47. First Optically Active Heptalenes and their Absolute Configuration[1])

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It is shown that dimethyl 7-isopropyl-5,10-dimethylheptalene-1,2-dicarboxylate (**1**) and dimethyl 5,6,8,10-tetramethylheptalene-1,2-dicarboxylate (**2**) can be resolved *via* the corresponding mono-acids and with the aid of optically active primary or secondary amines such as 1-phenylethylamine or ephedrine into the (–)-(*P*)- and (+)-(*M*)-enantiomeres, respectively. Characteristic for the (*P*)-chirality of the heptalene π-skeleton with C_2 or pseudo-C_2 symmetry are two (–)-CE's at the long wavelength region (450–300 nm) followed by at least one intense (+)-CE at wavelengths about or below 300 nm. The absolute configuration of the heptalenes was correlated with the well-established absolute configuration of (+)-(*R*)- and (–)-(*S*)-1-phenylethanol.

Introduction. – Some years ago, we reported [1] that dimethyl 7-isopropyl-5,10-dimethylheptalene-1,2-dicarboxylate (**1**)[5]) is the main product of the thermal reaction of guajazulene with dimethyl acetylenedicarboxylate (*cf.* [2]), and that it shows in its ^{1}H- as well as ^{13}C-NMR spectra the CH_3 groups of the i-Pr moiety in diastereotopic positions, also at higher temperatures. This was the first proof that heptalenes with substituents in the angular positions might also be configurationally stable enough in solution[6]) to be resolved into their antipodes at ambient temperature[7]). In the following part, we describe the optical resolution of **1** and of dimethyl 5,6,8,10-tetramethylheptalene-1,2-dicarboxylate (**2**), easily accessible by thermal reaction of 1,4,6,8-tetramethylazulene and dimethyl acetylenedicarboxylate (see *Exper. Part*).

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[1]) Presented in part by *H.-J. H.* at lectures in Basle (1980), 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.

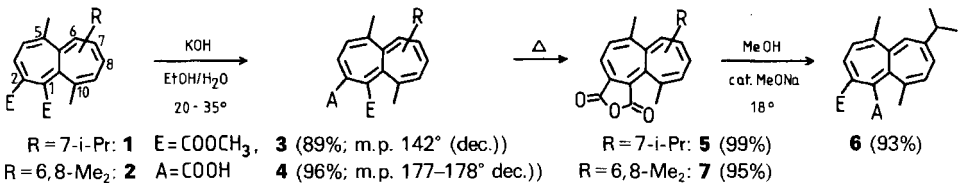
[5]) We use the numbering of the heptalene ring according to the IUPAC nomenclature. Thus, a hypothetical double bond shift in 1-methylheptalene will lead to the constitutionally isomeric 5-methylheptalene *etc.*

[6]) X-Ray analyses of dimethyl heptalene-1,2- [3] and -3,8-dicarboxylate [4] revealed a boot-like conformation for both seven-membered rings with global pseudo-C_2 and C_2 symmetry for the heptalene skeleton in the crystals, and torsional angles between C(1)–C(10a)–C(5a)–C(5) and C(6)–C(5a)–C(10a)–C(10) of 51.1°/53.8° and 37.9°, respectively. The X-ray analysis of **1** [5] showed that this highly substituted heptalene also possesses pseudo-C_2 symmetry with respect to its ring skeleton with the corresponding torsional angles of 63.0° and 62.4°.

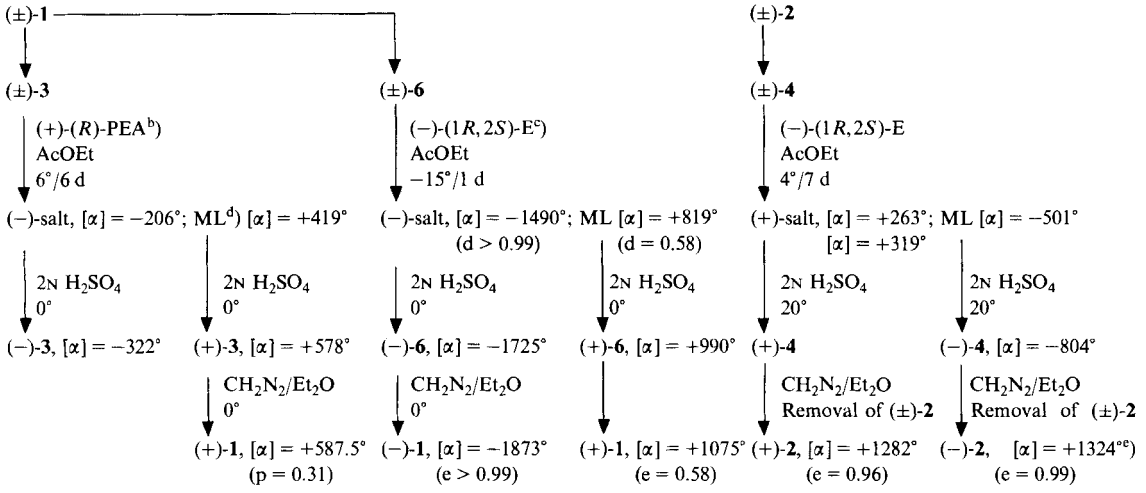
[7]) For a review on the evolution of heptalene chemistry, see [6], in which *Paquette* stated under the heading *Future Prospects:* 'Also, the weight of evidence has become sufficient to justify the beliefs... that an optically active heptalene with sufficiently high barriers to racemization will be prepared'. When we read this, we had just succeeded in a partial resolution of **1**.

Optical Resolution of Heptalenes 1 and 2. – Reaction of **1** and **2** with KOH in $EtOH/H_2O$ at 20–35° yields exclusively the 2-acids **3** and **4**[8]). Both acids decompose above their m.p.'s by loss of MeOH and form nearly quantitatively the corresponding 1,2-dicarboxylic anhydrides **5** and **7**[9]). These anhydrides react with nucleophiles preferentially at the carbonyl group at C(2) as demonstrated by the reaction of **5** with MeOH in the

Scheme 1



Scheme 2. *Results of the Optical Resolution of* (±)-**1** *and* (±)-**2**[a])



[a]) Specific rotations as $[\alpha]_D^{20}$ in acetone. [b]) PEA = 1-Phenylethylamine. [c]) E = Ephedrine. [d]) Mother liquor. [e]) Highest observed $[\alpha]_D^{20} = -1336°$; resolution with (+)-(*R*)-PEA.

Table 1. *Kinetic Parameters of Thermal Racemization of* (−)-**1** *and* (−)-**3**[a])

Parameter	(−)-**1**	(−)-**3**
$\Delta H^{\neq}$ ($KJmol^{-1}$)	89.6 ± 2.4	93.6 ± 6.5
$\Delta S^{\neq}$ ($Jdeg^{-1}\,mol^{-1}$)	− 37 ± 8	− 26 ± 21
$\Delta G^{\neq}$ ($KJmol^{-1}$)	100.6 ± 4.7	100.3 ± 13
$\tau_{1/2}$ (25°; h)	18	24

[a]) From polarimetric measurements in acetone in the temp. range of 20–46°.

[8]) Reaction with KOH in boiling $EtOH/H_2O$ gives the corresponding 1,2-di-acids which are also converted to the cyclic anhydrides upon heating above 200°.

[9]) The position of the double bonds in **5** is established by $^3J(3,4) = 7.0$ and $^3J(8,9) = 7.2$ Hz. It was further confirmed by an X-ray analysis [5].

presence of NaOMe at 18°[10]). By this way, also the 1-acids (*e.g.* **6**) of the heptalene-1,2-dicarboxylates can be prepared (see *Scheme 1*).

In a first attempt, we resolved the (±)-2-acid **3** with (+)-(*R*)-1-phenylethylamine in acetone or AcOEt.

The best results are shown in *Scheme 2*[11]). The kinetic parameters for the racemization of (−)-**1** and (−)-**3** are collected in *Table 1*. They show that both heptalenes are only moderately stable at room temperature with respect to their configuration, *i.e.* the coupled ring inversion of both seven-membered rings (*cf.* [8])[12]). We obtained better results when we resolved the (±)-1-acid **6** with (−)-(1*R*,2*S*)-ephedrine at −15°. According to the ^{1}H-NMR measurement[13]) of the corresponding (−)- and (+)-ephedrinium salts, the obtained (−)- and (+)-1-acids have e-values of about 1.00 and 0.58, respectively. These values should also be valid for **1**, since we performed the esterification of (−)- and (+)-**6** with CH_2N_2 in Et_2O at 0°[14]).

In a similar manner, we succeeded in the optical resolution of **2**[2])[3]) for which we expected a greater optical stability of its antipodes as compared to (+)- and (−)-**1** since all its angular positions (C(1), C(5), C(6) and C(10)) are substituted. Both (+)-(*R*)-1-phenylethylamine and (−)-(1*R*,2*S*)-ephedrine form easily separable diastereoisomeric salts with the 2-acid **4** of **2**. However, salt formation with (−)-(1*R*,2*S*)-ephedrine is better reproducible. Optically pure (e = 0.96–0.99) (−)- and (+)-**2** were easily obtained from the partially resolved 2-acids **4** by esterification with CH_2N_2 in Et_2O and removal of (±)-**2** by crystallization[15]). Since (+)- and (−)-**2** are optically stable up to 80°[16]), the e-values can be determined by established methods. Thus, the ^{1}H-NMR spectrum of (±)-**2** measured in $CDCl_3$ in the presence of Eu(hfc)$_3$ shows differences in the enantiomeric shifts for the signals of CH_3OOC–C(2). The respective G-values (*cf.* [11]) for this group are 5.76 and 6.00. A probe of (+)-**2** with $[\alpha]_D^{20} = +1192°$ (acetone) gave in the presence of Eu(hfc)$_3$ a (+)-**2**/(−)-**2** ratio of 94:6, *i.e.* e = 0.88 ± 0.02. Accordingly, it can be concluded that enantiomerically pure (e = 1.00) (+)-**2** has $[\alpha]_D^{20} = 1350 \pm 30°$ (acetone). This corresponds nicely with our highest observed $[\alpha]_D^{20}$-value for (−)-**2** of −1336° (acetone).

To be independent of optical standards such as Eu(hfc)$_3$, we chose another *'ab ovo'* method for the determination of the enantiomeric purity of (−)-**2**. The reaction of a

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[10]) Depending on the reaction conditions, the 1-acid **6** can be accompanied by up to 10% of the 2-acid **3**.

