48. Light-Induced and Thermal π-Skeletal Rearrangement of Heptalenes with Retention of Configuration[1])

by **Werner Bernhard**[2]), **Paul Brügger**[3]), **Peter Schönholzer, Roland H. Weber**[4]), and **Hans-Jürgen Hansen***

Central Research Units, *F. Hoffmann-La Roche & Co., Ltd.*, CH-4002 Basle

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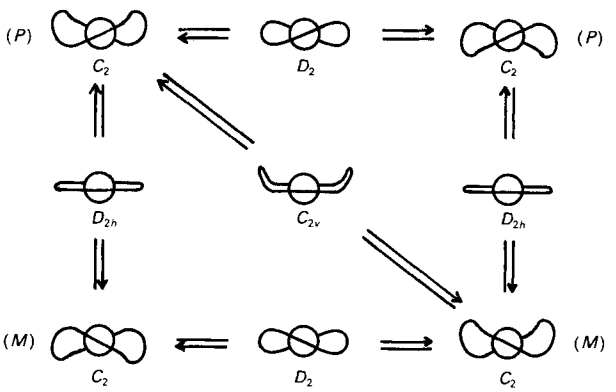
It is shown that dimethyl 5,6,8,10-tetramethyl- (**3**) and 8-(*tert*-butyl)-5,6,10-trimethylheptalene-1,2-dicarboxylate (**5**), and their derivatives rearrange reversibly on irradiation or on heating to yield the corresponding 1,6,8,10-tetramethyl- (**4**) and 8-(*tert*-butyl)-1,6,10-trimethylheptalene-1,2-dicarboxylate (**6**), and their derivatives by double-bond shift (π-skeletal rearrangement) *via* a transition state with D_2 symmetry as the highest possible one. This follows from the fact that (−)-(*P*)-**3** is photochemically as well as thermally rearranged to give (−)-(*P*)-**4** *i.e.* the π-skeletal rearrangement occurs with retention of configuration of the heptalene skeleton and without loss of optical purity.

Introduction. – Thermal π-skeletal rearrangements of heptalenes[5]), *i.e.* double-bond shifts (DBS) have so far been observed in heptalene itself ($E_a \approx 3.5$ kcal mol^{-1} [3]), in dimethyl heptalene-3,8-dicarboxylate ($E_a < 3.5$ kcal mol^{-1} [4]), 1,2-dicarboxylate ($T_C \approx -25$ °C[5]) and 1,6-dicarboxylate ($\Delta G^{\neq}_{233} = 14$ kcal mol^{-1} [6]) as well as in heptalene-



Scheme 1. *Topological Changes in a* C_2 *Loop as Models for* π*-Skeletal Rearrangement in Heptalene*

[1]) Presented in part by *H.-J. H.* at lectures in Vienna (1982), Berlin (1982), Lodz (1984), and Zurich (1985).

[2]) Part of the Ph. D. thesis of *W. B.*, No. 837, University of Fribourg/Switzerland, 1982. Present address: Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Universitätstr. 16, CH-8092 Zürich.

[3]) Part of the Ph. D. thesis of *P. B.*, No. 858, University of Fribourg/Switzerland, 1983.

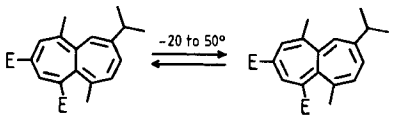
[4]) Part of the planned Ph. D. thesis of *R. H. W.*, University of Basle/Switzerland.

[5]) For a thermal σ-skeletal rearrangement of heptalenes, see [1]. We will report on this rearrangement in detail later in this journal [2].

1,6-dicarbaldehyde ($\Delta G^{\ddagger}_{233} = 9.9$ kcal mol^{-1} [6]). The DBS is degenerated, *i.e.* it leads to an isoenergetic structure in the parent compound and in symmetrically substituted (*e.g.* heptalene-3,8-dicarboxylate) with respect to the two relevant mirror planes (through C(5a), C(10a) and C(3), C(8)) in a hypothetical D_{2h} heptalene[6]). X-Ray analysis of heptalenes (*cf.* [2] [7] [8] and below) show that their ring skeleton possesses C_2 symmetry allowing the formulation of at least three different transition-state geometries for the DBS. These geometries can be classified according to the highest possible symmetry of their topology (*Scheme 1)* since *the stereochemical outcome of a given chemical transformation is determined by the highest attainable symmetry in the transition state*[7]). The symmetries are D_2, C_{2v} and C_{2h} or D_{2h}[8]) for heptalene itself and symmetrically substituted heptalenes (see above). There exist two modes (*via* C_{2v} and D_{2h} or $C_{2h}+D_2$) of the DBS accompanied by racemization and one mode (*via* D_2) which occurs with retention of configuration[9]). In an unsymmetrically substituted heptalene (*e.g.* (*P*)-1-methylheptalene[10])), all three pathways can be differentiated with chiral heptalenes, since the DBS *via* D_2 symmetry will lead to a constitutionally isomeric heptalene with the same configuration (*e.g.* (*P*)-5-methylheptalene), whereas a DBS *via* C_{2v} symmetry will result in a constitutionally isomeric heptalene with the inverted configuration (*e.g.* (*M*)-5-methylheptalene). On the other hand, a DBS *via* D_{2h} (or C_{2h} followed by D_2) symmetry will lead to racemization (*e.g.* (*PM*)-5-methylheptalene)[11]).

We have already reported [1] that dimethyl 9-isopropyl-1,6-dimethylheptalene-3,5-dicarboxylate (**1**)[12]) possesses, according to its ^{1}H- and ^{13}C-NMR spectra, CH_3 groups of the i-Pr moiety in diastereotopic positions despite the fact that the temperature depen-

Scheme 2



1 E = COOCH$_3$ **2**

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[6]) Disubstitution in heptalene with localized double bonds leads to 45 constitutionally isomeric heptalenes and to 45 additional enantiomers if the heptalene skeleton possesses C_2 symmetry (*cf.* [2] [7] [8]). If both substituents are identical the number of isomers is reduced to 25 of which the 1,5-, 2,4-, 1,10-, 2,9-, and 3,8-isomers should exhibit a degenerate DBS.

[7]) It is not relevant whether this symmetry is really attained by the atoms defining the topology (*e.g.* the C-atoms of the heptalene skeleton) at the same time, or only passed sequently. The highest attainable symmetry describes, so to speak, the 'Rubicon of symmetry' that has to be crossed simultaneously or sequently by the atoms.

