Benzo[*a*]heptalenes from Heptaleno[1,2-*c*]furans

Part I

Cycloaddition Reaction of Heptaleno[1,2-*c*]furans with Different Dienophiles

by **Peter Uebelhart**, **Christophe Weymuth**, and **Hans-Jürgen Hansen***

Organisch-chemisches Institut der Universität, Winterthurerstrasse 190, CH-8057 Zürich

Dedicated with great respect to Professor *Rolf Huisgen* on the occasion of his 85th birthday

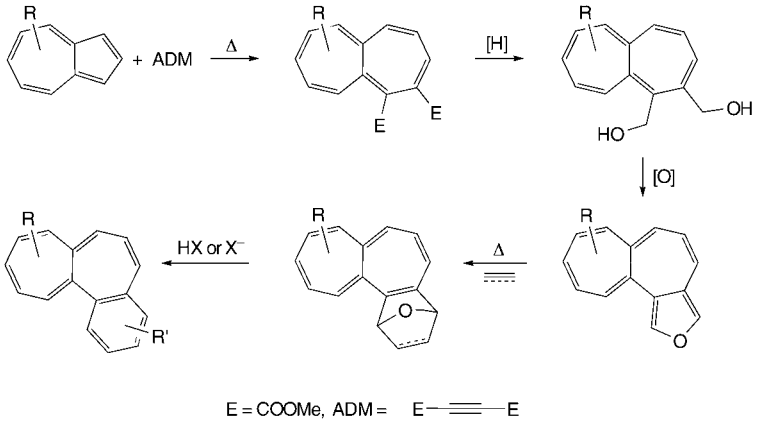
It is shown that heptaleno[1,2-*c*]furans **1**, which are available in two steps from heptalene-4,5-dicarboxylates by reduction and oxidative dehydrogenation of the corresponding vicinal dimethanols **2** with MnO_2 or IBX (*Scheme 4*), react thermally in a *Diels–Alder*-type [4 + 2] cycloaddition at the furan ring with a number of electron-deficient dipolarophiles to yield the corresponding 1,4-epoxybenzo[*d*]heptalenes (*cf. Schemes 6, 15, 17,* and *19*). The thermal reaction between dimethyl acetylenedicarboxylate (ADM) and **1** leads, kinetically controlled, *via* a sterically less-congested transition state (*Fig. 4*) to the formation of the (*M**)-configured 1,4-dihydro-1,4-epoxybenzo[*a*]heptalenes, which undergo a cyclic double-bond shift to the energetically more-relaxed benzo[*d*]heptalenes **4** (*Schemes 6* and *7*). Most of the latter ones exhibit under thermal conditions epimerization at the axis of chirality, so that the (*M**)- and (*P**)-stereoisomers are found in reaction mixtures. The (*P**)-configured forms of **4** are favored in thermal equilibration experiments, in agreement with AM1 calculations (*Table 1*). The relative (*P**,1*S**,4*R**)- and (*M**,1*S**,4*R**)-configuration of the crystalline main stereoisomers of the benzo[*d*]heptalene-2,3-dicarboxylates **4a** and **4f**, respectively, was unequivocally established by an X-ray crystal-structure determination (*Figs. 1* and *2*). Acid-induced rearrangement of **4** led to the formation of the corresponding 4-hydroxybenzo[*a*]heptalene-2,3-dicarboxylates **5** in moderate-to-good yields (*Schemes 8*, *13*, and *14*). When the aromatization reaction is performed in the presence of trifluoroacetic acid (TFA), trifluoroacetates of type **6** and **13** (*Schemes 8, 12,* and *13*) are also formed *via* deprotonation of the intermediate tropylium ions of type **7** (*Scheme 11*). Thermal reaction of **1** with dimethyl maleate gave the 2,3-*exo*- and 2,3-*endo*-configured dicarboxylates **14** as mixtures of their (*P**)- and (*M**)-epimers (*Scheme 15*). Treatment of these forms with lithium di(isopropyl)amide (LDA) at $-70°$ gave the expected benzo[*a*]heptalene-2,3-dicarboxylates **15** in good yields (*Scheme 16*). Fumaronitrile reacted thermally also with **1** to the corresponding 2-*exo*,3-*endo*- and 2-*endo*,3-*exo*-configured adducts **17**, again as mixtures of their (*P**)- and (*M**)-epimers (*Scheme 17*), which smoothly rearranged on heating in dimethoxyethane (DME) in the presence of Cs_2CO_3 to the benzo[*a*]heptalene-2,3-dicarbonitriles **18** (*Scheme 18*). Some cursory experiments demonstrated that hex-3-yne-2,5-dione and (*E*)/(*Z*)-hexa-3-ene-2,5-dione undergo also the *Diels–Alder*-type cycloaddition reaction with **1** (*Scheme 19*). The mixtures of the stereoisomers of the 2,3-diacetyl-1,4-epoxytetrahydrobenzo[*d*]heptalenes **22** gave, on treatment with Cs_2CO_3 in DME at 80°, only mixtures of the regioisomeric inner aldol products **24** and **25** of the intermediately formed benzo[*a*]heptalenes **23** (*Scheme 20*).

1. Introduction. – From the very beginning of the discovery and exploration of [4 + 2] cycloaddition reactions by *Diels* and *Alder* at the end of the twenties of the last century until today, furan and its derivatives have been proved as excellent enophiles reacting inter- as well as intramolecularly with almost all types of dienophiles (*cf.* [1] and literature cited there; for latest results, see [2][3]). The thus formed 7-oxabicyclo[2.2.1]heptenes or -heptadienes can be easily transformed on acid or base catalysis into cyclohexa-1,3-dienes or their corresponding benzene structures under

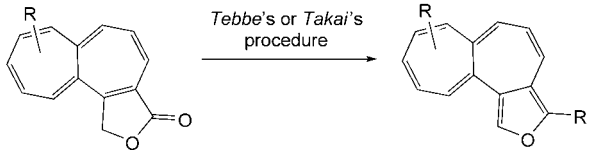
preservation or loss of the O-atom originating from the applied furan derivative. Chiral auxiliaries at the dienophiles induce high diastereoselectivities at the *endo*- and/or *exo*-7-oxabicycles, formed purely thermally or under acid catalysis at low temperature, so that *Diels–Alder* reactions with furans are often the key step in the synthesis of natural products (*cf.* [1][3]).

In view of the development of a new and variable synthetic entrance into the field of colchicinoids [4], we were interested in what way heptaleno[1,2-*c*]furans, which are easily accessible from heptalene-1,2- or -4,5-dicarboxylates by reduction and subsequent oxidative dehydrogenation [5][6], can be applied as enophiles in *Diels–Alder* reactions leading to 1,4-epoxybenzo[*a*]heptalenes. Provided that the following acid- or base-catalyzed aromatization takes place, a general five-step synthesis of benzo[*a*]-heptalenes starting with azulenes and dimethyl acetylenedicarboxylate (ADM) can be envisaged (*Scheme 1*). The *Diels–Alder* reaction of heptaleno[1,2-*c*]furans and symmetrically substituted alkenes or alkynes would give rise to the formation of benzo[*a*]heptalenes with substituents at C(2) and C(3), which may bear, in dependence of the applied reaction conditions in the aromatization step, an additional OH group (R′) at C(1) or C(4). Moreover, additional substituents at C(1) and/or C(4) of the formed benzo[*a*]heptalenes can principally be introduced at the stage of the corresponding heptaleno[1,2-*c*]furans, which are available, for example, from corresponding heptaleno[1,2-*c*]furanones according to *Tebbe*'s or *Takai*'s alkylidenation protocol (*Scheme 2*) [5][7].

Scheme 1

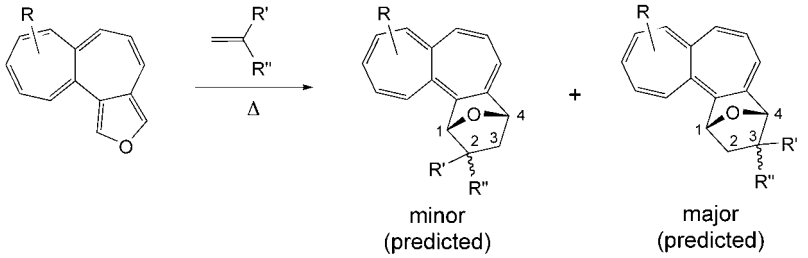


Scheme 2



In the case of mono- or 1,1-disubstituted alkenes as dienophiles, the formation of regioisomeric adducts has to be taken into account. Nevertheless, nucleophilic addition reactions to heptalene-4,5-dicarboxylates (see, *e.g.*, [8][9]), which all take place at the sterically less-hindered C=O group at C(4), support the assumption that the regioisomers with the alkene substituents at C(3) should prevail in the product mixtures (*Scheme 3*). The product composition of the cycloaddition step with alkenes may gain in complexity by formation of *exo*- and *endo*-isomers of the cycloadducts, as well as their double-bond-shifted (DBS) isomers. However, this complexity should not influence the yield of benzo[*a*]heptalene formation as long as both diastereoisomers and their DBS forms undergo the aromatization step equally well.

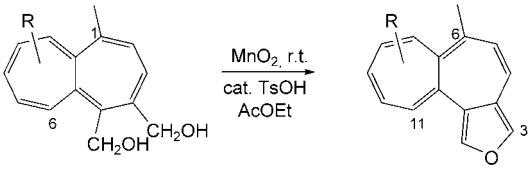
Scheme 3. *Formation of Regioisomers upon Cycloaddition of Dienophiles to Heptaleno[1,2-c]furans.* AM1 Calculations indicate that the structures displayed are more stable than their double-bond shifted (DBS) forms.