[11]) At temperatures above 20°, only one diastereoisomeric ammonium salt is obtained which shows that at these temperatures a dynamic equilibrium between (+)- and (−)-**3** is established. The racemic diester **1** can also be resolved by slow chromatography on triacetylcellulose (*cf.* [7]) with EtOH. The highest observed $[\alpha]_D^{20}$-values (EtOH) in one experiment, were −1068 ± 120° and +680 ± 50°. We thank Prof. Dr. *K. Schlögl* and Dr. *M. Widhalm*, Institut für Organische Chemie der Universität Wien, for these experiments performed in 1982.

[12]) The maximum symmetry of the C-skeleton of the heptalene ring in the transition state would be D_{2h} if the process occurs with bond length equalization or C_{2h} in the case of bond-length alternation (cf. [9]).

[13]) The ^{1}H-NMR spectrum of the diastereoisomeric ephedrinium salts in $CDCl_3$ show well-separated signals for the methoxycarbonyl group at C(1).

[14]) Whereas (±)-**1** is a nicely crystalline compound (m.p. 143–144°), (−)-**1**, with e ≃ 1.00, has only been obtained as an oil so far.

[15]) So far, we were not able to crystallize optically pure (−)- and (+)-**2**. Since (±)-**2** crystallizes very well (m.p. 124–125°), it can easily be removed.

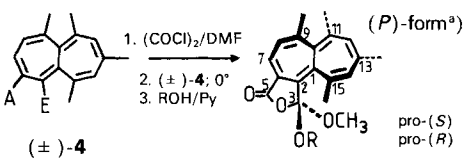
[16]) $\tau_{1/2}$ > 1000 h; racemization experiments of (+)-**2** (c = 1.4 × 10^{-3} mol) in tetralin at 145 and 169° gave $\tau_{1/2}$ = 96 and 13 min, respectively (*cf.* [9] [10]).

racemic compound (±)-**A** with itself will lead to *rac*-(A-A) and *meso*-(A-A). This reaction may be kinetically or thermodynamically controlled. In principle, the ratio *rac*-(A-A)/*meso*-(A-A) can easily be determined by standard methods (chromatography, NMR *etc.*). If we want to determine traces of one enantiomer in the other, and we know that under the reaction conditions the ratio *rac*-(A-A)/*meso*-(A-A) does not deviate much from 1 the amount of the formed *meso*-(A-A) will just reflect the enantiomeric purity e (*e.g.* 99% (+)-**A** + 1% (−)-**A** → 98% (+)-(A-A) + 2% *meso*-(A-A), *i.e.* e = 0.98)[17]).

In our case, we took advantage of the fact that the 2-acid **4**, in the presence of oxalyl chloride and *N*,*N*-dimethylformamide in MeCN, forms easily the stable racemic and *meso*-bis-2,2'-carboxylic anhydrides **10** in a ratio of 2:3[18]). Both diastereoisomers are easily separable by TLC, and less than 0.2% of the *meso*-form can be determined in the racemic form (detection by fluorescence quenching). Saponification of (−)-**2** (see *Scheme 1*) with $[\alpha]_D^{20} = -1324°$ yielded (−)-**4** with $[\alpha]_D^{20} = -1245°$ (acetone). Formation of the bis-2,2'-carboxylic anhydride **10** with this acid (*cf. Schemes 3* and *4*) led to a (−)-bis-2,2'-carboxylic anhydride which contained according to TLC less than 1% of the *meso*-form, *i.e.* e = 0.99. Thus, for enantiomeric pure (−)-**2** $[\alpha]_D^{20} = -1337°$ (acetone) which again is in excellent agreement with the highest observed value (see *Scheme 2*).

Absolute Configuration of the Optically Active Heptalenes 1 and 2. – Treatment of **4** with oxalyl chloride and *N*,*N*-dimethylformamide followed by addition of MeOH and pyridine gives – as we found – not the expected dimethyl dicarboxylate **2** (*cf.* [14]) but the isomeric compound **8** (*Scheme 3*)[19]). The same reaction with (±)-1-phenylethanol yields two diastereoisomers **9A** and **9B** which differ only in the configuration of the 1-phenylethoxy moiety.

Scheme 3



(±)-**4**

R = CH_3: **8** (83%; m.p. 173–174°)
(*S*)-PhCH(CH_3): **9A** (20%; m.p. 154–155°)[b])
(*R*)-PhCH(CH_3): **9B** (11%; m.p. 134–135°)

[a]) Only one enantiomer of the racemic compounds is shown.

[b]) Besides **9A** and **9B**, varying amounts (4–14%) of the 1,2-dicarboxylic anhydride **7** (*Scheme 1*) and of the bis-2,2'-carboxylic anhydride (**10**; *ca.* 18%) in racemic and *meso*-form (2:3) are formed.

This is exemplified by the following ^{1}H-NMR experiments and arguments: the dimethoxy compound **8** shows the signals of the CH_3O groups at 3.18 and 3.46 ppm (*cf. Table 2*). The *'cis'*-relationship of the CH_3O group at 3.18 ppm and CH_3–C(13) as well as the CH_3O group at 3.46 ppm and CH_3–C(15) is established by a NOE of about 1%. On

[17]) For the determination of e based on this principle, there are not very much examples in the literature (*cf.* [12]). For a general analysis of this principle, see [12]. We thank Prof. Dr. *W. Marty*, Institut de chimie, Université de Neuchâtel, for a preprint of his communication.

[18]) *Horeau* determined the enantiomeric purity of (+)- and (−)-2-phenylbutanoic acid in a similar manner (*cf.* [13]).

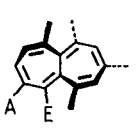
[19]) We will report on this reaction leading to the nearly unknown class (*cf.* [15] and examples cited therein) of 'hemi-ortho-anhydrides' later in this journal [16].

Table 2. *Chemical Shifts in the ^{1}H-NMR Spectra ($CDCl_3$) of* **8**, **9A**, *and* **9B**

H-Atoms	δ [ppm]			$\Delta\delta$ [ppm] (δ(**9A**)–δ(**9B**))
	8	**9A**	**9B**	
H–C(7)	7.244	7.163	7.260	– 0.097
H–C(8)	6.474	6.437	6.471	– 0.034
H–C(12)	6.163	6.144	6.128	0.016
H–C(14)	6.079	6.077	5.939	0.138
CH_3–C(9)	2.088	2.076	2.077	0
CH_3–C(11)	1.728	1.712	1.712	0
CH_3–C(13)	1.995	1.997	1.939	0.058
CH_3–C(15)	2.161	2.198	1.915	0.283
CH_3O–C(3)	3.181, 3.465	3.177	3.138	0.039
PhC*H*(CH_3)	–	5.333	5.329	0
PhCH(C*H*$_3$)	–	1.555	1.478	0.077

the other hand, the pro-(*S*)-configuration of the CH_3O group at 3.18 ppm follows also from its high-field shift compared with the other group at 3.46 ppm. The effect can be attributed to the shielding property of the C(1)=C(2) and C(14)=C(15) bond, since the pro-(*S*)-configurated CH_3O group, is, according to models, situated beneath these bonds. Both diastereomers **9A** and **9B** show only one signal for their CH_3O group at C(3), namely at 3.18 and 3.14 ppm, respectively, which clearly indicates that the 1-phenylethoxy moiety is (3*R*)-configurated (in the (*P*)-heptalene) in both diastereo-

Scheme 4



(–)-(*P*)-**4**
$[\alpha]_D^{20} = -1245°$ [a])

(–)-(*S*)-PEA → (–)-**9A** (24%) [b])
$[\alpha]_D^{20} = -1433°$

(+)-(*R*)-PEA → (–)-**9B** (24%) [c])
$[\alpha]_D^{20} = -1320°$

[a]) In acetone.
[b]) In addition, 14% of (–)-**7** ($[\alpha]_D^{20} = -2565°$) and 18.5% of (–)-**10** ($[\alpha]_D^{20} = -1510°$) were formed.
[c]) In addition, 4% of (–)-**7** ($[\alpha]_D^{20} = -2817°$) and 18.7% of (–)-**10** ($[\alpha]_D^{20} = -1162°$) were formed.

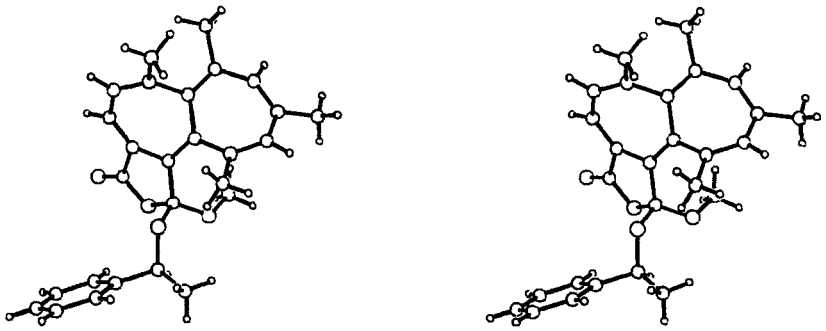


Fig. 1. *Stereoscopic projection of the X-ray diffraction structure of racemic 3-methoxy-9,11,13,15-tetramethyl-3-(1'-phenylethoxy)-4-oxatricyclo[8.5.0.0^{2,6}]pentadeca-1,6,8,10,12,14-hexaen-5-one* (**9A**) *showing its relative (P,3R,1'S)-configuration*

isomers[20]). Therefore, **9A** and **9B** differ only in the configuration of the 1-phenylethoxy group at C(3). Comparison of the chemical-shift differences between **9A** and **9B**, and inspection of models allow only one conclusion: **9A** possess the (1′*S*)- and **9B** the (1′*R*)-configuration. This follows from the high-field shift of H–C(14) and, especially of CH_3–C(15) in **9B** compared to **9A**. This high-field shift has to be attributed to the high