[8]) Calculations have shown that planar heptalene with localized double bonds (C_{2h} symmetry) is energetically favoured over planar heptalene with delocalized double bonds (D_{2h} symmetry) (*cf.* [9]). This indicates that both transition states are lying on energetically separated hypersurfaces.

[9]) A similar analysis based on the conformational changes in cycloheptatriene has already been performed for heptalene [10].

[10]) Numbering of the heptalene ring according to the IUPAC nomenclature (see Rule A-21).

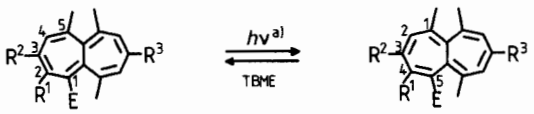
[11]) Models of the different transition states show that the non-bonding interactions in an idealized D_{2h} or C_{2h} transition state (*cf.*, however, *Footnote 7*) should be greater than in an idealized C_{2v} transition state (*e.g.* CH_3 groups at C(1) and C(10) exhibit non-bonded 1,5 C–C distances of about 1.8 (D_{2h} or C_{2h}) and 2.8 Å (C_{2v})).

[12]) Structure confirmed by an X-ray analysis [2]. The heptalene skeleton shows pseudo-C_2 symmetry with torsional angles between C(1)–C(10a)–C(5a)–C(5), and C(6)–C(5a)–C(10a)–C(10) of 58.1° and 60.3°, respectively.

dence (−20 to 50°) of the other signals indicate a rapid π-bond shift *(Scheme 2)*. This was the first indication that the DBS in heptalenes may occur without loss of the optical integrity. In the following, we report on experiments which clearly demonstrate that light-induced as well as thermal DBS in heptalenes occur *via* a transition state with D_2 symmetry.

Light-Induced and Thermal π-Skeletal Rearrangements. – When dimethyl 5,6,8,10-tetramethylheptalene-1,2-dicarboxylate (**3**) [8] in (*tert*-butyl) methyl ether (TBME) solution was exposed to normal laboratory light or irradiated with a high-pressure Hg lamp through a *Pyrex* filter, rapid and clean formation of a new heptalene **4** was observed *(Scheme 3)*. On the other hand, irradiation of **4** yielded again the mixture of **3** and **4**. A similar reversible photoreaction was observed when dimethyl 8-(*tert*-butyl)-5,6,10-trimethylheptalene-1,2-dicarboxylate (**5**; see *Exper. Part*) was irradiated in TBME solution. The double-bond isomer **6** was obtained in 65% yield. Again, the same ratio of **5**/**6** was reached when pure **6** was irradiated[13]).

Scheme 3



3 (54%)	$R^1 = E$, $R^2 = H$, $R^3 = CH_3$	**4** (46%)
5 (35%)	$R^1 = E$, $R^2 = H$, $R^3 = t\text{-}C_4H_9$	**6** (65%)
[3-$^2H_1$]-**3** (54%)	$R^1 = E$, $R^2 = D$, $R^3 = CH_3$	[3-$^2H_1$]-**4** (46%)
7 (56%)	$R^1 = A$, $R^2 = H$, $R^3 = CH_3$	**8** (44%) b)

a) High-pressure Hg lamp; TBME = (*tert*-butyl) methyl ether.
b) A = COOH; determined after esterification into **4**.

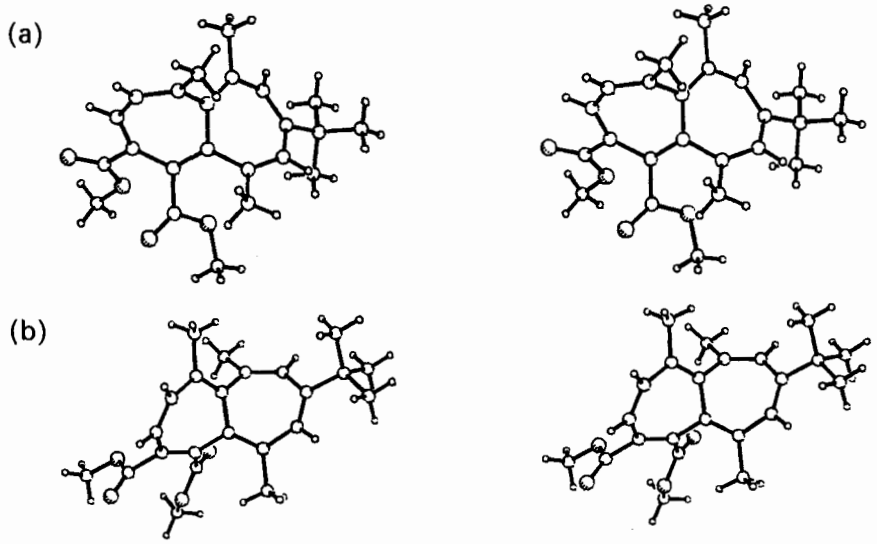


Fig. 1. *Stereoscopic projections of* (±)-**5** (a) *and* (±)-**6** (b). Both compounds are shown in the (*P*)-configuration.

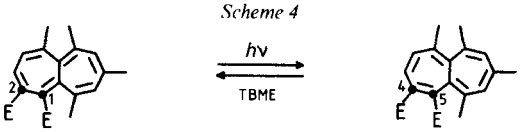
13) All 4 heptalenes (**3**–**6**) were completely photostable in the crystalline state.

Whereas the 2-acid **7** showed the same photochemically reversible π-skeletal rearrangement as **3** and **5** (see *Scheme 3*), the 1,2-dicarboxylic anhydride [8] of **7** remained unchanged after irradiation[14]).

The structure of the new heptalenes **3–6** was unequivocally determined by an X-ray analysis of the heptalenes **5** and **6** *(Fig. 1)*[15]).

The structure of **3** and **4** follows from a comparison of the spectral data of **3** and **4** with those of **5** and **6** (see *Exper. Part*). Additional structural information of **4** and **6** was obtained by $^3J(2,3) = 11.8$ and 12.0 Hz, respectively, which clearly indicates that a double bond is located between C(2), C(3)[16]). The position of H–C(3) in the ^{1}H-NMR spectra was determined by ^{2}H-labelling of **3** and **4** in position 3 (see *Scheme 3* and *Exper. Part*). Further information on the structural relation between **3** and **4** was obtained by the preparation and photochemical rearrangement of [1,2–$^{13}C_2$]-**3** (*Scheme 4, cf.* [2]). The difference between the ^{13}C,^{13}C-coupling constants (^{1}J) in **3** and **4** show unequivocally that a DBS had occurred (*cf.* ^1J (1,2) = 68.8 Hz and $^1J(2,3) = 53.7$ Hz in 1,3-butadiene [13], and for a similar ^1J ratio in *trans*-stilbene [14])[17]).

