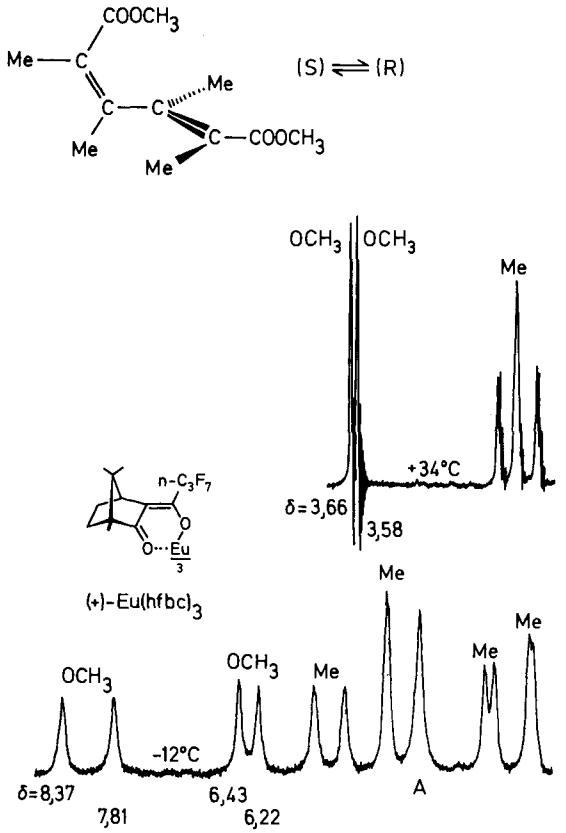



Figure 1. NMR (60 MHz) of the methyl protons of (*E,Z*)-**2** in $CCl_4$ before (top) and after (bottom) addition of 0.40 equivalents of (+)-Eu(hfbc)$_3$. The resonance designed A in the lower spectrum originates from the auxiliary compound

Table 6. Barriers $\Delta G_T^{\ddagger}$ to partial rotation about the central single bond

| | (*Z*,*Z*)-**2** | (*E*,*Z*)-**2** | (*E*,*E*)-**2** | (*E*,*Z*)-**7** |
|---|---|---|---|---|
| Solvent | $CCl_4/CFCl_3$ (2:1) | $CCl_4$ | $CCl_4/CFCl_3$ (2:1) | $CDCl_2CDCl_2$ |
| Aux. Comp. | (+)-Eu(hfbc)$_3$ | (+)-Eu(hfbc)$_3$ | (+)-Eu(hfbc)$_3$ | Eu(fod)$_3$ |
| Equivalents | 0.80 | 0.40 | 0.80 | 0.32 |
| $T$[K] | 257.7 | 286.2 | 298.5 | > 378 |
| $\Delta G_T^{\ddagger}$ [kJ mol$^{-1}$] | 58.5 ± 1.0 | 65.2 ± 0.6 | 73.5 ± 0.7 | > 83.5 |
| Method | a) | TAPIRS[12] | TAPIRS[12] | – |
| $^1$H NMR signals used | $OCH_3$ | $OCH_3$ | $OCH_3$ | $OCH^AH^B$ |

a) Simulation using extrapolated lineshape parameters[13].