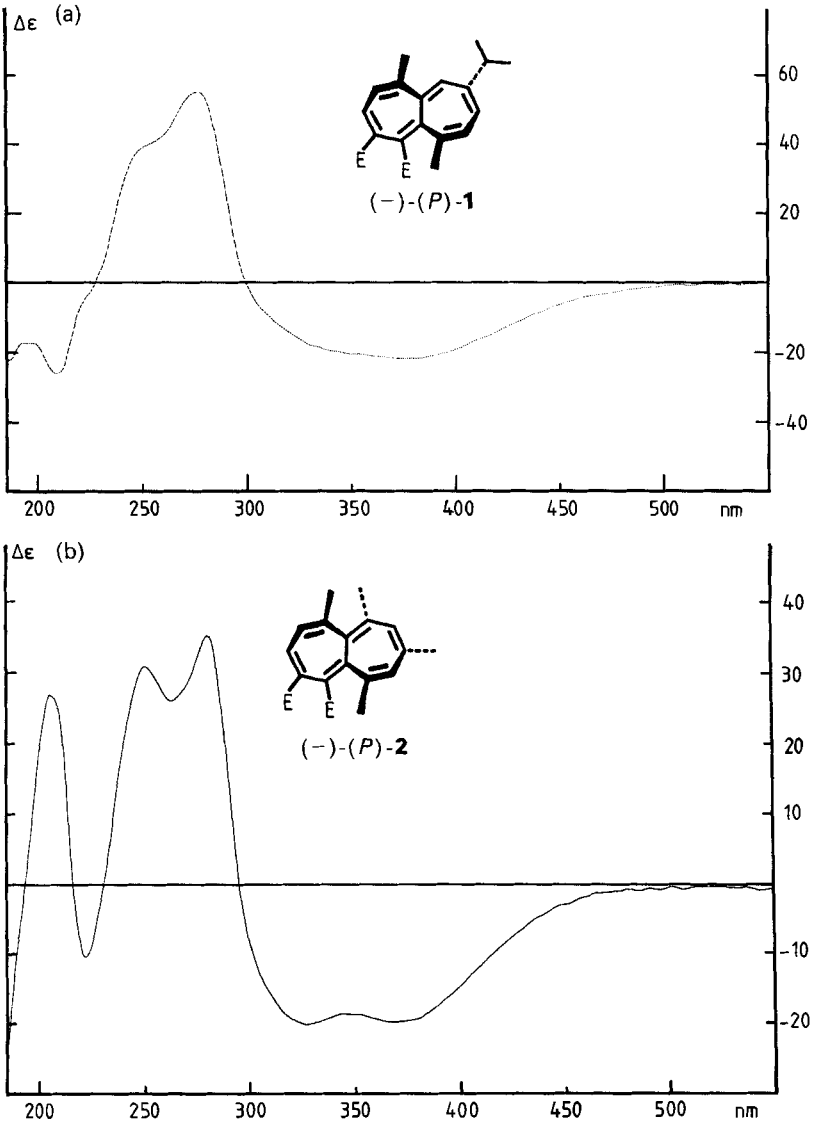


Fig. 2. *CD spectra of (−)-(P)-***1** (a) *and (−)-(P)-***2** (b) *in cyclohexane*

[20]) We observed this highly stereoselective reaction of **4** as well as of **3** also with other alcohols including CD_3OH [16].

anisotropy of the phenyl moiety influencing the shifts on steric grounds only in the diastereoisomer **9B** with the (1'*R*)-configurated 1-phenylethoxy group.

The decisive experiments correlating the (*S*)- and (*R*)-configuration of (−)- and (+)-1-phenylethanol, respectively, with the (*P*)-configuration of (−)-**4** are shown in *Scheme 4*. The reaction of (−)-**4** with (−)-(*S*)-1-phenylethanol gave the (−)-**9A** diastereoisomer and conversely with (+)-(*R*)-1-phenylethanol the (−)-**9B** form. Since **9A** and **9B** have the relative configuration (*PM*, 3*RS*, 1'*SR*) and (*PM*, 3*RS*, 1'*RS*), respectively, (−)-**4** must possess the (*P*)-configuration of the heptalene skeleton. We unequivocally confirmed the relative configuration of racemic **9A** by an X-ray analysis (*Fig. 1*)[21]).

Since (−)-**2** derived from (−)-**4**[22]) and (−)-**1** show nearly identical CD spectra (*Fig. 2*), there is no doubt that (−)-**1** has also (*P*)-configuration of the heptalene skeleton. Furthermore, as shown by the correlation of the CD spectra of (−)-(*P*)-1,2-bis(hydroxymethyl)-5,6-8-10-tetramethylheptalene ((−)-(*P*)-**11**, obtained by reduction of (−)-(*P*)-**4** with $LiALH_4$ in Et_2O), (−)-(*P*)-**2**, (−)-(*P*)-**9A**, and (−)-(*P*)-**7** (see *Scheme 4* and *Fig. 3*), the (*P*)-configuration of the heptalene skeleton is characterized by two (−)-CE of similar

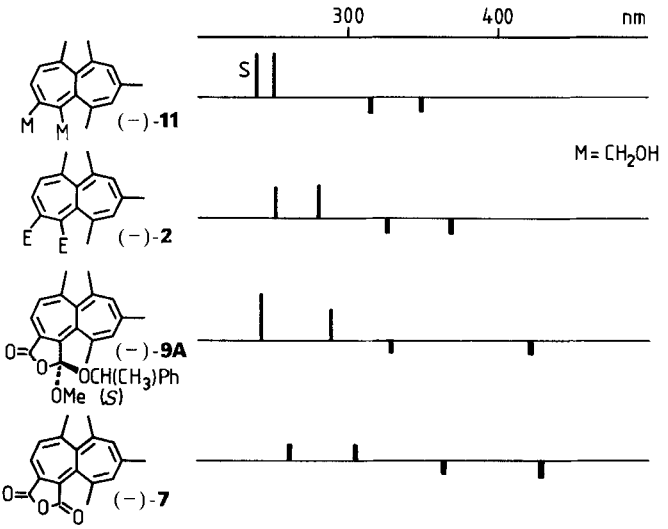


Fig. 3. *Schematic comparison of the CD spectra of (−)-***11**, *(−)-***2**, *(−)-***9A**, *and (−)-***7** *showing that all heptalene skeletons with* C_2 *symmetry possess* (P)*-configuration*

[21]) *Crystal Data.* Space group and cell dimensions: orthorhombic, *Pbca* with $a = 14.703$ (3), $b = 15.946$ (2) and $c = 18.915$ (3) Å; density $D = 1.25$ Mgm^{-3}, $Z = 8$. *Data collection. Crystal size:* $0.30 \times 0.35 \times 0.43$ mm^3; temp.: 170K; wavelength: 0.71069 Å; total data measured: 4378 (excluding standards), total data observed: 2901. The structure was determined by direct methods using 32 starting phase permutations. Refinement proceeded smoothly to convergence at $R = 0.0381$ with anisotropic refinement of all non-H-atoms. *Structural data of the heptalene skeleton. Bond lengths:* C(1)–C(2) = 1.351, C(2)–C(6) = 1.442, C(6)–C(7) = 1.352, C(7)–C(8) = 1.440, C(8)–C(9) = 1.345, C(9)–C(10) = 1.491, C(10)–C(11) = 1.346, C(11)–C(12) = 1.452, C(12)–C(13) = 1.352, C(13)–C(14) = 1.457, C(14)–C(15) = 1.341, C(1)–C(15) = 1.483 and C(1)–C(10) = 1.485 Å. *Torsional angles:* C(2)–C(1)–C(10)–C(9) = 61.8°, C(15)–C(1)–C(10)–C(11) = 61.7°, C(1)–C(2)–C(6)–C(7) = −29.5°, C(6)–C(7)–C(8)–C(9) = 25.2°, C(10)–C(11)–C(12)–C(13) = −27.8° and C(12)–C(13)–C(14)–C(15) = 30.1°.

[22]) The CD spectra of (−)-(*P*)-**4** and (−)-(*P*)-**2** are identical (see *Exper. Part*).

molecular ellipticities in the long-wavelength region (450–300 nm) and by at least one intense (+)-CE about or below 300 nm[23]).

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 physical department of the Central Research Units of *F. Hoffmann-La Roche & Co., Ltd.*, Basle for IR, NMR, mass, CD and ORD spectra as well as for GC, HPLC, and elemental analyses, and the measurement of optical rotations. 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 support by a scholarship. *H.-J. H.* thanks especially Prof. Dr. *W. Hug*, Institut de chimie physique de l'Université de Fribourg, for intense discussions on electronic transitions of chiral heptalenes.

Experimental Part

General. M.p. on a Büchi apparatus (model *510*). The values are not corrected. TLC on silica gel plates (*60-F-254* plates, *Merck*). Prep. TLC also on silica gel (*60-F-254* plates, *Merck*; dimension 20 × 20 cm; thickness of the silica gel layer 2 mm). Column chromatography (CC) on silica gel (70–230 mesh *ASTM*). Evaporation of solvents on a rotatory evaporator (RE) at 0–40° and 15 Torr. Bulb-to-bulb distillations in Büchi apparatus (model *GKR-50*). The temp. of the oven and the pressure (Torr) is given. All operations with **2** and its derivatives were performed by exclusion of light (*cf.* [9]). Optical rotations on a *Perkin-Elmer* instrument (model *241*); specific rotations as $[\alpha]_\lambda^T$ (T in °C) in acetone (c = g/ml). UV/VIS spectra on a *Beckman* spectrophotometer (model *Acta III*, 195–800 nm). Maxima and minima (λ_{max} and λ_{min}) are given in nm (log ε). CD (on a dichrographe *Mark II, Jobin Yvon*) and ORD[24]) spectra in cuvettes of 10 cm, 1 cm, 0.96 mm and 0.08 mm. Range of measurements 190–699 nm. IR spectra (film or KBr) on a *Nicolet-7199-FT*-IR-system or on a *Perkin-Elmer* IR spectrophotometer (model *599*). Band positions are given in cm^{-1}. ^{1}H-NMR spectra at 90, 270 or 400 MHz. Chemical shifts in ppm with respect to TMS (= 0) as internal standard; f.s. = fine structure. Coupling constants J in Hz, $J(1,2) = J$(H–C(1), H–C(2)) *etc.* ^{1}H-DR-NMR (^{1}H double-resonance experiments) at 400 MHz given in irradiated position→observed position. MS on *MS-9*, *MS 902* and *MM 7070* instruments; ionization at 70 eV; ions in m/z (rel. %).