Scheme 4



[1,2-^{13}C]-**3** $^1J(1,2) = 61.4$ Hz

● = ^{13}C

[4,5-$^{13}C_2$]-**4** $^1J(4,5) = 74.3$ Hz

[14]) Similar photo-induced, π-skeletal rearrangements were also observed with 1,2-bis(hydroxymethyl)-5,6,8,10-tetramethylheptalene [8] and 1,2,5,6,8,10-hexamethylheptalene [11].

[15]) *Crystal Data of* **5**. *Space group:* monoclinic $P2_1/n$ with $a = 6.351$ (1), $b = 17.875$ (5), and $c = 18.190$ (3) Å; density: 1.52 Mgm^{-3}, $Z = 4$. *Data collection.* Crystal size: 0.17 × 0.20 × 0.25 mm^3; temp.: 170 K, wave length: 0.71069 Å; total data measured: 4099 (excluding standards); total data observed: 2299; refinement proceeded smoothly to convergence at $R = 0.0458$ with anisotropic refinement of all non-H-atoms. *Structural data of the heptalene skeleton: Bond lengths:* C(1)–C(2) = 1.473, C(2)–C(3) = 1.355, C(3)–C(4) = 1.432, C(4)–C(5) = 1.345, C(5)–C(5a) = 1.493, C(5a)–C(6) = 1.346, C(6)–C(7) = 1.453, C(7)–C(8) = 1.357, C(8)–C(9) = 1.464, C(9)–C(10) = 1.338, C(10)–C(10a) = 1.490, C(10a)–C(5a) = 1.475, and C(10a)–C(1) = 1.354 Å. *Torsional angles:* C(5)–C(5a)–C(10a)–C(1) = 64.0°, C(6)–C(5a)–C(10a)–C(10) = 65.7°, C(10a)–C(1)–C(2)–C(3) = –31.0°, C(2)–C(3)–C(4)–C(5) = 32.6°, C(5a)–C(6)–C(7)–C(8) = –34.0°, C(7)–C(8)–C(9)–C(10) = 35.5°.

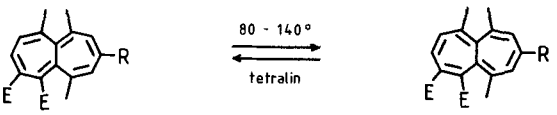
Crystal Data of **6**. *Space group:* triclinic $P\bar{1}$ with $a = 7.454$ (9), $b = 9.841$ (10), and $c = 15.280$ (18) Å; density: 1.15 Mgcm^{-3}, $Z = 2$. *Data collection.* Crystal size: 0.33 × 0.48 × 0.80 mm^3; temp.: 170 K; wave length: 0.71069 Å; total data measured: 4138 (excluding standards); total data observed: 2937; refinement proceeded smoothly to convergence at $R = 0.0493$ with anisotropic refinement of all non-H-atoms. *Structural data of the heptalene skeleton: Bond lengths:* C(1)–C(2) = 1.449, C(2)–C(3) = 1.342, C(3)–C(4) = 1.449, C(4)–C(5) = 1.355, C(5)–C(5a) = 1.480, C(5a)–C(6) = 1.352, C(6)–C(7) = 1.456, C(7)–C(8) = 1.357, C(8)–C(9) = 1.465, C(9)–C(10) = 1.338, C(10)–C(10a) = 1.481, C(10a)–C(5a) = 1.474, and C(10a)–C(1) = 1.355 Å. *Torsional angles:* C(5)–C(5a)–C(10a)–C(1) = 64.6°, C(6)–C(5a)–C(10a)–C(10) = 62.6°, C(10a)–C(1)–C(2)–C(3) = –32.4°, C(2)–C(3)–C(4)–C(5) = 35.0°, C(3)–C(4)–C(5)–C(5a) = 3.2° (*cf.* C(10a)–C(1)–C(2)–C(3) = –31.0° in **5**), C(5a)–C(6)–C(7)–C(8) = –34.0°, C(7)–C(8)–C(9)–C(10) = 36.0°. Originally, we assigned the structure of a 3,6,8,10-tetramethyl- and 8-(*tert*-butyl)-3,6,10-trimethylheptalene-1,2-dicarboxylate to **4** and **6**, respectively. We thank Prof. Dr. *K. Hafner* and Dipl.-Chem. *G. L. Knaup*, Institut für Organische Chemie, Technische Hochschule Darmstadt, for the information on their X-ray analysis of **4**, obtained by thermal isomerization of **3** (*cf.* [12] and below).

[16]) Compare the corresponding coupling constants $^3J(3,4) = 5.8$ and 6.0 Hz in **3** and **5**, respectively.

[17]) $^1J(2,3) \approx 72$ Hz in **3**. Thus, the ^1J (^{13}C,^{13}C) coupling constants in heptalenes are good probes for the presence of C–C ($^1J \approx 60$ Hz) or C=C bonds ($^1J \approx 70$ Hz) in the perimeter.

Since the isomerized heptalenes **4** and **6** accompanied **3** and **5**, respectively, to an extent of 10% also in the original mixture of the thermal reaction of dimethyl acetylenedicarboxylate and the corresponding azulenes (*cf.* [8] and *Exper. Part*), we looked also for a thermal isomerization of **3** and **5**. We found that these isomerizations occur easily at temperatures > 80° (*Scheme 5; cf.* [12]).

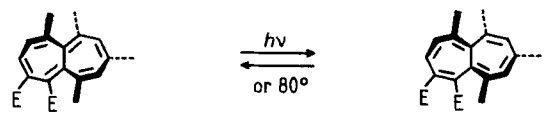
Scheme 5



R = CH_3:	**3** (88.7%)	100°	**4** (11.3%)
R = t-C_4H_9:	**5** (89.2%)	100°	**6** (10.8%)

The investigation of the temperature dependence of the equilibrium **3**⇆**4** (*cf.* the *Table* in *Exper. Part*) in tetralin yielded $\Delta H° = -10.0 \pm 1.4$ kJ mol^{-1}. $\Delta S° = -9.7 \pm 3.7$ JK^{-1}mol^{-1}, *i.e.* the enthalpy favours **3** and the entropy **4**. The rate ($k_{1,2}+k_{4,5}$)[18]) for the equilibration at 100° is for **3**/**4** 2.7 times faster than for **5**/**6**. This difference may reflect the greater buttressing effect of a t-Bu group as compared to a CH_3 group at C(8) in the transition state.[19]).