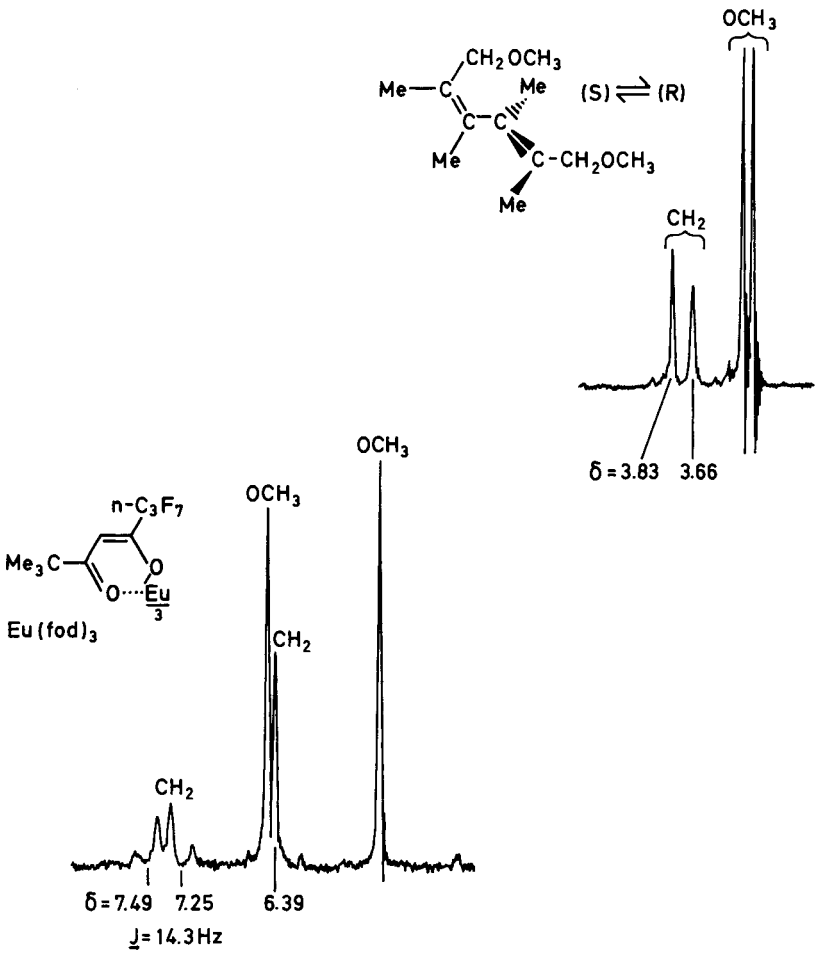



Figure 2. NMR of the methylene and methoxyl protons of (*E*,*Z*)-**7** in $CCl_4$ at 34°C before (top) and after (bottom) addition of 0.32 equivalents of Eu(fod)$_3$

because one of the $OCH_3$ signals was partially distorted by an overlapping resonance of the shift reagent. Therefore spectral simulation[13] using extrapolated[14] lineshape parameters was used to determine $\Delta G^{\neq}$. (*E,Z*)-**7** contains diastereotopic methylene protons such that addition of an optically active auxiliary compound should not be necessary to determine $\Delta G^{\neq}$. However, the anisochrony of the methylene protons in suitable solvents was too small to give rise to an AB spectrum. Addition of 0.32 equivalents of the achiral shift reagent $Eu(fod)_3$ shifts and splits one of the methylene signals into an AB-spectrum (Figure 2). Unfortunately the chemical shift difference of these diastereotopic methylene protons becomes very small at higher temperatures. An accurate determination of $\Delta G^{\neq}$ was therefore impossible and only a lower limit could be obtained.

The order of barrier heights (*E,E*) > (*E,Z*) > (*Z,Z*) is a reasonable one: In the crowded *s-trans*[4] transition state for (*Z,Z*)-**2** the two $CO_2CH_3$ groups can be turned out of coplanarity, thus minimizing non-bonded interactions. In contrast, the transition state for (*E,E*)-**2** suffers from Me/Me interactions which are more difficult to diminish. It is of interest to compare the barrier for (*E,E*)-**2** with its chloro analog where the methyl groups on the butadiene chain are replaced by chlorine. No experimental data exist; however, from increments known for (*E,E*)-tetrachlorobutadienes[3] the barrier can be estimated to $\Delta G^{\neq} \approx 54$ kJ mol$^{-1}$ which is considerably smaller than the value for (*E,E*)-**2**. The barrier of (*E,Z*)-**7** is higher by at least 18 kJ mol$^{-1}$ than the barrier found for (*E,Z*)-**2** (Table 6). This increase reflects a greater effective bulkiness of the $CH_2OCH_3$ group as compared to the $CO_2CH_3$ group.

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## Experimental Part

IR spectra: Beckman IR 4240 spectrometer. – Raman spectra: Coderg T 800 Raman instrument using the 5145 Å line of an Ar-LASER. – UV spectra: Shimadzu 210 UV spectrometer. – $^1H$ NMR spectra: Varian T-60 (CW mode, 60 MHz) and Bruker WH-90 (PFT mode, 8 K data points, 90 MHz). Temperature measurement was performed using methanol and the Van Geet formula. Cyclosilane-$d_{18}$ (Merck AG, Darmstadt) was used as internal standard for PFT $^1H$ NMR spectra and chemical shifts were converted to $\delta_{TMS}$ using $\delta_{TMS} - \delta_{cyclosilane} = -0.328$. – $^{13}C$ NMR spectra: PFT mode, 22.63 MHz, Bruker WH-90, 8 K data points under proton noise decoupling. – High-resolution mass spectra: Varian MAT-311 A spectrometer, 70 eV, direct insertion probe. – Photolysis: Hg high-pressure lamp TQ 150, photoreactor with forced circulation (Otto Fritz GmbH, Hofheim). – Analytical gas chromatograms: Varian 1860-42 chromatograph, 20 m glass capillary column (0.25 mm i. d.) with marlophen (split 1 : 6). – Preparative GC separations: APG 402 (Hupe & Busch), 2 m column (20 mm i. d.), filled with 10% Carbowax 20 M on Chromosorb P/DMCS (60 – 80 mesh).

(+)-Eu(hfbc)$_3$ was available from Regis Chemical Co., Morton Grove, Illinois, USA. – 1-Butyne was obtained commercially from Air Products GmbH, Hattingen, W.-Germany, and converted to 2-butyne as described by *Brandsma*[15]. Methyl 2,3-dimethyl-2-butenoate (**5**) was synthesized according to *Huston* and *Goerner*[16].