In the following, we will report on the general structural and mechanistic aspects of [4+2] cycloaddition reactions with heptaleno[1,2-*c*]furans, and the catalyzed rearrangements of their corresponding cycloadducts.

2. *Diels–Alder* Reactions with Heptaleno[1,2-*c*]furans. – 2.1. *Synthesis of Heptaleno[1,2-c]furans.* The heptaleno[1,2-*c*]furans **1a–d** were prepared by oxidative dehydrogenation of the corresponding heptalene-4,5-dimethanols **2a–d** with activated MnO_2 in CH_2Cl_2 at r.t. (*Scheme 4*). In variation of our earlier described procedure [5], we performed the reaction in the presence of catalytic amounts of 4-methylbenzenesulfonic acid (TsOH), whereby the yields of **1** were distinctly improved at the expense of the accompanying over-oxidized furanones **3**.

Scheme 4

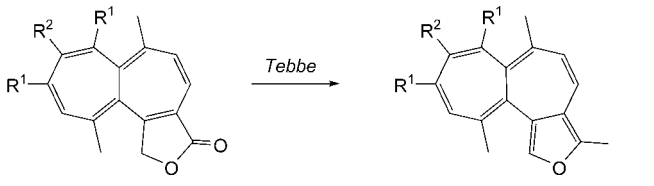


2a R = 9-^{i}Pr, 6-Me	**1a** R = 8-^{i}Pr, 11-Me (54% (94%[a]))	**3a** R = 8-^{i}Pr, 11-Me (<10%)
2b R = 6,8,10-Me_3	**1b** R = 7,9,11-Me_3 (53%)	**3b** R = 7,9,11-Me_3 (27%)
2c R = 8-^{i}Pr	**1c** R = 9-^{i}Pr (47%)	**3c** R = 9-^{i}Pr (n.d.[b]))
2d R = 8-^{t}Bu	**1d** R = 9-^{t}Bu (82%)	**3d** R = 9-^{t}Bu (n.d.)

[a]) Yield with IBX as oxidizing agent. [b]) Not determined, but present according to TLC.

The application of 1-hydroxy-1,2-benziodoxol-3(1*H*)-one 1-oxide (IBX) [10] as oxidizing agent in DMSO/acetone at r.t. [6] gave higher and better-reproducible yields of the heptalenofurans, since no heptalenofuranones at all are formed under these conditions. However, the handling of IBX seems not to be without problems (see literature cited in [10]), and for the preparation of larger amounts of **1**, MnO_2 is the much cheaper oxidant, which, in addition, can easier be removed from the reaction mixtures by simple filtration. Moreover, we were also interested in the furanones **3** as by-products, since two of them (**3a** and **3b**) have been transformed with *Tebbe*'s reagent into the corresponding new 3-substituted heptaleno[1,2-*c*]furans **1e** and **1f** (*Scheme 5*).

Scheme 5



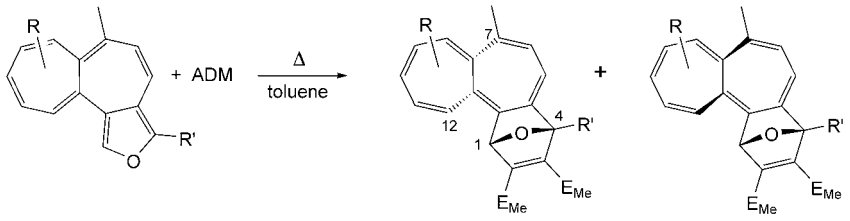
[a]) Equilibrium mixture of the DBS isomers [5]. [b]) Second values taken from [5]. [c]) Yield with respect to reacted **3b**, of which 17% were recovered because the reaction had been performed with an old sample of the *Tebbe* reagent.

2.2. *Adducts with Dimethyl Acetylenedicarboxylate* (ADM), *and Their Rearrangements.* The cycloaddition between the heptalenofurans **1** and ADM in toluene occurred smoothly at 80–130° (*Scheme 6*). The 1,4-dihydro-1,4-epoxybenzo[*d*]heptalene-2,3-dicarboxylates **4** were obtained as mixtures of epimeric (*P**)- and (*M**)-forms. We found no indication for the presence of the obligatorily built primary cycloadducts **4′**, the DBS isomers of **4**, in detectable amounts. This finding is in accordance with the results of AM1 calculations, which showed the ΔH_f° values of the observed products **4** to be 7–10 kcal/mol lower than those of **4′** (*Scheme 7*).

The spectroscopic structure determination of compounds **4** was unambiguous (see *Exper. Part*). On the other hand, the relative configuration of the epimers could not be derived unequivocally from their spectra, in particular their ^{1}H-NMR spectra. Therefore, we performed an X-ray crystal-structure analysis of **4a** and **4f**, which established the relative (*P**)-configuration for **4a** and the relative (*M**)-configuration for **4f** (*Figs. 1* and *2*, resp.). The other (*P**)- and (*M**)-configured products **4** could then be correlated by their ^{1}H-NMR and UV/VIS spectra (*Fig. 3*), as well as by thermal epimerization experiments in connection with AM1 calculations (*Table 1*). The latter showed that the (*P**)-epimers of **4**, where the epoxy bridge and C(12)–Me (**4a**, **4b**, **4e**, and **4f**) and C(12)–H (**4d**) are on opposite sides of the heptalene ring system, have slightly lower ΔH_f° values as compared with their (*M**)-pendants (see *Table 1*).

The thermal epimerization experiments performed with the pure forms of (*P**)-**4a** and -**4e**, and of (*M**)-**4b** and -**4f**, were in agreement with the calculated values, whereby the thermal equilibrium of the tetra- and pentamethyl substituted compounds **4b** and **4e**, respectively, with the much higher '*peri*'-hindrance for epimerization in comparison

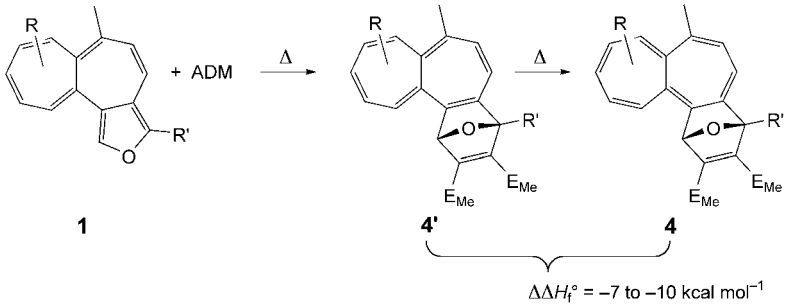
Scheme 6



1a[a])	80°, 70 h (87%)	(*P**)-**4a**[b]) (50%)	(*M**)-**4a** (37%)
1b	80°, 20 h (90%)	(*P**)-**4b** (14%)	(*M**)-**4b** (77%)
1d	100°, 0.8 h (>50%)	(*P**)-**4d** (50%)	(*M**)-**4d** (n.d.)
1e	120°, 3 h[c]) (91%)	(*P**)-**4e** (55%)	(*M**)-**4e** (36%)
1f	80°, 4 h (>65%)	(*P**)-**4f** (n.d.)	(*M**)-**4f**[d]) (65%)

[a]) See *Schemes 4* and *5* for substituents and their locations. [b]) (*P**,1*S**,4*R**)-Configuration (see *Fig. 1*). It means that the epoxy-O-atom and C(12)–R are on the opposite sides of the molecule. This rel. configuration will be applied in all the following *Schemes* and *Tables*. [c]) Plus an additional 3 h at 130°. [d]) (*M**,1*S**,4*R**)-Configuration (see *Fig. 2*). It means that the epoxy-O-atom and C(12)–R are on the same side of the molecule. This rel. configuration will be applied in all the following *Schemes* and *Tables.*

Scheme 7



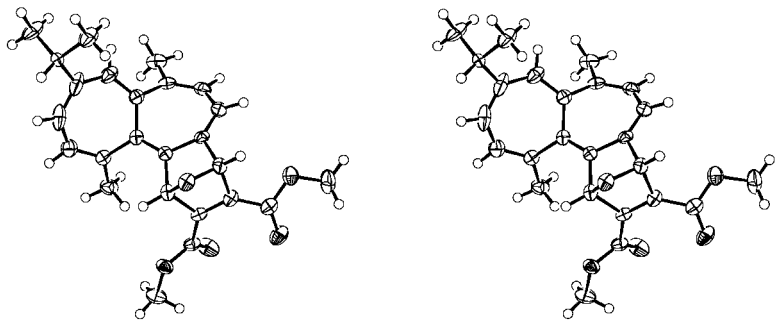


Fig. 1. *Stereoscopic view of the X-ray crystal structure of* (P*)-**4a** (only one of the two 10-(i-Pr) conformers found is shown)

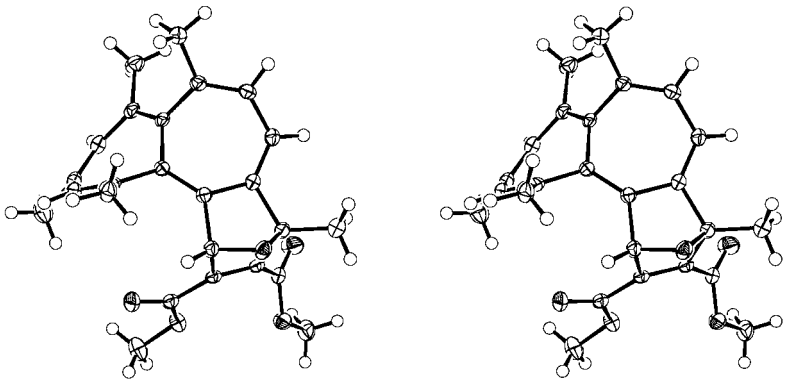


Fig. 2. *Stereoscopic view of the X-ray crystal structure of (*M**)-***4f***

with **4a** and **4e**, could not be attained due to massive side-product formation. Nevertheless, the (*P**)- and (*M**)-series of **4** could also be characterized by their UV/VIS spectra, which showed for all epimers distinct differences in the wavelength region above 300 nm (*Fig. 3*).