Scheme 6



(–)-(*P*)-**3** (–)-(*P*)-**4**[a])

[a]) Highest observed $[\alpha]_D^{20} = -1095°$ (acetone; e = 0.99).

Further information of the nature of the transition state for the DBS is achieved from the observation that (–)-(*P*)-**3** [8] rearranged photochemically as well as thermally to yield (–)-**4** (*Scheme 6; cf.* also [12]). A comparison of the CD spectra of (–)-(*P*)-**3** and (–)-**4** (*cf. Fig. 2*) clearly shows that (–)-(*P*)-**4** with two (–)-CE at 388 and 318 nm and a strong (+)-CE at 280 nm (*cf.* [8]) is also (P)-configurated. Thus, in the photochemical and thermal DBS in **3** and **4** a transition state with D_2 as the highest possible symmetry is involved [20]).

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[18]) $k_{1,2}$ = rate for the isomerization of the 1,2-diester and $k_{4,5}$ for that of the 4,5-diester.

[19]) It is of interest to note that **3** and **4** as well as **5** and **6** show identical MS (70 eV). This could be attributed to the fact that the thermal equilibration occurs before ionization. However, it is more likely that **3** and **4** as well as **5** and **6**, lead to the same M^+ ion under the conditions of measurement.

[20]) We observed thermal DBS at 20° with retention of configuration also in 5,5-dimethoxy-4-oxatricyclo[8.5.0.0^{2,6}]pentadeca-2(6),7,9,11,13,15-hexaen-3-ones (heptalene-1,2-dicarboxylic hemi-ortho-anhydrides) [15]. So far, we have performed no further experiments to elucidate the electronic nature of the photochemical reaction. It should be noted that *Nakajima et al.* [9d] [9e] calculated for C_{2h} heptalene a bond equalization in the S_1 and T_1 state, *i.e.* the symmetry is changed to D_{2h} in the lowest excited states of heptalene. Our preliminary PPP-CI calculations [16] of C_{2h} heptalene with twisted p-C AO's to simulate the C_2 symmetry of the heptalene skeleton show that bonding in the HOMO's results in a non-bonding state in the next following LUMO's which is qualitatively in agreement with our observed photochemical DBS in heptalenes.

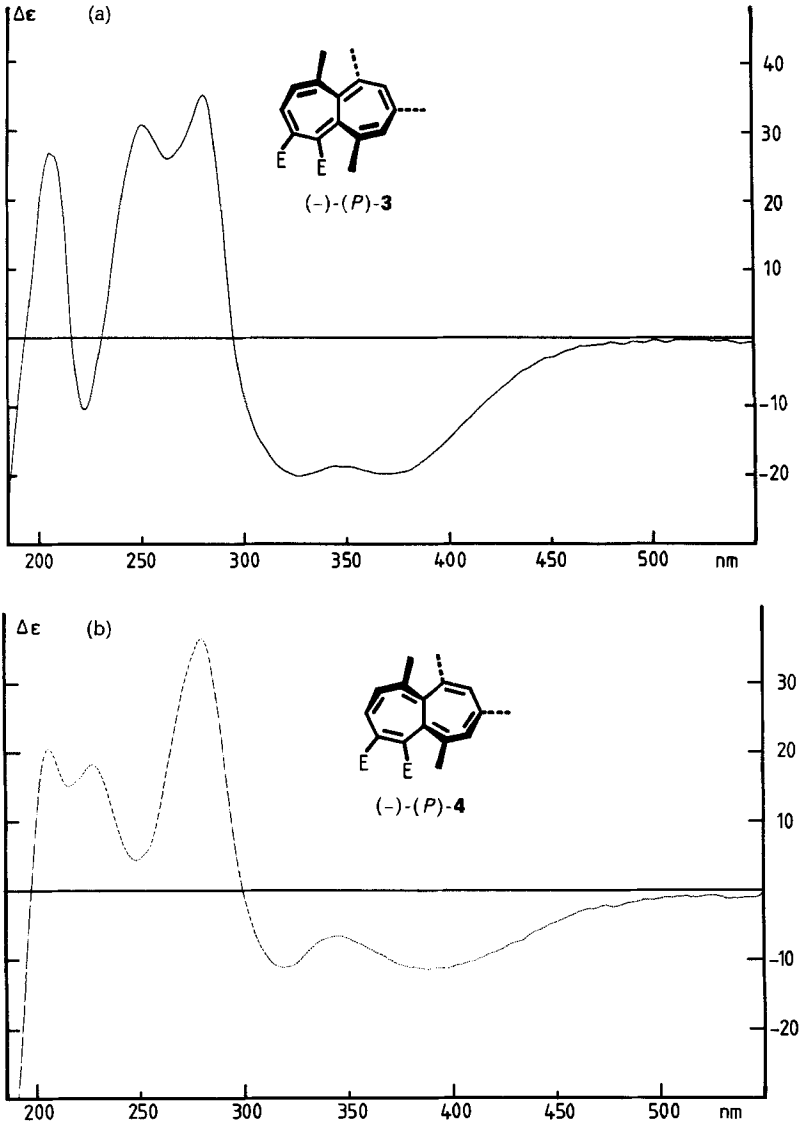

Fig. 2. *Comparison of the CD spectra* (cyclohexane) *of* (−)-(P)-**3** (a) *and* (−)-(P)-**4** (b) *derived photochemically or thermally from* (−)-(P)-**3**

The thermal DBS in **3** and **4** occurs at temperatures < 100° without racemization ($[k_{12} + k_{45}]/[k_{rac}(1,2)+k_{rac}(4,5)] \approx 400$ in tetralin at 100°). The photochemical DBS takes place also without measurable racemization at short irradiation times. Prolonged irradiation times lead to photoracemization[21]).

[21]) Optically active dimethyl 7-isopropyl-5,10-dimethylheptalene-1,2-dicarboxylate [8] shows also only a slow photoracemization.