1. *Dimethyl (–)-(***P***)- and (+)-(***M***)-7-Isopropyl-5,10-dimethylheptalene-1,2-dicarboxylate* ((–)-(*P*)- and (+)-(*M*)-**1**)[2])[3]). – 1.1. *Selective Saponification of* **1** *to the Corresponding* rac-*1-Methoxycarbonylheptalene-2-carboxylic Acid* ((±)-**3**). Finely crystalline diester **1** (15.0 g, 44 mmol) [1] was added at r.t. to a soln. of KOH (77.4 g, 1.38 mol) in H_2O (360 ml) and EtOH (360 ml). The yellow crystals of **1** were dissolved after *ca.* 6 h. The yellow soln. was neutralized with 25% aq. HCl and the precipitated **3** extracted with Et_2O, and washed with H_2O. The residue of the Et_2O phase (17 g) was recrystallized with Et_2O/hexane yielding 12.6 g (87.6%) yellow crystals of **3**. M.p. 140–142° (dec.). IR (KBr): 2633/2528 (COOH), 1736/1716 (COOR), 1682 (COOH), 1383/1370 ($C(CH_3)_2$). ^{1}H-NMR (270 MHz): 1.049 and 1.087 (2*d*, $^3J((CH_3)_2CH–C(7)) = 7.0$, $(CH_3)_2CH–C(7)$); 1.989 (br. *s*, $CH_3–C(10)$); 2.086 (*t*-like *s*, $^4J(CH_3–C(5), H–C(4)) \approx {}^5J(CH_3–C(5), H–C(3)) \approx 1.1$, $CH_3–C(5)$); 2.476 (*sept.*, $^3J((CH_3)_2CH–C(7)) = 7.0$, $(CH_3)_2CH–C(7)$); 3.690 (*s*, $CH_3OOC–C(1)$); 5.856 (br. *s*, H–C(6)); 6.131 (*dq*, $^3J(9, 8) = 6.5$, ^4J(H–C(9),

[23]) It should be possible to deduce the absolute configuration of the heptalenes also directly from their CD spectra. Unfortunately, all calculations of electronic transitions in heptalene itself were done with planar heptalene of D_{2h} or C_{2h} symmetry (cf. [17]). However, nearly all calculations of the PPP-CI-type indicate that the symmetry of the long-wavelength transitions are A,B,B,B (or A) (in C_2 symmetry). The longest-wavelength transition of A symmetry should be forbidden in planar heptalene and only be weakly allowed (*i.e.* of low intensity) in non-planar heptalene. If we assume that the CE of this transition is very weak and thus far not observed, the next two transitions of B symmetry would nicely correspond to the two (–)-CE of (P)-heptalenes provided that the C_2 rule of *Wagnière* and *Hug* [18] is applicable, which correlates the polarization and the sign of the long-wavelength CE of molecules with C_2 symmetry of the chromophore with the handedness of the chromophore. It should be noted that (*P*)-chirality of the heptalenes corresponds to a (*M*)-conformation of the central s-*trans*-butadiene moiety (C(1), C(10a), C(5a), C(6); *cf. Scheme 4*) and its attached ethylene groups (C(2), C(3) and C(7), C(8)). The (*M*)-conformation of s-*trans*-butadiene results in a (–)-CE of the long-wavelength transition (*cf.* [19]). We will report on this topic later in this journal.

[24]) Instrument constructed in our Physics Department.

CH_3–C(10)) = 1.3, H–C(9)); 6.193 (*dq*, $^3J(4, 3) = 6.5$, ^4J(H–C(4), CH_3–C(5)) = 1.5, H–C(4)); 6.270 (slightly splitted *d*, $^3J(8, 9) = 6.5$, H–C(8)); 7.554 (*dq*, $^3J(3, 4) = 6.5$, ^5J(H–C(3), CH_3–C(5)) = 1.0, H–C(3)); *ca.* 9.5 (br. *s*, HOOC–C(1)). MS: 326 (3, M^+), 294 (100, $M^+ - CH_3OH$). Anal. calc. for $C_{20}H_{22}O_4$ (326.40): C 73.60, H 6.79; found: C 73.31, H 6.91.

1.2. rac-*7-Isopropyl-5,10-dimethylheptalene-1,2-dicarboxylic Anhydride* ((±)-**5**[9]). Compound **3** (2.1 g, 6.4 mmol) was introduced in a bulb-to-bulb distillation tube and slowly heated up to 170° at 0.03 Torr. The extrusion of MeOH was indicated by an increase of the pressure (up to 0.1 Torr). The formed red-brownish coloured oil was quantitatively distilled (200°/0.03 Torr) and recrystallized with Et_2O/hexane to yield 1.75 g (93%) deeply-red-to-brown needles of (±)-**5**. M.p. 126–127°. UV (hexane): λ_{max} 224 (4.28), 263 (4.19), 313 (4.02), 368 (3.60), *ca.* 445 sh (3.1), absorption up till 600; λ_{min} 214 (4.27), 249 (4.13), 291 (3.91), 350 (3.57). IR (KBr): 1807/1757 (cyclic 5-membered anhydride). ^{1}H-NMR (360 MHz): 1.086 and 1.111 (2*d*, $^3J((CH_3)_2CH$–C(7)) = 7.0, $(CH_3)_2$CH–C(7)); 2.200 (br. *s*, CH_3–C(10)); 2.305 (br. *s*, CH_3–C(5)); 2.514 (*sept.*, $^3J((CH_3)_2CH$–C(7)) = 7.0, $(CH_3)_2CH$–C(7)); 5.944 (*s*, H–C(6)); 6.277 and 6.351 (2*d*, $^3J(8, 9) = 7.2$, H–C(8), H–C(9)); 6.446 (*d* with f.s., $^3J(4, 3) = 7.0$, ^4J(H–C(4), CH_3–C(5)) ≈ 1.4, H–C(4)); 7.141 (*d*, $^3J(3, 4) = 7.0$, H–C(3)). MS: 295 (22, $M^+ + 1$), 294 (100, M^+). Anal. calc. for $C_{19}H_{18}O_3$ (294.53): C 77.53, H 6.16; found: C 77.25, H 6.14.

1.3. rac-*7-Isopropyl-2-methoxycarbonyl-5,10-dimethylheptalene-1-carboxylic Acid* ((±)-**6**). Anhydride **5** (5.0 g, 17 mmol) was suspended in MeOH (100 ml) and NaOMe (1.5 g, 27.3 mmol) in MeOH (50 ml) added at 18°. An immediate change of the colour from red-brown to yellow indicated the formation of the 1-acid (±)-**6**. The soln. was acidified with 3N aq. HCl, extracted with Et_2O and the Et_2O extracts washed with H_2O. The residue of the extracts (5.5 g)[25] was recrystallized with Et_2O/hexane and yielded 5.2 g (93%) of pure **6**. M.p. 122.7–122.8° (dec.). IR (KBr): 1730/1700 (COOR), 1680 (COOH). ^{1}H-NMR (90 MHz): 1.06 (2*d*, $^3J((CH_3)_2CH$–C(7)) = 7.5, $\Delta\delta$ = 0.07 ppm, $(CH_3)_2$CH–C(7)); 2.06 (br. *s*, CH_3–C(5) and CH_3–C(10)); 2.48 (*sept.*, $^3J((CH_3)_2CH$–C(7)) = 7.5, $(CH_3)_2CH$–C(7)); 3.69 (*s*, CH_3OOC–C(2)); 5.85 (br. *s*, H–C(6)); 6.0–6.35 (several signals, H–C(4), H–C(8) and H–C(9)); 6.66 (br. *s*, COOH); 7.44 (*d* with f.s., $^3J(3, 4) = 6.5$, H–C(3)). MS: 326 (very weak, M^+), 294 (100, $M^+ - CH_3OH$). Anal. calc. for $C_{20}H_{22}O_4$ (326.40): C 73.60, H 6.79; found: C 73.44, H 6.84.

1.4. *(–)-(*P*)- and (+)-(*M*)-7-Isopropyl-1-methoxycarbonyl-5,10-dimethylheptalen-2-carboxylic Acid* ((–)-(*P*)- and (+)-(*M*)-**3**). 2-Acid (±)-**3** (3.26 g, 10 mmol) together with (+)-(*R*)-1-phenylethylamine (1.33 g, 11 mmol) were dissolved in AcOEt. The yellow soln. was concentrated (RE) to about 70 ml and stored in the refrigerator at 6° for 6 d. The formed, slightly yellow crystals (3.15 g) were separated from the mother liquor (ML) from which 1.6 g of a yellow-brown oil was obtained upon evaporation (RE) of the AcOEt. Crystals: $[\alpha]_D^{20} = -206°$ ($c = 1.42 \times 10^{-3}$); oil: $[\alpha]_D^{20} = +419°$ ($c = 1.29 \times 10^{-3}$).

The (–)- and the (+)-1-phenylethylammonium salts were treated at 0° with 2N H_2SO_4 and Et_2O and the thus obtained etheral extracts of (–)-(*P*)- and (+)-(*M*)-**3** washed with 2N H_2SO_4 and H_2O at 0°. The dried Et_2O extracts were evaporated at 0° and all residual solvent carefully removed in high vacuum at 0°. (–)-(*P*)-**3**: $[\alpha]_D^{20} = -322°$ ($c = 1.18 \times 10^{-3}$); (+)-(*M*)-**3**: $[\alpha]_D^{20} = +578°$ ($c = 1.02 \times 10^{-3}$). With respect to their optical lability the oily, partially resolved 2-acids were not further purified. According to the optical purity (p) of the dimethyl 1,2-dicarboxylate (–)-(*P*)-**1** *(cf. 1.7)*, obtained from the corresponding acid (–)-(*P*)-**6** the p-values for the acids can be estimated to be in the range of 0.17 (–322°) and 0.31 (+578°).

1.5. *(–)-(*P*)- and (+)-(*M*)-***6***. 1-Acid (±)-**6** (3.5 g, 10.7 mmol) was dissolved in AcOEt (170 ml) and combined with a soln. of (–)-(1*R*, 2*S*)-ephedrine (1.8 g, 10.9 mmol) in AcOEt (20 ml). The mixture was concentrated (RE) to 80 ml and stored for 24 h at –15°. The formed yellow crystals (2.0 g) were filtrated and washed with ice-cold AcOEt. M.p. 105°. $[\alpha]_D^{20} = -1490°$ ($c = 1 \times 10^{-3}$).

Evaporation (RE) of the ML yielded 3.3 g of semi-crystalline (+)-ephedrinium salt with $[\alpha]_D^{20} = +819°$ ($c = 1 \times 10^{-3}$). Since the (–)-ephedrinium salt showed in the ^{1}H-NMR (270 MHz) only one signal for CH_3OOC–C(2) at 3.653 ppm, the (+)-salt, however, two at 3.631 and 3.668 ppm in a ratio of 1:3.76 (21 and 79%)[26]), the diastereomeric purity (d) of the salts are > 0.99 and 0.58, respectively.

Decomposition of the salts with 2N H_2SO_4 at 0° *(cf. 1.3)* led to 1.3 g (37%) of (–)-(*P*)- and 1.9 g (54%) of (+)-(*M*)-**6** with $[\alpha]_D^{20} = -1725°$ ($c = 1 \times 10^{-3}$)[27]) and +990° ($c = 1 \times 10^{-3}$), respectively.