The product analysis (*Scheme 6*) and the epimerization experiments (*Table 1*) lead to the conclusion that the (*M**)-isomers of **4**, which emerge from the primarily formed (*M**)-isomers **4′** with retention of configuration by the DBS process [11], are the *kinetically* controlled products, whereas the (*P**)-isomers **4** and their progenitors **4′** represent the *thermodynamically* controlled products. The almost exclusive formation

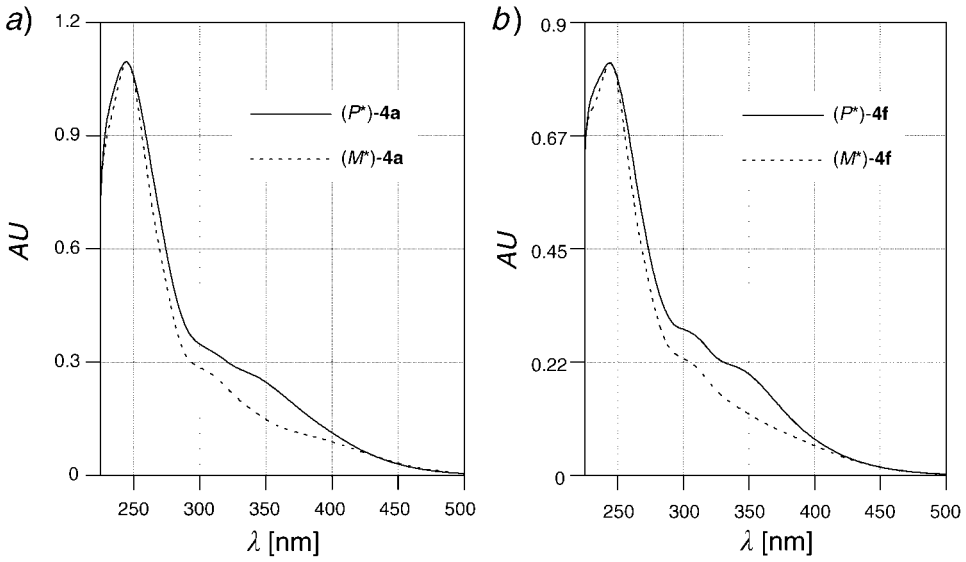


Fig. 3. *HPLC–UV/VIS Spectra of* a) (P*)*- and (*M*)-**4a**, *and* b) (P*)*- and (*M*)-**4f**. Solvent: hexane/(CH_2Cl_2 + 0.5% MeOH) 4 : 1.

Table 1. *AM1 Calculated Heat of Formation* (ΔH_f°) *of Epimers of Compound* **4**

Epimer	ΔH_f° [kcal/mol]	(*P**)/(*M**)	
		calculated[a])	observed[b])
(*P**)-**4a**	– 72.79	0.62	56 (100°/2 h)
(*M**)-**4a**	– 72.41	0.38	44
(*P**)-**4b**	– 68.34	0.59	[c])
(*M**)-**4b**	– 68.05	0.41	
(*P**)-**4d**	– 67.16	0.60	[d])
(*M**)-**4d**	– 66.83	0.40	
(*P**)-**4e**	– 76.22	0.68	58 (120°/2 h)
(*M**)-**4e**	– 75.62	0.32	42
(*P**)-**4f**	– 71.79	0.67	[e])
(*M**)-**4f**	– 71.25	0.33	

[a]) Calculated for the applied epimerization or reaction temperature on supposition that $\Delta H_f^\circ \approx \Delta G_f^\circ$. [b]) Values of separate epimerization experiments in toluene; in parentheses, temperature/time for the establishment of the equilibrium. [c]) Heating of pure (*M**)-**4b** at 100°/20 h gave $\leq$6% of (*P**)-**4b**; supplementary heating at 120°/23 h led to an (*M**)/(*P**) ratio of 65 : 35, still far away from equilibrium. Massive by-product formation impeded an establishment of the equilibrium. [d]) Epimerization experiments were not performed due to the low stability of (*P**)-**4d**. Nevertheless, (*P**)-**4d** was the main epimer in the original reaction mixture (*Scheme 6*). [e]) Heating of pure (*M**)-**4f** at 100°/20 h gave $\leq$6% of (*P**)-**4f**; supplementary heating at 120°/23 h led to an (*M**)/(*P**) ratio of 67 : 33, still far away from equilibrium. As in the case of (*M**)-**4b**, massive by-product formation impeded an establishment of the equilibrium.

of the (*M**)-epimers in the case of **4b** and **4f** speaks for a predominant [4 + 2] approach of ADM on the sterically less-hindered (*M**,1*re*,3*si*)-face of the heptaleno[1,2-*c*]furans **1**, which results in the formation of (*M**)-**4′**, followed by rapid isomerization to (*M**)-**4** (*Fig. 4*)[1]).

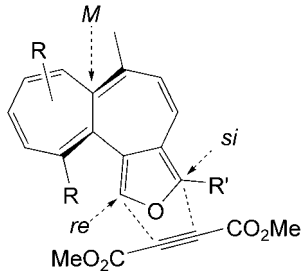
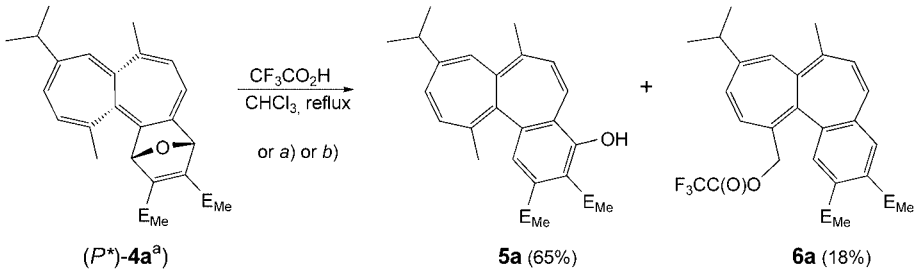


Fig. 4. *Favored approach of dimethyl acetylene-1,2-dicarboxylate in the [4 + 2] cycloaddition with the heptaleno[1,2-*c*]furans* **1**

Treatment of (*P**)-**4a** (or mixtures of (*P**)- and (*M**)-**4a**) in boiling $CHCl_3$ with 3 – 5 mol-equiv. of trifluoroacetic acid (TFA) induced a complete rearrangement. Two orange colored products, **5a** and **6a**, with **5a** as the main part, were isolated in 83% yield (*Scheme 8*). Compound **5a** crystallized from a hexane solution of the mixture in orange crystals. The TFA ester **6a** was isolated as an orange colored oil by HPLC separation of

[1]) DBS Processes in heptalenes occur more easily than the corresponding double-ring inversion processes, which lead to racemization or epimerization [11 – 13].

Scheme 8



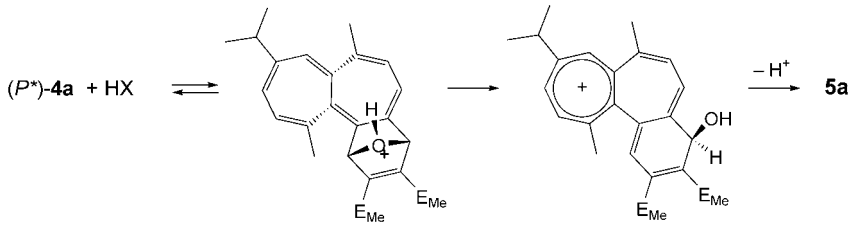
(*P**)-**4a**[a]) **5a** (65%) **6a** (18%)

a) MeOH, conc. HCl, 80°; 75% of **5a**[b]). *b*) Cyclohexane, *Amberlyst 15*, 80°; 64 % of **5a**[c]).
[a]) Or mixtures of (*P**)- and (*M**)-**4a**; for details see *Exper. Part.* [b]) Crude material; pure crystalline **5a**: 53%.
[c]) Crude material; pure crystalline **5a**: 48 %.

the residue of the mother liquor. The structures of both compounds were unequivocally established by their spectroscopic data (see *Exper. Part*). Typical for the benzo[*a*]-heptalenol **5a** is the sharp *singlet* at δ(H) 11.45 ppm for HO–C(4) in its ^{1}H-NMR spectrum ($CDCl_3$), indicating the involvement in an intramolecular H-bridge in a salicylic ester type substructure. Moreover, the UV/VIS spectrum of **5a** in EtOH, with the longest-wavelength heptalene band appearing as a shoulder at *ca.* 390 nm, changed dramatically when a base (MeONa) was added. The heptalene band appeared now as a broad, clear-defined maximum of fourfold intensity at 392 nm. The 4-position of the OH group was verified by ^{1}H-NOE experiments. The presence of a CF_3COO group in **6a** was evident from a strong IR absorption ($CHCl_3$) at 1782 cm^{-1}, characteristic for $\nu_{C=O}$ of trifluoroacetates, and distinctly separated from $\nu_{C=O}$ at 1727 cm^{-1}, attributable to the COOMe groups at C(2,3).