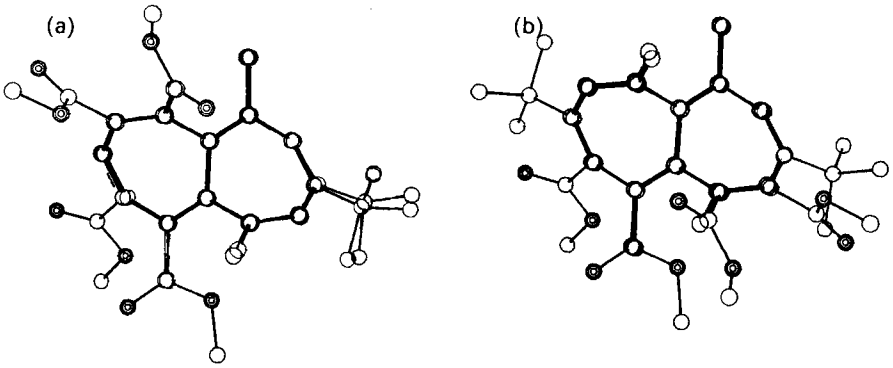

Fig. 3. *Matchings of the heptalene skeletons of* (P)-**5** (black) *and its double-bond isomer* (P)-**6** (red); a) *match of C(1)***5**/*C(1)***6** *to C(10)***5**/*C(10)***6**; b) *match of C(1)***5**/*C(6)***6**. *C(5)***5**/*C(10)***6**. *C(6)***5**/*C(1)***6** etc.

Fig. 3 shows the two possible matchings of the heptalene skeletons of (*P*)-**5** and its double-bond isomer (*P*)-**6** according to their X-ray structure. It clearly demonstrates that there are only marginal deviations in the two skeletons and their substituents in space. This allows the conclusion that the optical spectra of heptalenes [8] are strongly correlated with their configuration and that future CFF calculations (*cf.* [17]) will allow to describe energetically the different pathways of configurational and conformational changes of the heptalene skeleton.

We thank Dr. *P. Bischofberger*, Dr. *M. Cosandey* and *F. Nydegger*, Institut de chimie organique de l'Université de Fribourg, and our colleagues in the physics department of the Central Research Units of *F. Hoffmann-La Roche & Co., Ltd.*, Basle for CD, ORD, IR, NMR, mass spectra as well as for GC, HPLC and elemental analyses, and the measurement of optical rotations. PD Dr. *K. Müller* performed the matchings of the heptalene skeletons with the RIMG system [18]. We gratefully acknowledge partial support of this work by the *Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung*, and two of us (*P. B.* and *R. H. W.*) express their gratitude to the personnel department of *F. Hoffmann-La Roche & Co., Ltd.*, Basle for scholarship. *H.-J. H.* thanks especially Dipl.-Chem. *G. L. Knaup*, Technische Hochschule Darmstadt, for a discussion following the lecture of *H.-J. H.* in Zürich on the results of the thermal rearrangement of **3** and **4** investigated in Darmstadt.

Experimental Part

General. See [8]. Irradiation experiments were performed in (*tert*-butyl) methyl ether (TBME) at 10–14° with a Hg high-pressure lamp (*Hanau Quarzlampengesellschaft*, Type *TQ 150*) through a *Pyrex* filter (thickness 1.5 mm) under Ar.

1. Experiments with Dimethyl 5,6,8,10-Tetramethylheptalene-1,2-dicarboxylate (3) and its Derivatives. – 1.1. *Reversible Photochemical Formation of Dimethyl 1,6,8,10-tetramethylheptalene-4,5-dicarboxylate* (**4**) *from* **3**. Diester **3** (500 mg, 1.53 mmol) [8] was dissolved in TBME (250 ml) and irradiated during 4 h to yield a photostationary mixture of **3** (270 mg, 54%) and **4** (220 mg, 46%). The separation was achieved by prep. TLC (R_f (**3**) 0.38, R_f (**4**) 0.55 with hexane/Et_2O 1:1, or R_f (**3**) 0.55 and R_f (**4**) 0.63 with AcOEt/hexane/AcOH 50:50:1).

Diester **4**. M.p. 91–92°. UV (hexane): λ_{max} 206 (4.37), 234 sh (4.12), 270 (4.23), 310 sh (3.37), 388 sh (2.70); λ_{min} 228 (4.00), 249 (3.97). IR (KBr): 1734/1715 (COOR). ^{1}H-NMR (400 MHz, $CDCl_3/C_6D_6$): 1.607/1.540 (*s*, CH_3–C(1)); 1.688/1.765 (*s*, CH_3–C(6)); 1.912/1.793 (*d*-like *s*, ^4J (CH_3–C(8), H–C(7)) ≈ 1.2, CH_3–C(8)); 1.946/1.976 (*d*-like *s*, ^4J (CH_3–C(10), H–C(9)) ≈ 1.3, CH_3–C(10)); 3.633 and 3.745/3.374 and 3.455 (2 *s*, each 3 H, CH_3OOC–C(4), CH_3OOC–C(5)); 5.930/5.832 (br. *s*, H–C(9)); 6.015/6.001 (br. *s*, H–C(7)); 6.492 and 6.497/6.284 and 6.777 (*AB*, $J(AB) = {}^3J(3,4) = 11.8$, 2H, H–C(2), H–C(3)). ^{1}H-DR-NMR (C_6D_6): 1.540 (CH_3–C(1))→6.284 (*s* sharpening, H–C(2)) and 6.777 (*s* sharpening, H–C(3)); 1.765 (CH_3–C(6))→5.832 (*quint.*-like *s*, H–C(9)) and 6.001 (*s* sharpening, H–C(7)); 1.793 (CH_3–C(8))→ 1.976 (*s* sharpening, CH_3–C(10)) and 5.832 (*quint.*-like *s*, ^4J-

(H–C(9), CH_3–C(10)) ≈ ^4J(7,9) ≈ 1, H–C(9)); 1.976 (CH_3–C(10))→5.832 (*s* sharpening, H–C(9)) and 6.001 (*quint.*-like *s*, H–C(7)); 5.832 (H–C(9))→1.976 (*s*, CH_3–C(10)); 6.001 (H–C(7))→1.793 (*s*, CH_3–C(8)) and 1.976 (*s* sharpening, CH_3–C(10)) and 5.832 (*q*-like *s*, H–C(9)). ^{1}H-NOE: 1.762 (CH_3–C(6))→6.001 (H–C(7), 8%); 1.543 (CH_3–C(1))→6.284 (H–C(2), 12%). MS: Identical with that of **3** [8]. Anal. calc. for $C_{20}H_{22}O_4$ (326.39): C 73.60, H 6.79; found: C 73.58, H 6.78.

1.2. *Reversible Photochemical Formation of* **3** *from* **4**. 4,5-Dicarboxylate **4** (280 mg, 0.86 mmol) was irradiated in 250 ml TBME during 4 h: **3** (143 mg, 54%) and **4** (122 mg; 46%) were isolated with prep. TLC. A mixed m.p. (124–125°) of isolated **3** with an authentic sample of **3** [8] gave no depression.