1.6. *(+)-(*M*)-***1*** *from (+)-(*M*)-***3***. Compound (+)-**3** (from *1.4*, $[\alpha]_D^{20} = +578°$) reacted quantitatively with CH_2N_2 in Et_2O at 0° to yield the corresponding diester (+)-**1** as a yellow oil. $[\alpha]_D^{20} = +587.5°$ ($c = 1.11 \times 10^{-3}$;

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[25]) The ring-opening reaction of **5** was repeated several times. Up to 11% of the isomeric acid **3** could be detected by ^{1}H-NMR (80 MHz; signals for CH_3–C(10) at 2.02 and 2.09 ppm) in the crude acid **6**.

[26]) Salts of **6** are optically more stable than the corresponding salts of **3**.

[27]) $[\alpha]_{578}^{20} = -1860°$ and $[\alpha]_{546}^{20} = -2536°$ ($c = 1 \times 10^{-3}$).

[28]) P = peak, T = trough, sh = shoulder.

p = 0.31, according to *1.7*). ORD (dioxane, λ/ϕ)[28]): 699/1045, 589/2150, 441/9870 (P), 395/0, 370/−10210 (sh), 356/−16170, 332/−28940 (sh), 313/−44300, 299/−43100 (sh), 294/−45600 (P), 281/−6130 (sh), 279/0, 253/52300 (sh), 242/62200 (P).

1.7. *(−)-(P)- and (+)-(M)-**1**) from (−)-(P)- and (+)-(M)-**6***. The acid (−)-**6** ($[\alpha]_D^{20} = -1725°$) reacted quantitatively with CH_2N_2 in Et_2O at 0° to yield (−)-(*P*)-**1** as a yellow oil. $[\alpha]_D^{20} = -1873°$ ($c = 2.36 \times 10^{-4}$; e > 0.99 according to *1.5* and supposed that no racemization occurred at 0° in the course of the preparation of the diester *via* the free acid). ORD (dioxane, λ/ϕ) = 699/−3030, 589/−5980, 437/−27100 (T), 394/0, 295/181900 (P), 276/0, 243/−123860 (T), 238/106250 (sh), 235/112540. CD (cyclohexane, λ/θ; see also *Fig. 2*): 507/−1.77, 374.7/−71.9 (min), 350/−67.5 (sh), 276.8/181.8 (max), 255.0/133.3 (sh), 224.0/−12.7 (sh), 208.9/−85.9 (min). CD (dioxane): 503/−5.73, 384/−73.9 (min), 362/−68.0 (sh), 279.4/179.4 (max), 258.0/125.1 (sh), 225.0/−12.8 (sh), 211.3/−73.6 (min).

(+)-**6** ($[\alpha]_D^{20} = +990°$) yielded (+)-(*M*)-**1** with $[\alpha]_D^{20} = +1075°$ ($c = 1.05 \times 10^{-3}$).

1.8. *Thermal Racemization of (−)-(P)-**1** and (−)-(P)-**3** in Acetone.* The rates of racemization were measured in a thermostated polarimeter cuvette (100 mm) by following the decrease of α_D in acetone (c = 89.5 mmol/l for (−)-**3** and 14.7 mmol/l for (−)-**1**). According to $\ln(\alpha/\alpha_o) = -2\,k_{rac} \times t$ the following rate constants were determined for (−)-**3**: 1.40×10^{-4} s^{-1}/319.2 K, 7.01×10^{-5} s^{-1}/312.7 K, 1.98×10^{-5} s^{-1}/303.3 K, 1.08×10^{-5} s^{-1}/298.2 K and 5.94×10^{-6} s^{-1}/293.2 K, and for (−)-**1**: 1.48×10^{-4} s^{-1}/318.0 K, 2.93×10^{-5} s^{-1}/304.0 K, 1.40×10^{-5} s^{-1}/289.0 K and 7.88×10^{-6} s^{-1}/293.3 K.

2. *Dimethyl (−)-(P)- and (+)-(M)-5,6,8,10-Tetramethylheptalene-1,2-dicarboxylate* ((−)-(*P*)- and (+)-(*M*)-**2**)[2][3]). – 2.1. (±)-**2**. 1,4,6,8-Tetramethylazulene[29]) (12.5 g, 68 mmol) and dimethyl acetylenedicarboxylate (14 ml; 16.2 g, 114 mmol) were dissolved in freshly distilled tetralin (150 ml) and heated under N_2 during 3.5 h at 190°. Evaporation (RE at 75°/0.05 Torr) of the tetralin yielded 34.1 g of a dark oily residue. CC (1.6 kg silica gel, hexane/Et_2O 7:3) gave fractions containing 7.1 g (32%) of pure (±)-**2** and another set of fractions containing 7.6 g of pure dimethyl 4,6,8-trimethylazulene-1,2-dicarboxylate. Additional mixed fractions gave 2.4 g of heptalenes which contained besides some (±)-**2** about 1 g (4.5%) of dimethyl 1,6,8,10-tetramethylheptalene-4,5-dicarboxylate (*cf.* [9])[30]). (±)-**2**: yellow crystals after recrystallization from Et_2O/hexane, m.p. 124–125°. UV/VIS (cyclohexane): λ_{max} 213 (4.356), 235 sh (4.200). 251 sh (4.189), 263.5 (4.218), 319 sh (3.492), 374 sh (2.903); λ_{min} 244.0 (4.172); (dioxane): λ_{max} 263 (4.208), 274.0 sh (4.181), 322 sh (3.498), 367 sh (2.985). IR (KBr): 1737/1715 (COOR). ^{1}H-NMR (400 MHz: $CDCl_3/C_6D_6$, resp.): 1.744/1.561 (*s*, CH_3–C(6)); 1.962/1.817 (*d*-like *s*, ^4J(CH_3–C(8), H–C(7)) ≈ 1.3, CH_3–C(8)); 2.002/1.731 (*t*-like *s*, ^4J(CH_3–C(5), H–C(4)) ≈ ^5J(CH_3–C(5), H–C(3)) ≈ 1, CH_3–C(5)); 2.043/1.994 (*d*-like *s*, ^4J(CH_3–C(10), H–C(9)) ≈ 1.2, CH_3–C(10)); 3.691 and 3.706/3.265 and 3.449 (2*s*, CH_3OOC–C(1) and CH_3OOC–C(2)); 6.010/5.905 (br. *s* with f.s., H–C(9)); 6.145/6.019 (br. *s* H–C(7)); 6.269/5.895 (*dq*, ^3J(4,3) = 5.9/5.8, ^4J(H–C(4), CH_3–C(5)) = 1.4/1.45, H–C(4)); 7.525/7.701 (*dq*, ^3J(3, 4) = 5.9/5.8, ^5J(H–C(3), CH_3–C(5)) = 1, H–C(3)). ^{1}H-DR-NMR (400 MHz; $CDCl_3$): 6.269 (H–C(4))→2.002 (br. *s*, CH_3–C(5)); (C_6D_6): 1.561 (CH_3–C(6))→6.145 (*s* sharpening, H–C(7)); 1.731 (CH_3–C(5))→5.895 (*d*, ^3J(4, 3) = 5.8, H–C(4)) and 7.701 (*d*, ^3J(3, 4) = 5.8, H–C(3)); 1.817 (CH_3–C(8))→5.905 (*s* sharpening, H–C(9)) and 6.019 (*s* sharpening, H–C(7)); 1.994 (CH_3–C(10))→5.905 (*d*-like *s*, ^4J(9,7) ≈ 1, H–C(9)); 7.701 (H–C(1))→5.895 (*q*-like *s*, ^4J(H–C(4), CH_3–C(5)) ≈ 1.5, H–C(4)) and 1.731 (*d*, ^4J(CH_3–C(5), H–C(4)) ≈ 1.5, CH_3–C(5)). MS: 326 (94, M^+), 294 (11, $M^+ - CH_3OH$), 286 (8.5, $M^+ - CH_3C{\equiv}CH$), 279 (31, $M^+ - (CH_3 + CH_3OH)$), 267 (23, $M^+ - CH_3OOC\cdot$), 242 (9, $M^+ - HC{\equiv}CCOOCH_3$), 235 (26, $M^+ - (CH_3O\cdot + CH_3OH + CO)$), 228 (31, $M^+ - CH_3C{\equiv}CCOOCH_3$), 207 (25, $M^+ - (CH_3OOC\cdot + CH_3OH + CO)$), 184 (100, $M^+ - ADM$). Anal. calc. for $C_{20}H_{22}O_4$ (326.40): C 73.60, H 6.79; found: C 73.41, H 6.86.

Dimethyl 4,6,8-Trimethylazulene-1,2-dicarboxylate. Violet crystals, m.p. 141–142° (138–139° [2]). IR (KBr): 1717/1707 (COOR). ^{1}H-NMR (400 MHz): 2.6234 (*s*, CH_3–C(6)); 2.861 and 2.881 (2*s*, CH_3–C(4) and CH_3–C(8)); 3.925 and 3.998 (2*s*, CH_3OOC–C(1), CH_3OOC–C(2)); 7.118 and 7.141 (2 br. *s*, H–C(5), H–C(7)); 7.718 (*s*, H–C(3)). MS: 286 (64, M^+), 255 (100, $M^+ - CH_3O\cdot$), 254 (58, $M^+ - CH_3OH$). Anal. calc. for $C_{17}H_{18}O_4$ (286.33): C 71.31, H 6.34; found: C 71.35, H 6.53.

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[29]) The azulene (m.p. 44–45°) was prepared in an overall yield of 73% by *Vilsmeier* formylation [20] of 4,6,8-trimethylazulene [21] followed by reduction of the formed 1-formyl-4,6,8-trimethylazulene (m.p. 107–108°) with $NaBH_4/BF_3 \cdot Et_2O$ [22] in Et_2O/diglyme.

[30]) TLC of the mixed fractions showed, according to their yellow colour, the presence of further heptalenes, possibly dimethyl 3,6,8,10-tetramethylheptalene-1,2-dicarboxylate and rearranged products of this heptalene (*cf.* [9]). On exposure to normal laboratory light during several days, the heptalene ratio in the mixed fractions changed (TLC) (*cf.* [9]).