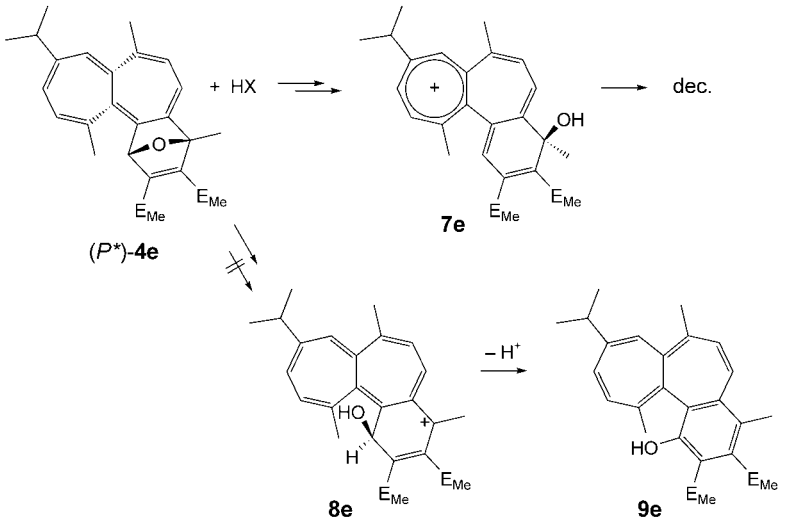
The formation of **5a** could be expected according to the formation of the intermediate cation **7a** (*Scheme 9*). However, the presence of the trifluoroacetate **6a** in the reaction mixture was surprising, since the rearrangement of *endo*-**4a**, induced by other H^+ sources, led only to **5a** in good yields (*Scheme 8*). The positive charge generated by cleavage of the epoxy bridge of protonated **4a** is well stabilized by the tropylium-like character of **7a**. The importance of this stabilization for the rearrangement of **4a** is also evident from the observation that the 4-Me substituted analogue **4e** of **4a** decomposed completely in the presence of *Amberlyst 15* as catalyst, and no indication for the formation of **8e** or **9** was found (*Scheme 10*). On the other hand,

Scheme 9



7a

Scheme 10

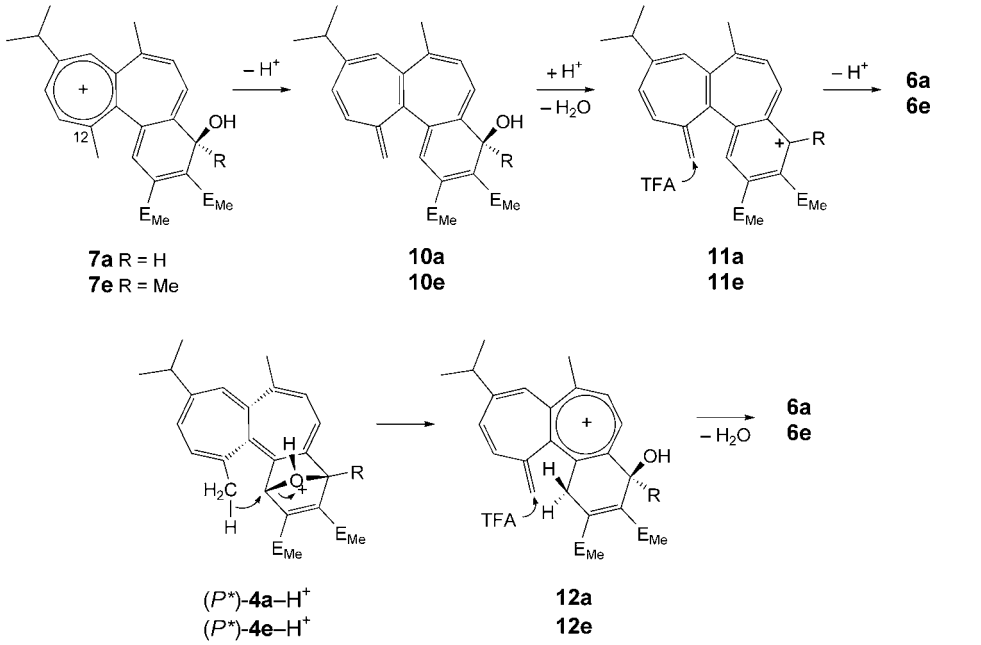


rearrangement of *endo*-**4e** with TFA resulted in the formation of the trifluoroacetate **6e** as analogue of **6a** in poor yield.

The above-mentioned observations indicate that cations of type **7a** or **7e** are, indeed, the decisive intermediates that must also be responsible for the formation of the trifluoroacetates **6a** and **6e**, respectively (*Scheme 11*). It seems that cation **7a** cannot be deprotonated solely at C(4) (→ **5a**), but also at Me–C(12), which results in the formation of the anellated heptafulvene **10a**. Acid-catalyzed removal of H_2O will then lead to cation **11a**, which finally should pick up TFA at CH_2=C(12), leading, after loss of H^+, to **6a**. This view is strongly supported by the sole formation of trifluoroacetate **6e** from **4e**, where only the last reaction channel is open. Nevertheless, the (*P**)-configured structures **4a** and **4e** offer another attractive pathway for the formation of the corresponding trifluoroacetates. The Me group at C(12) is perfectly disposed beneath C(1), with an interatomic distance of C(12)–CH_2H ··· C(1) of *ca.* 256 pm (according to MM2 calculations of protonated (*P**)-**4a** or -**4e**). In other words, a concerted hydride shift leading to the tropylium stabilized cations **12a** or **12e** might be possible, which then take up TFA and split off H_2O.

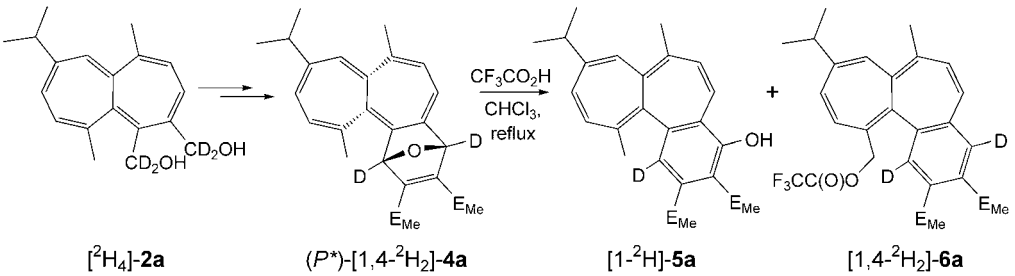
For the proof or disproof of the above hypotheses, we synthesized, [1,4-$^2H_2$]-**4a**, starting from fourfold deuterated **1a** (*Scheme 12*). The result of the rearrangement of the pure (*P**)-form of [1,4-$^2H_2$]-**4a** in TFA was clear. The formed trifluoroacetate [1,4-$^2H_2$]-**6a** showed no loss of deuterium at C(1). In case of formation of cation **12a** by a concerted hydride shift from Me–C(12), one would expect a certain loss of deuterium at C(1) of [1,4-$^2H_2$]-**6a** in the deprotonation step of the deuterated analogue of **12a**, taking into account that k_H/k_D may be >1, as has been observed in electrophilic aromatic substitutions of sterically encumbered substrates [14]. In other words, there is good evidence that cations of type **7** are also responsible for the formation of the trifluoroacetates of type **6** (see *Scheme 11*). Any further doubts were completely

Scheme 11



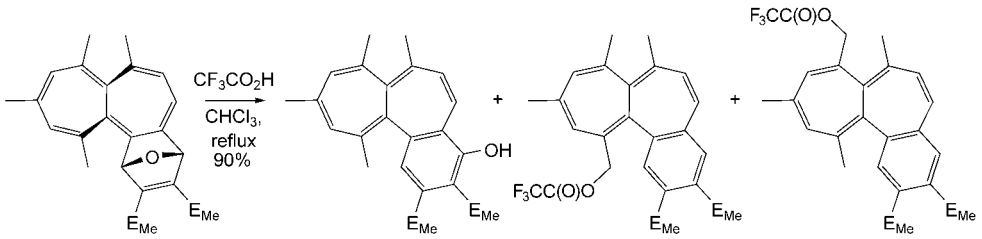
removed by the rearrangement of (*M**)-**4b** with TFA in boiling $CHCl_3$. No distinct epimerization to (*P**)-**4b** does occur in boiling $CHCl_3$ according to our epimerization experiments, so that a concerted hydride shift in protonated (*M**)-**4b** can be excluded. The formation of **6b** was yet observed, accompanied by the expected benzo[*a*]heptalen-4-ol **5b**, and, more strikingly, by a second trifluoroacetate, namely **13b** (*Scheme 13*).

Scheme 12



The separation of **5b**/**6b**/**13b** was difficult, since these compounds exhibit similar chromatographic behavior. Change of the stationary phase and the eluting solvent mixture on two different HPLC columns finally allowed their separation (see *Exper. Part*). The occurrence of **13b** in the reaction mixture is only compatible with its formation *via* cation **7b** as an analogue of **7a** and **7e**, respectively (*Scheme 12*), which can be deprotonated at Me–C(8), leading to **13b** *via* the corresponding anellated

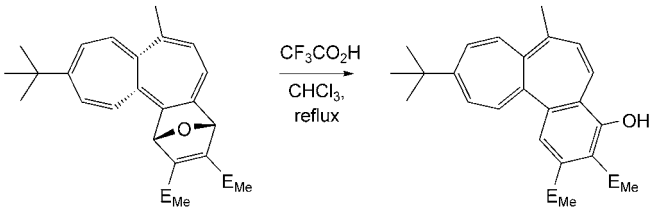
Scheme 13



heptafulvene, or at Me–C(12), resulting finally in **6b**. In principle, deprotonation of **7b** could also occur at Me–C(10). However, we found no indication for the presence of the corresponding 10-[(trifluoroacetoxy)methyl]benzo[*a*]heptalene-2,3-dicarboxylate in amounts $>3\%$ in the reaction mixture[2]).