1.3. *Formation of* **4** *from* **3** *by Exposure to Normal Laboratory Light* (neon tubes). Compound **3** (280 mg, 0.86 mmol) was dissolved in 5 ml tetralin and exposed to normal laboratory light on the bench during 30 d. Separation with prep. TLC yielded **4** (15.5 mg, 5.5%) and unchanged **3** (260 mg).

1.4. *Irradiation of Dimethyl 5,6,8,10-Tetramethyl[3-$^2H_1$]heptalene-1,2-dicarboxylate* ([3-$^2H_1$]-**3**). – 1.4.1. *Synthesis of [3-$^2H_1$]-***3** (*cf.* [8]). 1,4,6,8-Tetramethyl[3-$^2H_1$]azulene (3.0 g, 16.3 mmol)[22]) was dissolved in freshly distilled tetralin (40 ml), and, after addition of dimethyl acetylenedicarboxylate (ADM), (3.93 g, 27.7 mmol) the soln. was heated during 3 h at 190°. The solvent was removed by distillation (100°/0.04 Torr) and the residue (4.8 g) separated by CC (Et_2O/hexane 1:1) to yield after crystallization dimethyl 4,6,8-trimethyl[3-$^2H_1$]azulene-1,2-dicarboxylate (1.05 g, 22%). (m.p. 141–142°, ^{1}H-NMR (90 MHz): 7.70 (*s*, 0.12 H, H–C(3))), [3-$^2H_1$]-**3** (1.11 g, 21%), and a fraction of 0.5 g which contained mainly *dimethyl 1,6,8,10-tetramethyl[3-$^2H_1$]heptalene-4,5-dicarboxylate* ([3-$^2H_1$]-**4**; *cf. 1.4.2*).

[3-$^2H_1$]-**3**: m.p. 123–124°. ^{1}H-NMR (90 MHz, standard for integration CH_3OOC–C(1) and CH_3OOC–C(2) at 3.69 and 3.70): 6.02 (br. *s* with fs, 1.03 H, H–C(9)); 6.15 (br. *s*, 1.06 H, H–C(7)); 6.19 (*q*, ^4J(H–C(4), CH_3–C(5) ≈ 1.5, 1.00 H, H–C(4)); 7.53 (*dq*, 0.10 H, H–C(3)); CH_3–C(6), CH_3–C(8), CH_3–C(5), CH_3–C(10) at 1.74, 1.96, 2.00 and 2.04, respectively: MS: 327/326 (100/13, M^+), 242 (M^+–DC≡CCOOCH$_3$, 13), 185 (100, M^+–ADM); degree of deuteration 88%.

1.4.2. *Irradiation of [3-$^2H_1$]-***3**. Compound [3-$^2H_1$]-**3** (600 mg, 1.83 mmol) was irradiated in TBME (250 ml) for 4 h to yield after prep. TLC [3-$^2H_1$]-**4** (280 mg, 48%) and [3-$^2H_1$]-**3** (300 mg, 52%).

*[3-$^2H_1$]-***4**: ^{1}H-NMR (400 MHz, C_6D_6): 1.541 (*s*, CH_3–C(1)); 1.764 (*s*, CH_3–C(6)); 1.793 (*d*-like *s*, CH_3–C(8)); 1.975 (*d*-like *s*, CH_3–C(10)); 5.831 (br. *s*, H–C(9)); 6.001 (br. *s*, H–C(7)); 6.283 (br. *s* with *d* satellite, H–C(2)); 6.775 (*d*, 0.12 H, H–C(3)); 3.375 and 3.454 (2*s*, integration standard, CH_3OOC–C(1) and CH_3OOC–C(2)). ^{1}H-NOE: 1.543 (CH_3–C(1))→6.283 (H–C(2), 11%); 1.765 (CH_3–C(6))→6.001 (H–C(7), > 5%), MS: identical with that of [3-$^2H_1$]-**3**; degree of deuteration 88%.

1.5. *Irradiation of Dimethyl 5,6,8,10-Tetramethyl[1,2-$^{13}C_2$]heptalene-1,2-dicarboxylate* ([1,2-$^{13}C_2$]-**3**). [1,2-$^{13}C_2$]-**3** (119 mg, 0.36 mmol) (prepared by reaction of [1,2-$^{13}C_2$]ADM (*cf.* [2]) with 1,4,6,8-tetramethylazulene) was irradiated in TBME during 4 h. Prep. TLC yielded [1,2-$^{13}C_2$]-**4** (41 mg, 49%) and [1,2-$^{13}C_2$]-**3** (43 mg, 51%).

*[1,2-$^{13}C_2$]-***4**: ^{13}C-NMR (100.62 MHz)[23]): 17.54 (*q*, ^3J(H–C(2)) = 4, CH_3–C(1)); 17.62 (*q*, ^3J(H–C(7)) = 3.5, CH_3–C(6)); 22.36 (*q*, ^3J(H–C(9)) = 6.5, CH_3–C(10)); 25.13 (*q*, ^3J(H–C(7)) = 7, ^3J(H–C(9)) = 3.5, CH_3–C(8)); 52.24 and 52.42 (2*q*, CH_3OOC–C(1), CH_3OOC–C(2)); 126.25 (*d* with *d* satellite ^1J(H–C(3)) ≈ 164, ^1J(3,4) = 57, C(3)); 128.71 (*d*, ^1J(5,4) = 74.3, C(5)); 129.71 and 130.27 (2*d*, *sept.*-like. ^1J(H–C(7)) = 154 and J(H–C(9)) = 153, C(7), C(9)); 137.01 (*d*, ^1J(4,5) = 74.3, C(4)); 166.75 and 167.75 (2*s*, CH_3OOC–C(1), CH_3OOC–C(2)); *s* at 123.29, 128.93, 132.62, 133.56, 139.02 and 139.53 (C(5), C(5a), C(6), C(8), C(10) and C(10a); not assigned).

*[1,2-$^{13}C_2$]-***3**: ^{13}C-NMR (100.62 MHz): 122.44 (*d*, ^1J(1,2) = 61,4, C(1)); 131.46 (*d*, ^1J(2,1) = 61.4, C(2)); 139.15 (*s* with *d* satellite, ^1J(3,2) ≈ 72, C(3)).

1.6. *Irradiation of 1-Methoxycarbonyl-5,6,8,10-tetramethylheptalene-2-carboxylic Acid* (**7**). 2-Acid **7** (200 mg, 0.64 mmol) [8] was irradiated in TBME (250 ml) during 4 h. TLC (AcOEt/hexane/AcOH 50:50:1) showed the presence of **7** (R_f 0.27) and *5-methoxycarbonyl-1,6,8,10-tetramethylheptalene-4-carboxylic acid* (**8**) (R_f 0.19) in a ratio of 1:1. The acids were separated and identified *via* their dimethylesters (CH_2N_2 in Et_2O at 20°): **3** (108 mg; 56%) and **4** (85 mg; 44%).