2.2. *Selective Saponification of* **2** *to the Corresponding* rac-*1-Methoxycarbonylheptalene-2-carboxylic Acid* ((±)-**4**). Finely powdered diester **2** (5.3 g, 16.2 mmol) was added to a soln. of KOH (20 g) in EtOH/H_2O 1:1 (200 ml) kept at 35–40°. After stirring for 4 h, a clear yellow soln. was formed which was acidified with 25% aq. HCl under ice-cooling. The precipitated 2-acid **4** was extracted with Et_2O, washed with H_2O and dried. The acid was recrystallized with Et_2O/hexane, 4.91 g (96%). M.p. 159–160° (Et_2O/hexane; dec.) and 177–178° (Et_2O; dec.). IR (KBr): 1740/1724 (COOR), 1680 (COOH). ^{1}H-NMR (90 MHz): 1.74 (*s*, CH_3–C(6)); 1.96 and 2.02 (*d*-like *s*, $J \approx 1.2$, 3H and *m*, 6H, CH_3–C(5), CH_3–C(8), and CH_3–C(10)); 3.67 (*s*, CH_3OOC–C(1)); 6.01 (br. *s* with f.s., H–C(7)); 6.14 (br. *s*, H–C(9)); 6.27 (*q*-like *d*, $^3J(4, 3) = 5.9$, ^4J(H–C(4), CH_3–C(5)) = 1.45, H–C(4)); 7.61 (*q*-like *d*, $^3J(3, 4) = 5.9$, ^5J(H–C(3), CH_3–C(5)) ≈ 1, H–C(3)); 10.9 (br. *s*, HOOC–C(2)). MS: 312 (47, M^+), 280 (100, $M^+ - CH_3OH$). Anal. calc. for $C_{19}H_{20}O_4$ (312.37): C 73.06, H 6.45; found: C 72.91, H 6.66.

2.3. rac-*5,6,8,10-Tetramethylheptalene-1,2-dicarboxylic Anhydride* ((±)-**7**). Acid **4** (1.0 g, 3.20 mmol) was heated in a bulb-to-bulb tube at 180°/0.05 Torr till the evolution of MeOH had ceased. The brown-red residue was distilled at 230°/0.05 Torr to yield 0.95 g (95%) (±)-**7** as a red oil which was crystallized from Et_2O/hexane; m.p. 151–152°. UV (hexane): λ_{max} 225 (4.2), 265 (4.1), 304 (3.9), 350 sh (3.5), 430 sh (3.0); λ_{min} 246 (4.0), 298 (3.9). IR (KBr): 1811 and 1759 (cyclic 5-membered anhydride). ^{1}H-NMR (400 MHz): 1.813 (*s*, CH_3–C(6)); 2.057 (*d*-like *s*, $J = 1.2$, CH_3–C(8)); 2.103 (*s* with f.s., $J \approx 1.3$, CH_3–C(5)); 2.270 (*d*-like *s*, $J = 1.2$, CH_3–C(10)); 6.275 (br. *s*, H–C(7)); 6.300 (br. *s* with f.s., $J \approx 1.3$, H–C(9)); 6.540 (*dq*, $^3J(4, 3) = 6.5$, ^4J(H–C(4), CH_3–C(5)) = 1.5, H–C(4)); 7.295 (*d* with f.s., $^3J(3, 4) = 6.5$, ^5J(H–C(3), CH_3–C(5)) ≈ 0.6, H–C(3)). ^{1}H-DR-NMR: 2.057 (CH_3–C(8))→6.275 (H–C(7), *s* sharpening) and 6.300 (*q*-like *s*, $^4J(9, 7) \approx {}^4J$(H–C(9), CH_3–C(10)) ≈ 1.5, H–C(9)); 2.104 (CH_3–C(5))→6.540 (*d*, $^3J(4,3) = 6.5$, H–C(4)) and 7.295 (*d*, H–C(3)); 2.272 (CH_3–C(10))→6.275 (*q*-like *s*, $^4J(7, 9) \approx {}^4J$(H–C(7), CH_3–C(8)) ≈ 1.3, H–C(7)) and 6.300 (*d*-like *s*, $^4J(9, 7) \approx 1.3$, H–C(9)). ^{1}H-NOE: 2.057 (CH_3–C(8))→6.275 (H–C(7), 9%) and 6.300 (H–C(9), 9%); 2.272 (CH_3–C(10))→6.300 (H–C(9), 11%). MS: 280 (100, M^+). Anal. calc. for $C_{18}H_{16}O_3$ (280.32): C 77.12, H 5.75; found: C 77.15, H 5.81.

2.4. rac- *and* meso-*Bis(1-methoxycarbonyl-5,6,8,10-tetramethylheptalene-2-carboxylic) Anhydride* ((±)- and *meso*-**10**). To a mixture of DMF (0.18 ml, 2.3 mmol) and MeCN (2 ml) was added oxalyl chloride (0.083 ml, 1 mmol) in MeCN (1.5 ml) at 0°. The suspension of *N,N*-dimethyl-*N*-chloromethylideneammonium chloride was diluted with MeCN (1 ml), and (±)-**4** (0.250 g, 0.8 mmol) introduced under stirring. After 5 min at 0°, a second portion of (±)-**4** (0.250 g, 0.8 mmol) and MeCN (2 ml) was added. The mixture was briefly warmed up to 10°. After cooling to 0° a soln. of pyridine (0.2 ml, 2.5 mmol) in MeCN (1 ml) was added. After 20 min at 0°, the mixture was poured on to ice and extracted with Et_2O. The Et_2O extracts were washed with H_2O and dried ($MgSO_4$). Evaporation (RE) of Et_2O gave 0.53 g of a 2:3 mixture of (±)- and *meso*-**10**. The bis-anhydrides were separated by repeated prep. TLC with CH_2Cl_2/Et_2O on silica gel.

meso-**10**: m.p. 224–225° (dec.); $R_f = 0.26$ (Et_2O/hexane 1:1). UV (cyclohexane): λ_{max} 214 (4.36), 262 (4.18), 285 sh (4.10), 326 sh (3.52), 378 sh (3.02); λ_{min} 247 (4.16). IR (KBr): 1780/1734 (anhydride), 1714 (COOR). ^{1}H-NMR (270 MHz): 1.756 (*s*, CH_3–C(6)); 1.968 (*d*-like *s*, ^4J(CH_3–C(8), H–C(7)) ≈ 1, CH_3–C(8)); 2.022 (*s* with f.s., CH_3–C(5)); 2.042 (*d*-like *s*, ^4J(CH_3–C(10), H–C(9)) ≈ 1, CH_3–C(10)); 3.669 (*s*, CH_3OOC–C(1)); 6.013 (br. *s*, H–C(9)); 6.154 (br. *s*, H–C(7)); 6.268 (*dq*, $^3J(4,3) = 6.0$, ^4J(H–C(4), CH_3–C(5)) = 1.5, H–C(4)); 7.496 (*q*-like *d*, $^3J(3, 4) = 5.8$, ^5J(H–C(3), CH_3–C(5)) = 0.9, H–C(3)). MS: 606 (18, M^+), 326 (10), 295 (100). Anal. calc. for $C_{38}H_{38}O_7$ (606.72): C 75.23, H 6.31; found: C 75.18, H 6.51.

(±)-**10**: m.p. 216–217° (dec.); $R_f = 0.20$ (Et_2O/hexane 1:1). UV (cyclohexane): λ_{max} 214.5 (4.49), 264 (4.33), 280 sh (4.29), 324 sh (3.67), 366 sh (3.22); λ_{min} 247 (4.30). IR (KBr): 1789/1729 (anhydride and COOR). ^{1}H-NMR (270 MHz): 1.746 (*s*, CH_3–C(6)); 1.969 (*d*-like *s*, ^4J(CH_3–C(8), H–C(7)) ≈ 1, CH_3–C(8)); 2.025 (br. *s* with f.s., CH_3–C(5)); 2.046 (*d*-like *s*, ^4J(CH_3–C(10), H–C(9) ≈ 1, CH_3–C(10)); 3.679 (*s*, CH_3OOC–C(1)); 6.016 (br. *s*, H–C(9)); 6.149 (br. *s*, H–C(7)); 6.278 (*dq*, $^3J(4, 3) = 6.0$, ^4J(H–C(4), CH_3–C(5)) = 1.5, H–C(4)); 8.514 (*d* with f.s., $^3J(3, 4) = 6.0$, ^5J(H–C(3), CH_3–C(5)) ≈ 1, H–C(3)). MS: 606 (17, M^+), 326 (9), 295 (100). Anal. calc. for $C_{38}H_{38}O_7$ (606.72): C 75.23, H 6.31; found: C 75.44, H 6.61.

2.5. rac-*1,2-Bis(hydroxymethyl)-5,6,8,10-tetramethylheptalene* ((±)-**11**). To a soln. of $LiALH_4$ (0.55 g, 14.5 mmol) in dried Et_2O (15 ml), a soln. of **2** (2.0 g, 6.1 mmol) in Et_2O (150 ml) was added with stirring. After 4.5 h at r.t., an additional portion of $LiALH_4$ (0.1 g) was added to the mixture. After 1 h, the mixture was decomposed under ice-cooling with H_2O (0.55 ml, 30 mmol), 15% KOH soln. (0.55 ml) and again H_2O (1 ml). The inorg. salts were removed by filtration and the Et_2O extract washed with H_2O and dried ($MgSO_4$). Evaporation of Et_2O (RE) gave 1.31 g (79%) (±)-**11** as pale yellow crystals which were recrystallized from Et_2O. M.p. 153–155°. UV (cyclohexane): λ_{max} 214.5 (4.193), 247.0 sh (4.279), 254.5 (4.316), 296 sh (3.504), 348 sh (2.892); λ_{min} 227.5 (4.049). IR (KBr): 3217 (OH). ^{1}H-NMR (270 MHz): 1.714 (*s*, CH_3–C(6)); 1.990 (*s*, CH_3–C(8), CH_3–C(10)); 2.102 (*d*, ^4J(CH_3–C(5), H–C(4)) = 1.3, CH_3–C(5)); 2.63–2.74 (several signals, 2H, 2 OH); 4.24–4.42 (several signals, 4H, $HOCH_2$–C(1) and $HOCH_2$–C(2)); 5.999 (*quint.*-like br. *s*, H–C(9)); 6.082 (br. *s*, H–C(7)); 6.141 (*dq*, $^3J(4, 3) = 6.0$, ^4J(H–C(4),

CH_3–C(5)) = 1.5, H–C(4)); 6.514 (*d*, ^3J(3,4) = 6.0, 1H, H–C(3)). MS: 270 (70, M^+), 230 (13, $M^+ - CH_3C{\equiv}CH$), 184 (100, $M^+ - HOCH_2C{\equiv}CCH_2OH$). Anal. calc. for $C_{18}H_{22}O_2$ (270.37): C 79.96, H 8.20; found: C 79.80, H 8.36.