Whereas the rearrangement of (*M**)-**4b** in cyclohexane in the presence of *Amberlyst 15* failed, the *t*-Bu substituted 1,4-epoxide **4d** gave, with TFA in boiling $CHCl_3$, the expected benzo[*a*]heptalen-4-ol **5d** in poor yield only, but 73% with respect to recovered starting material (*Scheme 14*).

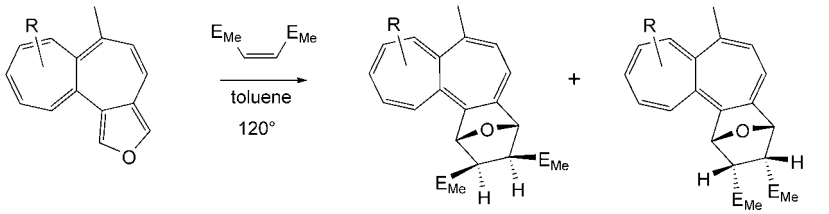
Scheme 14



2.3. *Adducts with Dimethyl Maleate* (DM), *and Their Rearrangement.* Heating of the heptaleno[1,2-*c*]furans **1a–c** with an excess of DM (3–30 mol-equiv.) in toluene at 120° led to the formation of the corresponding *cis*-configured 1,4-epoxy-1,2,3,4-tetrahydrobenzo[*d*]heptalene-2,3-dicarboxylates **14** (*Scheme 15*). The main part of the products represented the 2,3-*exo*-adducts, easily recognizable by the absence of measurable ^3J coupling constants between H–C(1)/H–C(2) and H–C(3)/H–C(4), in agreement with the *endo*-position of H–C(2) and H–C(3) [15], and, in turn, with the *exo*-position of the COOMe group at these C-atoms. As a result, the ^{1}H-NMR signals of H–C(1) and H–C(4) appeared as slightly broadened *singlets*, and those of H–C(2) and H–C(3) displayed a clear *AB* pattern, with $^3J_{AB} = 9.5$ Hz, indicating *cis*-relation of

[2]) This finding is in accordance with AM1 calculations of the epimers of the 8-, 10-, and 12-methylidenedihydrobenzo[*a*]heptalene-4-ols, which showed the 8- and 12-methylidene forms to be by 2.4–3.3 kcal/mol lower in ΔH_f° than the 10-methylidene structure.

Scheme 15



1a[a])	23 h (77%)	2,3-*exo*-**14a** (59%)[b])	2,3-*endo*-**14a** (18%)[c])
1b	72 h (93%)	2,3-*exo*-**14b** (93%)[d])	2,3-*endo*-**14b** (<5%)[e])
1c	48 h (59%)	2,3-*exo*-**14c** (50%)[f])	2,3-*endo*-**14c** (8.5%)[f])

[a]) See *Schemes 4* and *5* for substituents and their locations. [b]) Crystallization gave 2,3-*exo*-(*P**)-**14a** as pure epimer. At 120°, an equilibrium mixture of 75% 2,3-*exo*-(*P**)-**14a** and 25 % 2,3-*exo*-(*M**)-**14a** is established (see text). [c]) Mixture of 2,3-*endo*-(*P**)- and 2,3-*endo*-(*M**)-**14a** in a ratio of 3:1. [d]) The crystalline material represented a 43:57 mixture of 2,3-*exo*-(*P**)- and 2,3-*exo*-(*M**)-**14b**. The equilibrium mixture at 120° consisted of 65% 2,3-*exo*-(*P**)- and 35% 2,3-*exo*-(*M**)-**14b** (see text). [e]) Trace amounts. [f]) Pure epimers of 2,3-*exo*- and 2,3-*endo*-**14c**, resp.; presumably both (*P**)-configured. Yields are given with respect to reacted **1c**.

these two H-atoms. In contrast to these findings, the 2,3-*endo*-adducts, such as 2,3-*endo*-**14a**, showed *doublets* for the signals of H–C(1) and H–C(4), with $^3J(1,2)$ and $^3J(3,4)$ being in the range of 4.5–5.0 Hz, and for those of H–C(2) and H–C(3) double *doublets* with $^3J(2,3) = 11$ Hz were observed.

We found no indication for a thermal interconversion of 2,3-*exo*- and 2,3-*endo*-**14a**, which speaks for a kinetically controlled formation of these isomers. Indeed, heating of **14a** or **14b** in toluene (1% solution) at 120° did not lead to a retro-*Diels–Alder* reaction. However, thermal equilibration between the two epimers with respect to the axis of chirality at the heptalene core was observed (see footnotes in *Scheme 16* below). The relative (*P**)- and (*M**)-configuration of the 2,3-*exo*-epimers could easily be distinguished due to a distinct ^{1}H-NOE between Me–C(12) and H_{endo}–C(2), which is only possible in the (*P**)-configuration, where the interatomic distance between H_{endo}–C(2) and the closest H-atom of Me–C(12) amounts to 237–238 pm according to AM1 calculations.

The assignment of the relative configuration of 2,3-*exo*- and 2,3-*endo*-**14c** at the axis of chirality (see footnotes in *Scheme 15*) are based on a comparison of the ^{1}H-NMR chemical shifts (see *Exper. Part*) of H–C(2) and H–C(3), as well as Me–C(7), with those of 2,3-*exo*-(*P**)- and 2,3-*endo*-(*P**)-**14a**.

A clear indication of the relative configuration at the axis of chirality is also given by distinct differences in the UV/VIS spectra of the epimers of 2,3-*exo*-**14a** and -**14b**. The spectrum of 2,3-*exo*-(*P**)-**14a** (*Fig. 5*, *a*) as well as that of 2,3-*endo*-(*P**)-**14a** (*Fig. 5*, *b*) exhibits, in the wavelength region above 300 nm, a broad well-formed maximum at 338–339 nm. In contrast to this, their (*M**)-counterparts show an extended flat maximum at 329–335 nm (*Fig. 5*). The corresponding maximum of 2,3-*exo*-(*P**)-**14b** is shifted to shorter wavelengths (319 nm; see *Exper. Part*), and 2,3-*exo*-(*M**)-**14b** shows only an extended shoulder at 311 nm.

These findings are in agreement with AM1 calculations of the sets of epimers, which indicate that the (*P**)-forms possess the smaller *cisoid* torsion angles at the axis of chirality compared with their corresponding (*M**)-configured forms, independently of

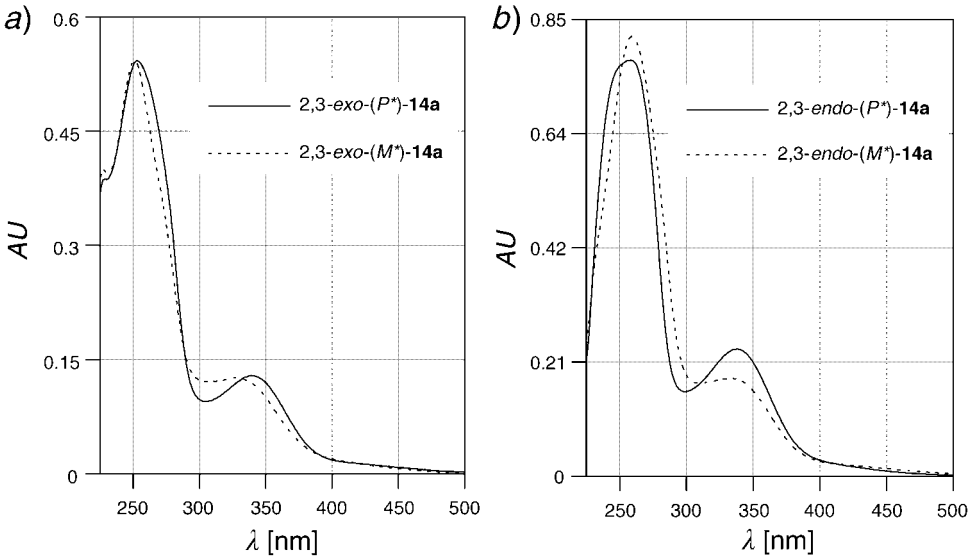


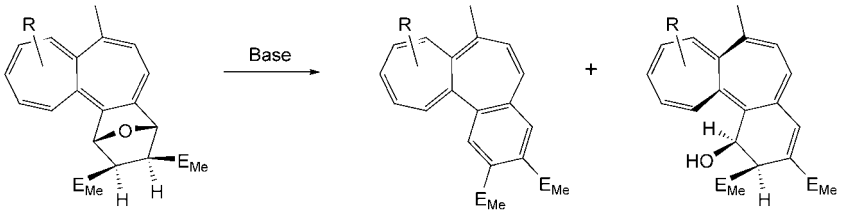
Fig. 5. *HPLC–UV/VIS Spectra of* a) *2,3*-exo-(P*)- *and* (M*)-**14a**, *and* b) *2,3*-endo-(P*)- *and* (M*)-**14a**. Solvent: hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1.

the 2,3-*exo*- or 2,3-*endo*-configuration. Moreover, compounds **14a**, with only three occupied *peri*-positions, show smaller torsion angles at the axis of chirality than compounds **14b**, with all four *peri*-positions occupied. We had reported earlier that the position of the long-wavelength heptalene absorption band is dependent on the degree of twisting of the heptalene skeleton in such a way that the specific heptalene conjugation is reduced in highly twisted heptalenes and, thus, the heptalene absorption bands are hypsochromically displaced (see, *e.g.*, [5][16] and below).