*Dimethyl 1,2,3,4-tetramethyl-3-cyclobutene-1,2-dicarboxylate* (**1**): Synthesized according to *Criegee* and coworkers[5]. – $^1$H NMR (+34°C, $CCl_4$): δ = 1.24 (s, 6H), 1.59 (s, 6H), 3.54 (s, 6H).

*Dimethyl (E,Z)-2,3,4,5-tetramethyl-2,4-hexadienedioate* ((*E,Z*)-**2**): Obtained according to *Adam*[6] by thermolysis of **1** in a closed glass tube. – UV (methanol): $\lambda_{max}$ = 222 nm (ε = 14500). – MS, molecular ion: Calc. 226.1205, Found 226.1202. – $^1$H NMR (+26°C, $CDCl_3$): δ = 1.70 (q, *J* = 1.45 Hz, 3H), 1.87 (q, *J* = 1.05 Hz, 3H), 1.93 (q, *J* = 1.05 Hz, 3H), 2.13 (q, *J* = 1.45 Hz, 3H), 3.68 (s, 3H), 3.75 (s, 3H).

*Photochemical E-Z isomerization of (E,Z)-***2**: A 1% solution of (*E,Z*)-**2** in *n*-hexane was irradiated for 2 h in the above mentioned photoreactor using a quartz lamp tube. The reaction was followed by GC analysis of samples taken at different times.

*Dimethyl (E,E)-2,3,4,5-tetramethyl-2,4-hexadienedioate* ((*E,E*)-**2**) was isolated from the photoreaction product by liquid chromatography using a lowbar silica gel column (Merck, Darmstadt) and petrolether/ether (4:1 v/v) with a flow of 150 ml/min. (*E,E*)-**2** was eluted first and was well separated from the strongly overlapping peaks of the other isomers. After removing the solvent the compound was purified by microdistillation, b. p. 50°C/0.01 mbar. – UV (methanol): $\lambda_{max}$ = 223 nm (ε = 15500). – MS, molecular ion: Calc. 226.1205, Found 226.1200. – $^1$H NMR (+34°C, $CCl_4$): δ = 1.72 (q, *J* = 1.5 Hz, 6H), 2.04 (q, *J* = 1.5 Hz, 6H), 3.68 (s, 6H).

*Dimethyl (Z,Z)-2,3,4,5-tetramethyl-2,4-hexadienedioate* ((*Z,Z*)-**2**): Isolation from the photolysis mixture was performed with the aid of preparative gas chromatography on Carbowax 20 M. (*Z,Z*)-**2** showed the lowest retention time and could be well separated from the other components. B. p. 73°C/0.5 mbar. – UV (methanol): $\lambda_{max}$ = 223 (ε = 11600). – MS, molecular ion: Calc. 226.1205, Found 226.1201. – $^1$H NMR (+34°C, $CCl_4$): δ = 1.83 (broad s, 12H), 3.56 (s, 6H).

*cis-3,4-Bis(methoxymethyl)-1,2,3,4-tetramethyl-1-cyclobutene* (**6**): To 1.7 g (10 mmol) of *cis*-3,4-bis(hydroxymethyl)-1,2,3,4-tetramethyl-1-cyclobutene[5] and 3.4 g (24 mmol) of $CH_3I$ in 10 ml of absol. dimethoxyethane 0.65 g (80% in mineral oil, 22 mmol) of NaH was added in 2 portions[17]. After 10 min another 0.4 ml of $CH_3I$ was added, the mixture stirred for 1.5 h at room temperature, and the solvent removed in vacuo. After addition of 50 ml of ether, NaI was removed by filtration. The crude product was treated a second time as described and the product chromatographed on silica gel, petrolether (40–60°C)/ether (2:1) being the eluents. The yield was 1.0 g (50%). – IR(film): 1690, 1430, 1180, 1080 cm$^{-1}$. – $^1$H NMR (+34°C, $CCl_4$): δ = 0.98 (s, 6H), 1.43 (s, 6H), 3.22 (s, 6H), 3.25, 3.35 (AB, *J* = 8.8 Hz, 4H).

*(E,Z)-1,6-Dimethoxy-2,3,4,5-tetramethyl-2,4-hexadiene* ((*E,Z*)-**7**): 1.0 g of **6** was heated under $N_2$ atmosphere in a closed glass tube for 2 h at 210°C. The crude product was chromatographed on silica gel using petrolether (40–60°C)/ether (2:1) as eluents. Pure (*E,Z*)-**7** was obtained in 50% yield. – UV (*n*-hexane): No maximum above 200 nm. ε = 340 (260 nm), 1500 (240), 4100 (220). – IR(film): 2977, 2915, 2811, 1756, 1722, 1668, 1447, 1382, 1371, 1189, 1093 cm$^{-1}$. – $^1$H NMR (+34°C, $CCl_4$): δ = 1.48 (q, 3H), 1.67 (broad s, 9H), 3.13 (s, 3H), 3.20 (s, 3H), 3.64 (broad s, 2H), 3.82 (broad s, 2H).

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