2.6. rac-*3,3-Dimethoxy-9,11,13,15-tetramethyl-4-oxatricyclo[8.5.0.0^{2,6}]pentadeca-1,6,8,10,12,14-hexaen-5-one* ((±)-**8**): To a cooled soln. (–20°) of DMF (0.47 g, 6.5 mmol) in MeCN (2 ml) was added oxalyl chloride (0.19 ml, 2.2 mmol) in MeCN (2 ml) (*cf.* [14]). The suspension of the formed iminium salt was diluted with MeCN (2 ml), and 2-acid **4** (0.625 g, 2.0 mmol) was added. The acid dissolved under warming up to 2° within 10 min. The yellow-orange soln. was cooled again to –20° and MeOH (0.25 ml, 5 mmol) dissolved in pyridine (0.5 ml, 6.2 mmol) were added within 5 min. The dark orange mixture was extracted with CH_2Cl_2 and the extracts washed with 20% $KHCO_3$-soln. and H_2O. The residue of the CH_2Cl_2 extracts was further purified by prep. TLC (Et_2O/hexane 1:1) to yield 0.54 g (83%) (±)-**8** which was recrystallized with Et_2O/hexane; 0.46 g (±)-**8** as yellow-orange crystals, m.p. 173–174°. UV (hexane): λ_{max} 212.0 (4.35), 246 (4.24), 267 (4.22), 321 sh (3.56), 396 sh (2.90); λ_{min} 227 (4.11), 256 (4.17). IR (KBr): 1774 (5-ring lactone). ^{1}H-NMR (270 MHz): see *Table 3*; ^3J(7, 8) = 6.5, ^4J(12, 14) ≈ 1.3, ^4J(H–C(8), CH_3–C(9)) ≈ 1.4, ^4J(H–C(12), CH_3–C(13)) ≈ 1.3, ^4J(H–C(14), CH_3–C(15)) ≈ 1.3, ^5J(H–C(7), CH_3–C(9)) ≈ 0.7. ^{1}H-NOE: 1.728 (CH_3–C(11))→6.163 (H–C(12), 10.7%); 1.995 (CH_3–C(13))→3.181 (CH_3O–C(3), 1%), 6.079 (H–C(14), 9%) and 6.163 (H–C(12), 10.7%); 2.088 (CH_3–C(9))→6.079 (H–C(14), 1.4%) and 6.163 (H–C(12), 1.1%) and 6.474 (H–C(8), 11%); 2.161 (CH_3–C(15))→6.079 (H–C(14), 10.3%); 3.465 (CH_3O–C(3))→2.161 (CH_3–C(15), 0.8%). MS: 326 (53, M^+), 295 (43, $M^+ - CH_3O^\cdot$), 294 (62, $M^+ - CH_3OH$), 208 (38, $M^+ - C_4H_6O_4$), 207 (42, $M^+ - (H_3COOC^\cdot + CH_3OH + CO)$), 193 (100). Anal. calc. for $C_{20}H_{22}O_4$ (326.39): C 73.60, H 6.79; found: C 73.69, H 6.91.

2.7. *(PM,3RS,1′SR)- and (PM,3RS,1′RS)-3-Methoxy-9,11,13,15-tetramethyl-3-(1′-phenylethoxy)-4-oxatricyclo[8.5.0.0^{2,6}]pentadeca-1,6,8,10,12,14-hexaen-5-one* ((±)-**9A** and (±)-**9B**, resp.). According to *2.6*, **4** (0.8 g, 2.6 mmol) reacted with 0.77 g (6.3 mmol) *rac*-1-phenylethanol in 0.65 ml pyridine. Workup and extraction with CH_2Cl_2 yielded 1.75 g of a brownish red oil which was separated by prep. TLC (Et_2O/hexane 1:1) to give 498 mg (47%) of (±)-**9A**/(±)-**9B** 1:1, 107 mg (15%) of **7**, and 226 mg of an orange oil from which, after crystallization, 44 mg (5.7%) of *meso*- and (±)-**10** could be isolated. The diastereoisomers (±)-**9A** (221 mg, 19.7%) and (±)-**9B** (104 mg, 9.8%) were separated by fractional crystallization from Et_2O/hexane.

(±)-**9A**: Orange crystals, m.p. 154–155°; R_f = 0.49 (hexane/Et_2O 7:3). UV (cyclohexane): λ_{max} 211.5 (4.351), 216 sh (4.294), 247 (4.186), 268 (4.164), 313 sh (3.595), 396 (2.862); λ_{min} 229 (4.086), 257 (4.132), 368 (2.826); (dioxane): λ_{max} 249 (4.239), 271 (4.229), 318 sh (3.659), 400 (2.977); λ_{min} 259 (4.188), 368 (3.907). IR (KBr): 1777 (5-ring lactone). ^{1}H-NMR (270 MHz): see *Table 3*; *J* as in **8** (see *2.6*). ^{1}H-DR-NMR: 6.077 (H–C(14))→2.198 (*s*, CH_3–C(15)); 6.144 (H–C(12))→1.997 (*s*, CH_3–C(13)); 6.437 (H–C(8))→2.076 (br. *s*, CH_3–C(9)) and 7.179 (br. *s*, H–C(7)). MS: 416 (100, M^+), 294 (61), 280 (44), 208 (41), 193 (69), 178 (32), 165 (28), 105 (88). Anal. calc. for $C_{27}H_{28}O_4$ (416.52): C 77.86, H 6.78; found: C 77.83, H 6.57.

(±)-**9B**: Yellow-orange crystals, m.p. 134–135°; R_f = 0.54 (hexane/Et_2O 7:3). UV (cyclohexane): λ_{max} 211.5 (4.431), 216 sh (4.376), 247.5 (4.258), 268 (4.239), 313 sh (3.663), 400 (2.973); λ_{min} 227.5 (4.075); 257 (4.203), 370 (2.927); (dioxane): λ_{max} 249 (4.238), 270.5 (4.233), 312 sh (3.714), 400 (2.977); λ_{min} 258.5 (4.191), 370 (2.919). IR (KBr): 1766 (5-ring lactone). ^{1}H-NMR (270 MHz): see *Table 3*; *J* as in **8** (see *2.6*). ^{1}H-DR-NMR: 5.939 (H–C(14))→1.915 (*s*, CH_3–C(15)); 6.128 (H–C(12))→1.939 (*s*, CH_3–C(13)); 6.471 (H–C(8))→2.077 (br. *s*, CH_3–C(9)) and 7.260 (br. *s*, H–C(7)). MS: 416 (90, M^+), 294 (50), 280 (43), 208 (39), 193 (71), 178 (35), 165 (32), 105 (100). Anal. calc. for $C_{27}H_{28}O_4$ (416.52): C 77.86, H 6.78; found C 77.76, H 7.06.

2.8. *(–)-(P)- and (+)-(M)-1-Methoxycarbonyl-5,6,8,10-tetramethylheptalene-2-carboxylic Acid* ((–)-(*P*)- and (+)-(*M*)-**4**). – 2.8.1. *Resolution with (+)-(R)-1-Phenylethylamine.* 2-Acid (±)-**4** (3.13 g, 10 mmol) and (+)-(*R*)-amine (1.34 g, 11 mmol) were dissolved in AcOEt and the soln. concentrated (RE) to a volume of 35 ml. Yellow crystals started to deposite after 15 d at 4°. The crystallization was complete after additional 7 d at 4°. The crystals (0.75 g) were separated from the ML and washed with ice-cooled AcOEt. Crystals: $[\alpha]_D^{20}$ = +946° ($c = 1.04 \times 10^{-3}$); yellow semi-solid from ML (3.47 g): $[\alpha]_D^{20}$ = –189° ($c = 1.12 \times 10^{-3}$); yellow semi-solid from washing (0.3 g): $[\alpha]_D^{20}$ = +144° ($c = 1.14 \times 10^{-3}$).

Determination of d of the (+)-Salt. The (+)-salt (57 mg, 0.12 mmol) was treated at 0° with 2N H_2SO_4 and Et_2O, and (+)-**4** directly converted into (+)-**2** with CH_2N_2 in Et_2O. Obtained (+)-**2** (43 mg) was combined with Eu(hfc)$_3$ (104.3 mg), and the ^{1}H-NMR measured in $CDCl_3$ at 90 MHz. ^{1}H-NMR of an analogously prepared sample with (±)-**2** (last number in brackets G values; *cf* [11]): 1.95 and 2.01 (2*s*, each 1.5H, CH_3–C(6), 0.3), 2.36 and 2.46 (2 br. *s*, each 3H, CH_3–C(8) and CH_3–C(10)); 2.96 (br. *s* with f.s. CH_3–C(5), 1.45); 5.21 and 5.22 (*s*, total 3H, CH_3OOC–C(1), 2.3), 6.5–6.9 (several signals, total 3H, H–C(4), H–C(7) and H–C(9)); 7.52 (*s*, 1.5H, CH_3OOC–C(2), 5.76) and 7.68 (*s*, 1.5H, CH_3OOC–C(2), 6.00), 12.44 (br. *dd*, H–C(3), 7.4). The signals at 7.52 and 7.68 of the optically active probe gave a ratio of 94:6, *i.e.* d of the (+)-salt = 0.88 ± 0.02.

Treatment of the (–)-salt (3.47 g) with 2N H_2SO_4 and Et_2O at 0° yielded (–)-**4** with $[\alpha]_D^{20}$ = –309° ($c = 1.21 \times 10^{-3}$).

2.8.2. *Resolution with (−)-(1R,2S)-Ephedrine.* 2-Acid (±)-**4** (5.0 g, 16 mmol) and (−)-ephedrine (2.9 g, 17.5 mmol) were dissolved in AcOEt and the soln. concentrated (RE) to 80 ml. Yellow crystals were formed after 7 d at 4°. Filtration and drying gave crystalline (+)-ephedrinium salt (5.47 g) with $[\alpha]_D^{20} = +263°$ ($c = 1.08 \times 10^{-3}$; after one recrystallization from AcOEt, 4.63 g with $[\alpha]_D^{20} = +319°$ ($c = 1.14 \times 10^{-3}$)) and 2.85 g of (−)-ephedrinium salt as semi-solid from the ML with $[\alpha]_D^{20} = -501°$ ($c = 1.16 \times 10^{-3}$). The (−)-ephedrinium salt was treated with 2N H_2SO_4 and Et_2O to yield 1.7 g of optically enriched (−)-**4** with $[\alpha]_D^{20} = -804°$ ($c = 1.13 \times 10^{-3}$).

The (+)-ephedrinium salt was directly converted into (+)-**2** (see *2.9*).