The assignments of the relative configuration of the 1,4-epoxy products **14** lead to the conclusion that, for steric reasons, the *exo*-arrangement of DM in the [4+2] transition state, with the carboxylate substituents pointing away from the heptalene skeleton, is strongly favored. We also assume, in analogy to the ADM addition experiments, that DM uptake occurs for the (*M**)-configured heptaleno[1,2-*c*]furans on the (1*re*,4*si*)-side of the furan part (*cf. Fig. 4*). However, the higher reaction temperature (120°, toluene) effects, in all cases investigated, rapid (*M**/*P**)-epimerizations at the axis of chirality, so that both epimers are found in the original product mixtures.

The aromatization of 2,3-*exo*-(*P**)-**14a** with lithium diisopropylamide (LDA) in THF/hexane at −70° took place smoothly and furnished the corresponding benzo[*a*]-heptalene-2,3-dicarboxylate **15a** in 90% yield (*Scheme 16*). Treatment of the mixture of epimers of 2,3-*exo*-**14b** (*cf. Scheme 15*) under the same conditions gave two products: the expected **15b** and a more-polar compound, which we assumed – on the basis of the ease of its acid-catalyzed transformation into **15b** (5N HCl/CH_2Cl_2, r.t.), and according to its characteristic ^{1}H-NMR and UV/VIS spectra – to be a ring-opened form of type **16b**. Its relative (*M**,1*R**,2*R**)-configuration was finally corroborated by an X-ray crystal-structure determination (*Fig. 6*).

Scheme 16



(*P**)-**14a**[a])	LDA[b]); –70°, 1 h	**15a** (90%)	**16a** (n.o.)
(*P*/M**)-**14b**	LDA[b]); –75°, 1 h	**15b** (62%)	**16b** (30%)
(*P**)-**14c**	Cs_2CO_3[c]); 80°, 3.5 h	**15c** (12.5%)	**16c** (n.o.)[d])

[a]) See *Schemes 4* and *5* for substituents and their locations. [b]) In THF/hexane. [c]) In 1,2-dimethoxyethane (DME). [d]) Not observed. As further products, 2-*exo*,3-*endo*-(*P**)- and 2-*endo*,3-*exo*-(*P**)-**14c** were found in a 1:1 ratio (total yield: 41%).

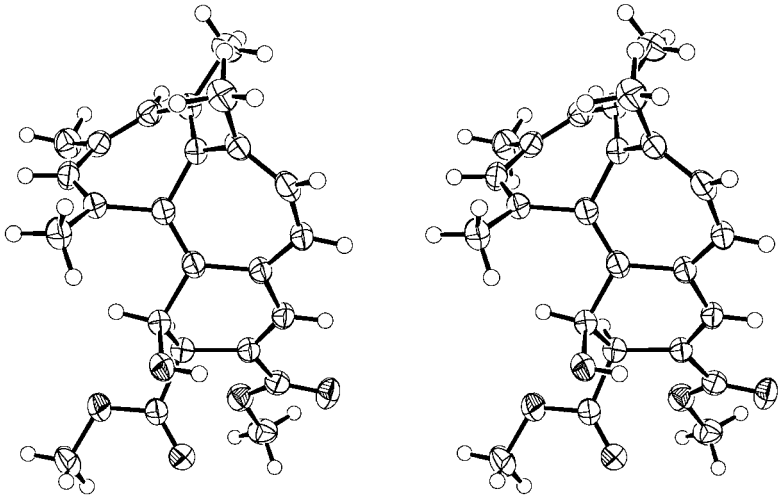


Fig. 6. *Stereoscopic view of the X-ray crystal structure of (*M*,*1*R*,*2*R*)-**16b**

The crystal structure of **16b**, which had been recrystallized from CH_2Cl_2/hexane, is quite interesting. The lattice of the monoclinic crystals is made of H-bonded dimers of **16b**, whereby two centrosymmetrically arranged molecules form mutual H-bonds between their OH groups at C(1) and the s-*cis*-oriented C=O parts of their methyl ester moieties at C(3) (*Fig. 7*). Two third of the small clefts that are generated between the centrosymmetric H-bonded dimers are occupied by loosely incorporated CH_2Cl_2 molecules, which tend to leave the crystals within several hours at room temperature and normal pressure, so that the crystals become opaque. It might be that the s-*cis*-conformation of the C=O group at C(3) in relation to the conjugated C(3)=C(4) bond is a result of the observed dimer formation in the crystals for which the s-*cis* conformation is spatially essential.

The AM1 calculation of the structure of **16b** reproduced very well the X-ray crystal structure, with only slight deviations in the torsion angles (*Table 2*). But it led to two

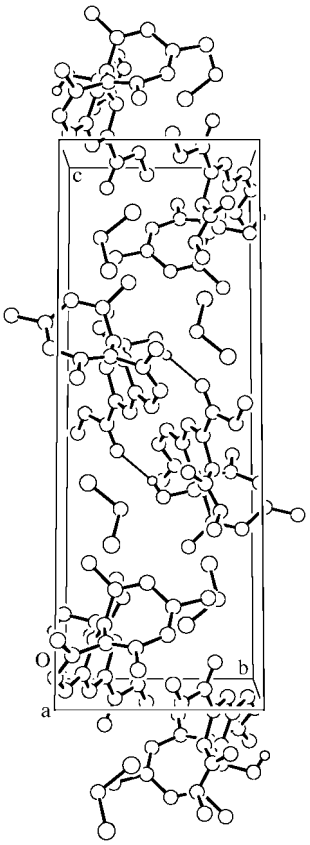


Fig. 7. *Crystal packing of the centrosymmetric, H-bonded dimers of (*M**,1*R**,2*R**)*-**16b** (for the sake of clarity, H-atoms not involved in H-bonds are omitted)

Table 2. *Selected X-Ray Crystal-Structural and Calculated Data* (heat of formation and torsion angles) *for Compound (*M**,1*R**,2*R**)*-**16b**

Parameter	X-Ray	AM1	
	s-*cis*	s-*cis*	s-*trans*
ΔH_f° [kcal/mol]	−130.1	−130.2	–
Θ (C(4a)−C(12b)−C(1)−OH) [°]	72.9 (3)	77.0	77.1
Θ (C(3)−C(2)−C(1)−OH) [°]	−80.6 (2)	−86.3	−87.2
Θ (OC−C(2)−C(3)−C(4)) [°]	−136.8 (3)	−137.6	−136.5
Θ (OC−C(2)−C(1)−C(12b)) [°]	167.7 (2)	163.3	162.6
Θ (C(7)−C(7a)−C(12a)−C(12b)) [°]	−63.8 (3)	−63.2	−63.1
Θ (C(8)−C(7a)−C(12a)−C(12)) [°]	−63.1	−62.9	−62.8
Θ (O=C−C(3)−C(4)) [°]	17.7 (4)	14.7	−160.5

conformations of almost equal ΔH_f° values, showing the C(4)=C(3)−C=O fragment with either s-*cis*- or s-*trans*-conformation. One can suppose, therefore, that crystallization of racemic **16b** in solution starts with a molecular recognition process of the antipodes of s-*cis*-**16b** steered by mutual intermolecular H-bond formation, which results in dimer generation.

The source of **16b** must be the (*M**)-configured epimer of 2,3-*exo*-**14b**, which is present in the starting crystal mixture in a proportion of 57% (*cf. Scheme 15*). An epimerization at the heptalene axis of chirality can be excluded because of the low reaction temperature. The results of the isomerization reaction at $-75°$ indicate that all (*P**)-form of 2,3-*exo*-**14b** had reacted, whereas less than half of the (*M**)-form had been transformed into **15b**. Most of it is found as the ring-opened form **16b**. In other words, the rate-determining step must be the second elimination step, which takes place more easily in the (*P**)- than in the (*M**)-epimer. The conformation of the six-membered ring of **16b** in the crystals as well as in the calculated structure exhibits the OH group at C(1) in a pseudo-axial position, and the MeOCO group at C(2) in a pseudo-equatorial position (see the corresponding torsion angles in *Table 2*). The OH group – or the oxido group under the strong basic conditions – would be in the correct stereochemical position for an elimination reaction. However, the (*M**)-configured heptalene part is inclined towards the bonding sphere of C(2)–C(3) in a way that a linear attack of the sterically encumbered base (LDA) on H–C(2) must be hindered.

AM1 calculations of the structure of the corresponding (*P**)-configured epimer of **16b**, which should result from the base-induced ring opening of (*P**)-**14b**, indicate just the opposite spatial situation (*Fig. 8*). H–C(2) is exposed to the open side of the molecule, so that a linear uptake of H–C(2) by LDA can take place. Moreover, the ΔH_f° value of (*P**)-**16b** – with the same conformation of the six-membered ring as has been found in the crystal structure as well as for the calculated structure for (*M**)-**16b**, and with the OH group at C(1) in pseudo-axial and the MeOCO group at C(2) in pseudo-equatorial position – is 5 kcal/mol above that of (*M**)-**16b**. The AM1 calculations also showed that (*P**)-**16b** should finally occupy an energetically more-relaxed conformation, lying 4 kcal/mol below the one with the OH group in pseudo-axial position, but still 0.5 kcal/mol above the analogous conformation of (*M**)-**16b**. The energetically relaxed conformation of (*P**)-**16b** bears the OH group at C(1) in pseudo-equatorial position, and the MeOCO group at C(2) in pseudo-axial position,