1.7. *Irradiation of (–)-(P)-***3**. Compound (–)-(*P*)-**3** (200 mg, 0.6 mmol) with $[\alpha]_D^{20} = -1336°$ (acetone, $c = 1.26 \times 10^{-3}$; e > 0.99) [8] was dissolved in TBME (250 ml) and irradiated during 40 min at 14–15°. Prep. TLC yielded (–)-(*P*)-**3** (76 mg, 54%) with $[\alpha]_D^{20} = -1261°$ ($c = 1.09 \times 10^{-3}$, p = 0.94) and (–)-(*P*)-**4** (65 mg, 46%) with

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[22]) Prepared by deuteration of 1,4,6,8-tetramethylazulene (3.0 g) [8] with D_2O (16.1 ml) and D_2SO_4 (11.6 ml) at 20°.

[23]) Multiplicities from the 'off-resonance' spectrum; coupling constants from the 'gated-decoupled' spectrum.

$[\alpha]_D^{20} = -1077°$ (acetone, $c = 1.15 \times 10^{-3}$). The ^{1}H-NMR (90 MHz, $CDCl_3$) of (−)-(*P*)-**4** (26 mg) was measured in the presence of $Eu(hfc)_3$ (89.2 mg). Signals of (+)-(*M*)-**4** (measured separately) could not be detected, *i.e.* (−)-(*P*)-**4** had e > 0.97 (*cf.* [8]).

*(−)-(P)-***4**: ORD (dioxane): 699/−1830, 448/−14830 (T), 400/0, 340/26110 (sh), 299/110350 (P), 280/0, 268/−75240 (T), 247/−7140 (P). CD (dioxane): 550/−7.02, 507.7/−7.39, 397.1/−40.57 (min), 343/−22.64 (max), 321/−32.67 (min), 281.1/113.46 (max), 251.3/12.64 (min), 227.4/53.51 (max), 219.8/47.30 (min), 206.1/76.27 (max); (cyclohexane, *cf. Fig. 2b*): 508.0/−3.12, 387.8/−37.74 (min), 344.8/−21.73 (max), 318/−36.59 (min), 279.6/120.46 (max), 272 (sh)/103, 248.1/14.45 (min), 227.0/60.18 (max), 216/50.01 (min), 206.2/67.83 (max), 186 (sh)/−140.

1.8. *Thermal Rearrangement of (−)-(P)-***4** *into (−)-(P)-***3**. (−)-(*P*)-**3** (109 mg) with $[\alpha]_D^{20} = -1313°$ ($c = 0.95 \times 10^{-3}$) [8] was dissolved in TBME (250 ml) and irradiated for 2 h at 15°. Prep. TLC yielded (−)-(*P*)-**3** (51.7 mg, 52%) with $[\alpha]_D^{20} = -1271°$ ($c = 1.09 \times 10^{-3}$, p ≈ 0.96) and (−)-(*P*)-**4** (47.6 mg, 48%) with $[\alpha]_D^{20} = -1095°$ ($c = 1.36 \times 10^{-3}$, p > 0.97; *cf. 1.7*). (−)-(*P*)-**4** was dissolved in cyclohexane (1.5 ml) and heated for 4 h at 80°. The cyclohexane was evaporated (RE) and the residue separated by prep. TLC to yield (−)-(*P*)-**3** (20 mg, 50%) with $[\alpha]_D^{20} = -1218°$ ($c = 0.99 \times 10^{-3}$, p ≃ 0.92) and (−)-(*P*)-**4** (20 mg, 50%).

1.9. *Thermal Equilibration Experiments with* **3** *and* **4**. Solns. (0.5 p.c.) of **3** and **4** in freshly distilled tetralin were prepared and heated in ampoules under strict exclusion of O_2 and light, and analyzed by HPLC (see *Table*).

Table. *Results of Thermal Equilibrations of* **3** *and* **4**

Temp.	Heating period	Starting material[a])			
		1,2-diester **3**		4,5-diester **4**	
[K]	[h]	**3** [%]	**4** [%]	**3** [%]	**4** [%]
353.2	5	90.4	9.6	90.4	9.6
373.2	2	88.6	11.4	88.7	11.3
393.2	2	86.7	13.3	86.8	13.2
413.2	2	85.2	14.8	85.3	14.7

[a]) Analysis by HPLC on *Lichrosorb* 5 μm (column: 50 cm) with hexane/AcOEt 85:15; detection at 265 nm.

From the *Table* follows: $\Delta H° = -10.0 \pm 1.4$ kJ mol^{-1} and $\Delta S° = -9.7 \pm 3.7$ JK^{-1}mol^{-1}, *i.e.* $\Delta G° = -7.1$ kJ mol^{-1} in favour of **3**. The kinetic of the equilibration of **4** at 100° yielded ($k_{12} + k_{45}$) = 10.2×10^{-4} s^{-1}, *i.e.* $\tau_{½}$ (100°) = 11 min. On the other hand, the racemization of (+)-(*M*)-**3** [8] in tetralin ($[\alpha]_D^{20} = +164°$) at 100, 145, and 169° yielded ($k_{rac}(1,2) + k_{rac}(4,5)$) = 0.026 (100°), 1.21 (145°), and 8.76×10^{-4} s^{-1} (169°), *i.e.* $\tau_{½}$ (100°) = 4.5×10^3 min.

2. Experiments with Dimethyl 8-(*tert*-Butyl)-5,6,10-trimethylheptalene-1,2-dicarboxylate (5). – 2.1. *Synthesis of* **5**. 6-(*tert*-Butyl)-1,4,8-trimethylazulene (7.0 g, 30.9 mmol)[24]) and ADM (7.35 g, 52 mmol) were dissolved in freshly distilled tetralin (70 ml) and heated at 180° for 4 h under N_2 and with exclusion of light. Tetralin was distilled off (RE, 40–50°/0.01 Torr) and the residual dark blue oil subjected to CC (hexane/Et_2O 7:3) to yield **5** (2.95 g, 26%), dimethyl 6-(*tert*-butyl)-4,8-dimethylazulene-1,2-dicarboxylate (4.45 g, 44%), dimethyl [6-(*tert*-butyl)-4,8-dimethylazulene-1-yl]fumarate (47 mg, 0.4%) and heptalene mixed fractions (*ca.* 0.8 g) which contained mainly *dimethyl 8-(*tert*-butyl)-1,6,10-trimethylheptalene-4,5-dicarboxylate (***6**, *cf. 2.2*).