2.9. *Optically Pure (−)-(P)- and (+)-(M)-***2**. – 2.9.1. *From the 1-Phenylethylammonium Salts of* **4**. The (+)-salt (300 mg, 0.69 mmol; see *2.8.1*) was decomposed with 2N H_2SO_4 and the acid extracted with Et_2O. The dried Et_2O extracts were treated with CH_2N_2 and (+)-(*M*)-**2** purified with prep. TLC to yield 230 mg with $[\alpha]_D^{20} = +1193°$ ($c = 1.12 \times 10^{-3}$). Since the (+)-salt had $d = 0.88 \pm 0.02$, it can be concluded that enantiomerically pure (e = 1.00) (+)-(*M*)-**2** has $[\alpha]_D^{20} = +1350 \pm 30°$. The diester was dissolved in *t*-butyl methyl ether and kept at 4°. After some time, 20 mg of yellow crystals ($[\alpha]_D^{20} = +436°$ ($c = 1.09 \times 10^{-3}$)) were deposited; (+)-**2** from the ML showed $[\alpha]_D^{20} = +1235°$ ($c = 1.03 \times 10^{-3}$; e = 0.915).

The acid (−)-**4** from *2.8.1* was esterified with CH_2N_2 to yield (−)-(*P*)-**2** with $[\alpha]_D^{20} = -312°$ ($c = 1.42 \times 10^{-3}$). The yellow diester (2.45 g) was dissolved in Et_2O/hexane to yield 1.90 g yellow crystals with $[\alpha]_D^{20} = -71.6°$ and 0.55 g of a yellow oil with $[\alpha]_D^{20} = -999°$ ($c = 1 \times 10^{-3}$); (−)-(*P*)-**2** was further purified by prep. TLC and crystallization from *t*-butyl methyl ether. This procedure yielded 400 mg of (−)-(*P*)-**2** as a yellow oil with $[\alpha]_D^{20} = -1336°$ ($c = 1.26 \times 10^{-3}$, $p > 0.99$). The crystals (15 mg) isolated from *t*-butyl methyl ether soln. showed $[\alpha]_D^{20} = -371°$ ($c = 1.04 \times 10^{-3}$).

2.9.2. *From the Ephedrinium Salts of* **4**. The (+)-salt with $[\alpha]_D^{20} = +319°$ was decomposed with 2N H_2SO_4, and the liberated acid (+)-**4** directly transformed into the (+)-(*M*)-diester (3.5 g) with CH_2N_2. Racemic diester was removed by two crystallizations to yield (+)-(*M*)-**2** (1.12 g, 21.5%) with $[\alpha]_D^{20} = +1280°$ ($c = 1.04 \times 10^{-3}$; p = 0.96). The (−)-acid from the (−)-salt with $[\alpha]_D^{20} = -804°$ was purified *via* the (−)-**2**; 1.7 g of (−)-**4** furnished 1.66 g of (−)-**2** with $[\alpha]_D^{20} = -882°$ ($c = 1.11 \times 10^{-3}$). Removal of the racemic diester by crystallization (Et_2O/hexane) led to (−)-**2** (1.18 g, 22.6%) with $[\alpha]_D^{20} = -1324°$ ($c = 1.02 \times 10^{-3}$) and a p-value of ≥ 0.99, *i.e.* $[\alpha]_D^{20} = -1337°$ for optically pure (−)-**2**.

The selective saponification of (−)-(*P*)-**2** yielded (−)-(*P*)-**4** with $[\alpha]_D^{20} = -1245°$ ($c = 0.93 \times 10^{-3}$).

The 2-acid (−)-(*P*)-**4** gave (−)-**10** (see *2.10*) the TLC analysis of which showed the presence of $< 1\%$[31]) of *meso*-**10**, *i.e.* $e \geq 0.99$ for (−)-**4** and (−)-**2**.

*(−)-(P)-***4** *with* $[\alpha]_D^{20} = -1245°$: ORD (dioxane): 699/−2340, 417/−26360 (T), 376/0, 343/16300 (sh), 293/160520 (P), 270/17100 (T), 266/29480 (P), 256/0, 239/−50040 (T). CD (cyclohexane): 369.1/−61.32 (min), 351.9/−56.87 (max), 327.2/−60.30 (max), 280.0/124.31 (max), 260.3/80.84 (min), 251.2/86.45 (max), 222.1/−43.00 (min), 205.3/89.34 (max). CD (dioxane): 374.0/−63.70 (min), 342.9/58.04 (max), 332.0/60.00 (min), 280.6/112.16 (max), 263.7/76.39 (min), 252.1/90.05 (max), 223.4/−39.37 (min), 205.5/101.20 (max).

*(−)-(P)-***2** *with* $[\alpha]_D^{20} = -1324°$: ORD (dioxane): 699/−2380, 418/−28040 (T), 374/0, 340/16000 (sh), 293/156600 (P), 274/19140 (T), 269/22850 (P), 258/0, 239/−71820 (T). CD (cyclohexane; *cf. Fig. 2*): 550/−3.55, 369.2/−65.17 (min), 344.0/−61.64 (max), 326.7/−66.46 (min), 279.9/116.09 (max), 263.2/85.68 (min), 250.7/101.61 (max), 222.5/−34.02 (min), 205.0/88.64 (max). CD (dioxane): 550/−3.29, 372.6/−68.18 (min), 346.2/−62.98 (max), 327.8/−66.21 (min), 281.4/113.76 (max), 265.2/81.49 (min), 253.1/95.57 (max), 223.2/−41.33 (min), 205.1/110.29 (max).

2.10. *(−)-(P)-***11**. Compound (−)-(*P*)-**4** (311 mg) with $[\alpha]_D^{20} = -1245°$ was reduced with $LiALH_4$ as described for **2** (see *2.5*). The Et_2O extracts yielded 162.6 mg (50.4%) from which (−)-(*P*)-**11** was obtained as pale yellow crystals (75.3 mg) with $[\alpha]_D^{20} = -878°$ ($c = 1.19 \times 10^{-3}$). The ML yielded also (−)-(*P*)-**11** as yellow oil with $[\alpha]_D^{20} = -749°$.

*(−)-(P)-***11** *with m.p. 147–148° and* $[\alpha]_D^{20} = -878°$: CD (cyclohexane): 345/−49.60 (sh), 315/−59.83 (min), 251.1/218.23 (max), 241/201000 (sh), 224.4/94.37 (min), 216.4/124.20 (max). CD (dioxane): 349/−57.07 (min), 340.3/−56.17 (max), 314.9/−63.84 (min), 251.4/253.89 (max), 240/228.00 (sh), 224.7/92.64 (min), 216.9/122.16 (max).

2.11. *(−)-(P,3R,1′S)-***9A** *and (−)-(P,3R,1′R)-***9B**. The reaction of (−)-(*P*)-**4** (300 mg, 0.96 mmol) with $[\alpha]_D^{20} = -1245°$ with (−)-(*S*)-1-phenylethanol ($e \geq 0.99$)[32]) as described for **4** yielded after prep. TLC (−)-**9A** (98 mg,

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[31]) The sensitivity of the method was tested with (±)- and meso-**10**. Dilution technique showed that less than 0.2% of meso-**10** in (±)-**10** could safely be identified (quenching of the fluorescence indicator of the TLC plate).

[32]) We thank Dr. *B. Wipf*, Central Research Units of *F. Hoffmann-La Roche & Co., Ltd.*, Basle, for the microbial preparation of this compound.

24%) with $[\alpha]_D^{20} = -1433°$ ($c = 1.12 \times 10^{-3}$), (−)-**10** (54 mg, 18%) as yellow oil which showed the presence of less than 1% of the *meso*-**10** and an $[\alpha]_D^{20} = -1510°$ ($c = -1.28 \times 10^{-3}$), and (−)-(*P*)-**7** (37 mg, 14%) as dark red oil with $[\alpha]_D^{20} = -2565°$ ($c = 1.19 \times 10^{-3}$).

In a similar manner, the reaction of (−)-(*P*)-**4** (303 mg, 0.97 mmol) with (+)-(*R*)-1-phenylethanol (e = 0.94, *Selectchemie AG*, Zurich) led to (−)-**9B** (98 mg, 24%) as a yellow oil with $[\alpha]_D^{20} = -1320°$ ($c = 1.01 \times 10^{-3}$), (−)-**10** (55 mg, 19%) as yellow oil which contained less than 1% of *meso*-**10** and showed $[\alpha]_D^{20} = -1162°$ ($c = 1.23 \times 10^{-3}$), and (−)-(*P*)-**7** (11 mg, 4%) as dark red oil with $[\alpha]_D^{20} = -2817°$ ($c = 1.00 \times 10^{-3}$).

*(−)-(*P,3R,1'S*)*-**9A**: ORD (dioxane): 699/−2945, 467/−23030 (T), 420/0, 366/36570 (P), 351/34050 (T), 301/129250 (P), 289/0 280/−63070 (T), 270/0, 258/82040 (P), 249/0, 238/−135620 (T). CD (dioxane): 420.8/−64.73 (min), 353.7/−29.53 (max), 328.0/−39.20 (min), 288.7/106.84 (max), 267.7/−2.63 (min), 242.4/201.65 (max), 225.6/98.99 (min), 212.8/178.38 (max). CD (EPA, −180°): 415.8/−82.73 (min), 350.5/−21.93 (max), 326.4/−49.84 (min), 287.2/153.75 (max), 264.8/−10.85 (min), 244.1/237.43 (max), 241.9/236.46 (sh), 225.2/91.03 (min), 211.2/292.20 (max).

*(−)-(*P,3R,1'R*)*-**9B**: ORD (dioxane): 699/−2658, 467/−21960 (T), 424/0, 362/37700 (P), 353/36630 (T), 303/121200 (P), 282/0 (T), 258/133230 (P), 246/0, 236/−84390 (T). CD (dioxane): 416.9/−58.26 (min), 354.8/−24.31 (max), 332.6/−31.40 (min), 288.7/100.09 (max), 268.6/4.90 (min), 242.9/208.29 (max), 224.0/85.41 (min), 213.5/108.93 (max). CD (cyclohexane): 409.0/−57.91 (min), 353.3/−27.69 (max), 330.8/−36.93 (min), 287.3/99.50 (max), 267.5/21.77 (min), 241.4/235.00 (max), 221.6/84.86 (min), 212.3/103.38 (max).

*(−)-(*P*)*-**7**: CD (cyclohexane)[33]: 428/−32.28 (min), 395/−29.53 (max), 358/−38.94 (min), 305.1/33.92 (max), 299.2/25.05 (min), 260.1/69.01 (max), 224.8/35.36 (min), 210.3/62.98 (max).

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