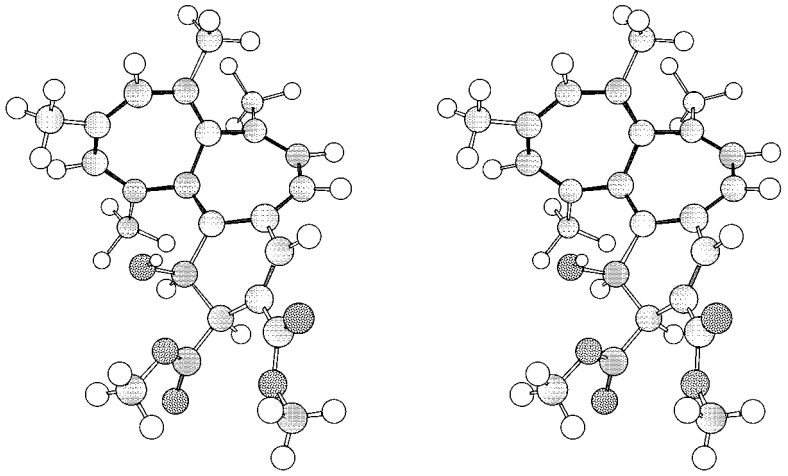


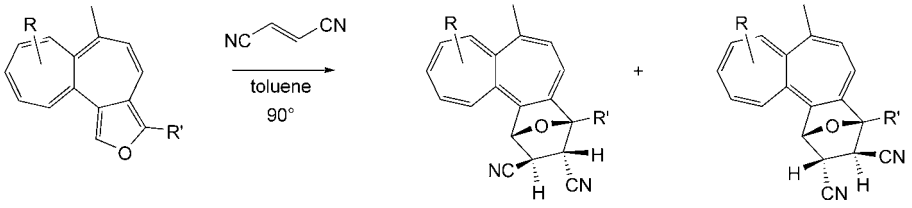
Fig. 8. *Stereoscopic view of the AM1-calculated, energetically non-relaxed structure of (*P*,*1*R*,*2*R*)-**16b**

whereby the C=O group of MeOC(O)–C(3) is still in an s-*cis* arrangement with C(3)=C(4). In other words, the energetically relaxed form of (*P**)-**16b**, or of its oxido variant, is not suited for a concerted elimination reaction leading to **15b**. Since the ring-opening reaction of (*P**)-**14b** at $-75°$ must first lead to the analogous (*P**)-form of (*M**)-**16b**, we suppose that the second elimination step of the corresponding oxido intermediate of (*P**)-**16b** takes place before the conformational change to the energetically relaxed form occurs.

The isomerization of 2,3-*exo*-(*P**)-**14c** with Cs_2CO_3 as base in boiling 1,2-dimethoxyethane (DME), an aromatization procedure that we used with great success in the case of 1,2,3,4-tetrahydro-1,4-epoxybenzo[*d*]heptalene-2,3-dicarbonitriles **17** (see *Sect. 2.4*), was not very effective since we observed mainly *cis* → *trans* isomerization at the C(2)–C(3) bond, which led to an almost 1:1 mixture of 2-*exo*,3-*endo*-(*P**)- and 2-*endo*,3-*exo*-(*P**)-**14c**, beside small amounts of the expected dimethyl benzo[*a*]heptalene-2,3-dicarboxylate **15c** (*Scheme 16*). Both *trans*-configured isomers of **14c** exhibited almost identical UV/VIS spectra, with a well-separated broad maximum at 349 nm (hexane), which speaks clearly for their relative (*P**)-configuration[3]). The (*P**)-configuration of 2-*exo*,3-*endo*-**14c** was additionally confirmed by the observation of a distinct ^{1}H-NOE effect between H_{endo}–C(2) and H–C(12), whose interatomic distance amounts to 318 pm according to an AM1 calculation.

2.4. *Adducts with Fumaronitrile* (FN), *and Their Rearrangement.* The thermal cycloaddition of the heptaleno[1,2-*c*]furans **1** and FN in toluene at 90° occurred smoothly and in high yields, and led, in all cases, to varying mixtures of the 2-*exo*,3-*endo*- and 2-*endo*,3-*exo*-configured products **17**, which consisted of the corresponding (*P**)- and (*M**)-epimers (*Scheme 17*). The mixtures were not separated, since ^{1}H-NMR analyses permitted the structure assignment of all four isomeric forms. Nevertheless, 2-

Scheme 17



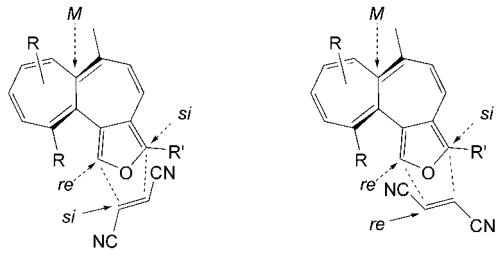
1a[a])	2.5 h (86%)	2-*exo*,3-*endo*-**17a** (44/17%)[b])	2-*endo*,3-*exo*-**17a** (29/10%)[b])
1b	15 h (94%)	2-*exo*,3-*endo*-**17b** (80/14%)[c])	2-*endo*,3-*exo*-**17b** (3.5/2.5%)
1c	3.5 h (71%)	2-*exo*,3-*endo*-**17c** (93/<1%)[d])	2-*endo*,3-*exo*-**17c** (7/<1%)[d])
1e	2.5 h (>90%)	2-*exo*,3-*endo*-**17e** (42/19%)	2-*endo*,3-*exo*-**17e** (29/10%)

[a]) See *Schemes 4* and *5* for substituents and their locations. [b]) In parentheses, rel. percentages of (*P**)- (first value) *vs.* (*M**)-epimer. [c]) The equilibrium mixture in toluene solution (1%) at 90° after 2.75 h contained 88% of the (*P**)- and 12% of the (*M**)-epimer. [d]) ^{1}H-NMR (600 MHz) detection limit: *ca.* 1%.

[3]) It is of interest to note once more that the absorption maximum of the discussed heptalene bands moved in the series of the (*P**)-configured 1,4-epoxy substrates 2,3-*exo*-**14b** → 2,3-*exo*-**14a** → 2-*exo*,3-*endo*-**14c** from 320 to 339 and finally to 349 nm, in agreement with the flattening of the heptalene π-system due to the decrease in the number of *peri*-substituents at the heptalene core.

exo,3-*endo*-(*P**)-**17a**–**c** could be obtained in pure form by crystallization. The relative (*P**)-configuration of 2-*exo*,3-*endo*-**17b** was established by ^{1}H-NMR measurements on the basis of a strong NOE between H_{endo}–C(2) and Me–C(12). The structure of the other isomers was correlated by their chemical ^{1}H-NMR shifts and their UV/VIS spectra.

Heating of 2-*exo*,3-*endo*-(*P**)-**17b** in toluene at 90° led to an equilibrium mixture consisting of 88% of the (*P**)- and 12% of the (*M**)-epimers (see footnote in *Scheme 17*). We conclude, therefore, that all the other isolated mixtures represent also equilibrium mixtures of the (*P**)/(*M**)-epimers, and the relative percentages that we found for the 2-*exo*,3-*endo*- and 2-*endo*,3-*exo*-**17** forms reflect the ratio to which the two diastereoisomeric transition states (TS1 and TS2) were passed (*Scheme 18*; see also *Scheme 7* and *Fig. 4*). We assume, on steric grounds, that, as in the case of the ADM and DM addition reactions, primarily the (*M**)-configured 1,2,3,4-tetrahydro-1,4-epoxybenzo[*a*]heptalenes are formed, which, after the DBS process, epimerize thermally to the equilibrated (*P**)/(*M**)-mixtures of **17**.



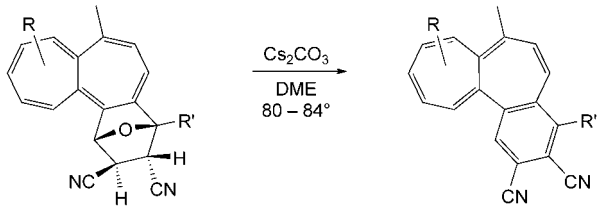
The isomerization of compounds **17** to the corresponding benzo[*a*]heptalene-2,3-dicarbonitriles **18** took place smoothly in the presence of Cs_2CO_3 in hot DME (*Scheme 18*). All products were crystalline, their color varying from orange (**18b**) *via* red (**18a**, **18e**) to dark red (**18c**), in correspondence with the decreasing number of *peri*-substituents around the central heptalene σ-bond. In *Table 3* are summarized the data of the three longest-wavelength heptalene absorption bands of the dinitriles **18**. The positions of heptalene bands I and II correspond very well with the AM1 calculated trend of the size of the average torsion angle (Θ_{av}) at the central σ-bond.

Table 3. *UV/VIS Longest-Wavelength Heptalene Absorption Bands of the Benzo[*a*]heptalene-2,3-dicarbonitriles* **18**

Compound	Θ_{av} [a])	λ_{max} [nm] (log e)[b])			Crystal color
	[°]	I	II	III	
18a	60.8	416 (sh, 3.13)	355 (3.55)	303 (4.17)	red
18b	62.8	401 (sh, 3.21)	350 (3.55)	309 (4.28)	orange
18c	56.7	441 (sh, 2.98)	362 (3.69)	304 (4.28)	dark red
18e	60.7	394 (sh, 3.26)	346 (3.54)	304 (4.13)	red

[a]) Avarage value of the two torsion angles at the central σ-bond of the heptalene part. [b]) See [16] for the assignment of absorption bands.