Diester **5**: pale yellow crystals, m.p. 135–137°. UV (cyclohexane): λ_{max} 213 (4.36), 259 (4.24), 278 sh (4.14), 316 sh (3.53), 365 sh (2.95); λ_{min} 241.5 (4.18). IR (KBr): 1715 (br., COOR), 1388/1368 (*t*-Bu). ^{1}H-NMR (400 MHz): 1.184 (*s*, *t*-Bu); 1.762 (*s*, CH_3–C(6)); 1.960 (*d*-like *s*, ^4J(CH_3–C(10), H–C(9)) ≈ 1.2, CH_3–C(10)); 2.029 (br. *s*, CH_3–C(5)); 3.677 and 3.703 (2*s*, each 3H, CH_3OOC–C(1), CH_3OOC–C(2)); 6.194 (br. *s*, H–C(7)); 6.226 (*quint.*-like *s*, $^4J(9,7) \approx {}^4J$ (H–C(9), CH_3–C(10)) ≈ 1.2, H–C(9)); 6.265 (*dq*, $^3J(4,3) = 6.0$, ^4J (H–C(4), CH_3–C(5)) = 1.35, H–C(4)); 7.505 (*dq*, $^3J(3,4) = 6.0$, ^5J (H–C(3), CH_3–C(5)) ≈ 0.8, H–C(3)). ^{1}H-DR-NMR: 1.960 (CH_3–C(10))→6.226 (*d*-like *s*, $^4J(9,7) \sim 1.5$, H–C(9)); 2.029 (CH_3–C(5))→6.265 (*d*, $^3J(4,3) = 6.0$, H–C(4)) and 7.505 (*d*, $^3J(3,4) = 6.0$, H–C(3)); 6.226 (H–C(9))→1.960 (*s*, CH_3–C(10)); 6.265 (H–C(4))→2.029 (*s* sharpening, CH_3–C(5)) and 7.505 (br. *s*, H–C(3)); 7.505 (H–C(3))→2.029 (*d*-like *s*, ^4J (CH_3C(5), H–C(4)) = 1.35,

[24]) The azulene (m.p. 47–48°) was prepared in analogy to 1,4,6,8-tetramethylazulene [8] in an overall yield of 42% by *Vilsmeier* formylation of 6-(*tert*-butyl)-4,8-dimethylazulene [19] and reduction of the formed 6-(*tert*-butyl)-1-formyl-4,8-dimethylazulene (m.p. 90–91°) with $NaBH_4/Et_2O \cdot BF_3$ in diglyme/Et_2O [20].

CH_3–C(5)). MS: 368 (100, M^+), 353 (24, $M^+ - 15$), 337 (14, $M^+ - CH_3O^\cdot$), 328 (4, $M^+ - H_3CC{\equiv}CH$), 321 (27, $M^+ - (CH_3^\cdot + CH_3OH)$), 309 (21, $M^+ - H_3COOC^\cdot$), 286 (26, $M^+ - (CH_3)_3CC{\equiv}CH$), 284 (7, $M^+ - HC{\equiv}CCOOCH_3$), 270 (28, $M^+ - CH_3C{\equiv}CCOOCH_3$), 226 (66, $M^+ - ADM$). Anal. calc. for $C_{23}H_{28}O_4$ (368.47): C 74.97, H 7.66; found: C 74.87, H 7.42.

*Dimethyl 6-(*tert*-Butyl)-4,8-dimethylazulene-1,2-dicarboxylate.* Dark blue crystals, m.p. 122–123°. IR (KBr): 1720–1713 (br. COOR), 1363/1376/1397 (*t*-Bu). ^{1}H-NMR (80 MHz): 1.46 (*s*, *t*-Bu); 2.91 and 2.94 (2 superimp. *s*, CH_3–C(4), CH_3–C(8)); 3.92 and 3.99 (2*s*, each 3H, CH_3OOC–C(1), CH_3OOC–C(2)); 7.37 (br. *s*, H–C(5), H–C(7)); 7.69 (*s*, H–C(3)). MS: 328 (94, M^+), 296 (100, $M^+ - CH_3OH$). Anal. calc. for $C_{20}H_{20}O_4$ (328.41): C 73.15, H 7.37; found: C 73.07, H 7.35.

2.2. *Reversible Photochemical Formation of* **6** *from* **5**: A soln. of **5** (291 mg, 0.79 mmol) in TBME (250 ml) was irradiated at 18° during 1 h under Ar. TBME was evaporated (RE) and the residue subjected to prep. TLC (hexane/Et_2O 3:1) to yield **6** (184 mg, 65%) and **5** (99 mg, 35%). Irradiation of pure **6** under the same conditions led to **5**/**6** in the same ratio.

Diester **6**: yellow crystals, m.p. 88–90°. UV (cyclohexane): λ_{max} 214 (4.29), 230 sh (4.20), 269 (4.32), 304 sh (3.57), 375 (2.71): λ_{min} 247 (4.12), 352 (2.65). IR (KBr): 1732/1720 (COOR), 1371/1362 (*t*-Bu). ^{1}H-NMR (270 MHz): 1.135 (*s*, *t*-Bu); 1.697 (*s*, CH_3–C(1)); 1.739 (*s*, CH_3–C(6)); 2.031 (*d*-like *s*, ^4J (CH_3–C(10), H–C(9)) = 1.3, CH_3–C(10)); 3.729 and 3.828 (2*s*, each 3H, CH_3OOC–C(4) and CH_3OOC–C(5)); 6.132 (br. *s*, H–C(7)); 6.232 (*quint.*-like *s*, $^4J(9,7) \approx {}^4J$ (H–C(9), CH_3–C(10)) ≈ 1.5, H–C(9)); 6.563 and 6.577 (*AB*, $J(AB) = {}^3J(2,3) = 12.0$, H–C(2) and H–C(3)). MS: identical with that of **5**; *cf. 2.1.* Anal. calc. for $C_{23}H_{28}O_4$ (368.47): C 74.97, H 7.66; found: C 74.77, H 7.85.

2.3. *Thermal Equilibrations of* **5** *and* **6**. Solns. (0.5 p.c.) of pure **5** and **6** in freshly distilled tetralin were heated at 100° under N_2 and exclusion of light. HPLC (*cf. Table*) after 15, 30, 45 and 300 min yielded $(k_{1,2} + k_{4,5}) = 3.78 \times 10^{-4}\ s^{-1}$ with $([5]/[6])_{100} = 89.2/10.8\%$.

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