Scheme 18



2-*exo*,3-*endo*-**17a**[a])[b])	2 h	**18a** (65%)
2-*exo*-3-*endo*-**17b**	1 h	**18b** (86%)
2-*exo*,3-*endo*-**17c**	18 h	**18c** (44%)
17e[c])	2.5 h	**18e** (93%)

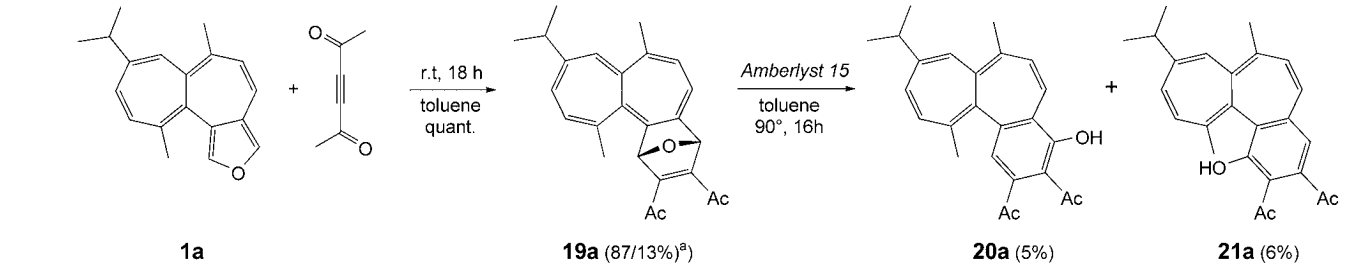
[a]) See *Schemes 4*, *5*, and *18* for substituents and their locations. [b]) The crystallized (*P**)-epimer was used in the case of **17a**–**c**. [c]) Raw mixture of stereoisomers used.

2.5. *Further Cycloaddition and Rearrangement Experiments.* Oxidative dehydrogenation of a *meso*/*racemo*-mixture of hex-3-yne-2,5-diol with CrO_3/H_2SO_4 [17] gave hex-3-yne-2,5-dione, which reacted already at r.t. in toluene with **1a** to give a *ca.* 7:1 mixture of the (*M**)- and (*P**)-forms of the corresponding 2,3-diacetyl-1,4-dihydro-1,4-epoxybenzo[*d*]heptalene **19a** (*Scheme 19*). Treatment of **19a** with *Amberlyst 15* in cyclohexane led mostly to destruction of **19a**. However, the ^{1}H-NMR spectrum ($CDCl_3$) of the crude material after the reaction exhibited two sharp *singlets* at δ(H) 12.06 and 11.54 ppm, respectively, typical for intramolecular H-bonds in 2-hydroxyacetophenones. Therefore, we assume that the expected acid-catalyzed isomerization of **19a** had taken place to a small extent, whereby the corresponding 4-hydroxy- and 1-hydroxybenzo[*a*]heptalenes **20a** and **21a**, respectively, had been formed. These reactions were not further investigated.

The oxidation of 2,5-dimethylfuran with '3-chloroperbenzoic acid' in CH_2Cl_2 at 0° results in (*Z*)-hex-3-ene-2,5-dione almost quantitatively [18], which readily isomerizes to the (*E*)-form on standing over longer periods of time at 0°, on heating, or in the presence of silica gel. Therefore, we were not surprised to find that the reaction of **1a** or **1b** with freshly prepared hex-3-ene-2,5-dione in toluene at 120° gave mainly the *trans*-configured adducts 2-*endo*,3-*exo*- and 2-*exo*,3-*endo*-**22a** and -**22b**, respectively (*Scheme 19;* for structural assignments, see *Exper. Part*). Treatment of the crystalline 2-*endo*,3-*exo*-(*P**)-adduct with Cs_2CO_3 in DMF at room temperature gave, in a non-optimized yield of 40%, not the expected **23a**, but just the cyclic aldol form **24a** as a mixture of the (*P**)- and (*M**)-forms (*Scheme 20*).

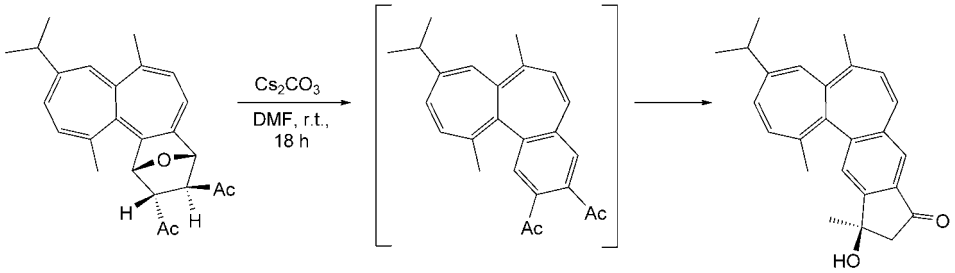
Finally, we studied the cycloaddition of heptalenofuran **1a** with phenyl ethenesulfonate. Heating of both reactants in toluene at 120° led to the regioisomeric cycloadducts *exo*-**25a** and *exo*-**26a** (and, presumably, *endo*-**26a**) in an almost quantitative total yield (*Scheme 21*). All three types of isomers appeared in the crude reaction mixture as (*P**)- and (*M**)-epimers in a thermodynamically controlled (*P**)/(*M**) ratio of *ca.* 5:1. The two main components, *exo*-(*P**)-**25a** and *exo*-(*P**)-**26a**, were obtained in pure crystalline form after chromatography and separation by preparative HPLC. Their relative (*P**)-configuration was evident from their UV/VIS spectra, since both

Scheme 19



[a]) 87:13 Mixture of the (*M**)- and (*P**)-epimers. [b]) Crystalline compound, (*P**)-configured according to its UV/VIS spectrum. On standing in solution at r.t., the (*M**)-epimer was slowly formed. [c]) Possibly present, but not searched for. [d]) Crystalline compound, (*P**)-configured according to its UV/VIS spectrum. [e]) Crystalline (*P**)-epimer (20%), (*M**)-epimer (5%), mixed with other forms. [f]) Crystalline (*M**)-epimer; (*P**)-epimer not found in amounts > 1%. [g]) Mainly one pure epimer; rel. axial configuration not determined. The other epimer was present in amounts of *ca.* 1.5%.

Scheme 20



22a[a]) **23a** (*P**)-**24a**[b])

[a]) The pure (*P**)-epimer was used. [b]) A 4:3 mixture of (*P**)- and (*M**)-**24a** was obtained in a non-optimized yield of at least 40%. A crude second chromatographic fraction (*ca.* 50%) contained presumably the other structurally isomeric epimers with exchanged C=O and $HOCH_2$ functions (see *Exper. Part*).

epimers exhibited clear broad maxima at 337 and 334 nm (in hexane), respectively, as has also been found for the main form of *endo*-**26a**[4]).

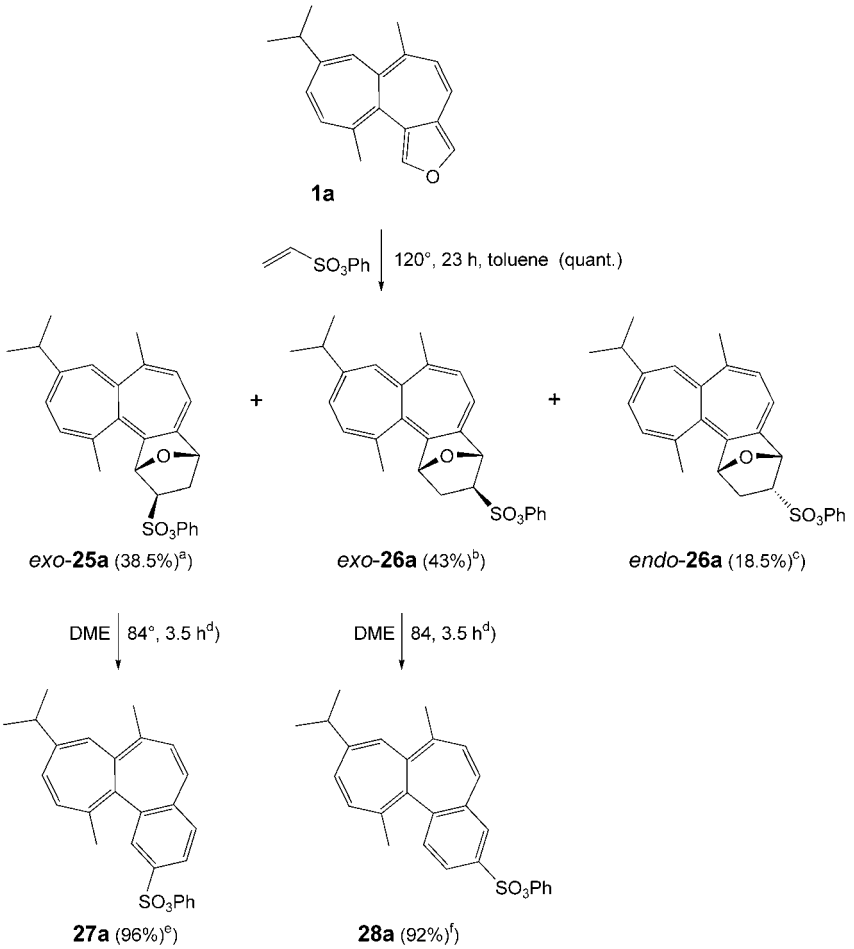
The structures of the regioisomers were in accord with their base-catalyzed rearrangement into the corresponding benzo[*a*]heptalene-sulfonates **27a** and **28a**, respectively, which occurred smoothly with Cs_2CO_3 in boiling DME (*Scheme 21*). Noteworthy is the position of the longest-wavelength heptalene absorption band of both isomers. It appears for **27a** at 344 nm in hexane, and at 349 nm in MeCN, and is hypsochromically shifted to 334 nm for **28a** in hexane, and to 337 nm in MeCN, respectively. The remote phenylsulfonyloxy substituent at the benzo part should not have a steric influence on the twisting of the heptalene core. Indeed, AM1 calculations of both structures provided almost the same cisoid torsion angles at the central σ-bond. The hypsochromic shift by 10 nm (hexane) or 12 nm (MeCN) of the longest-wavelength heptalene band in going from **27a** to **26a** must, therefore, be the result of an electronic effect. We assume, according to the slight positive solvent shift, that the excited state of **27a** has a more-pronounced charge-transfer character than that of **28a**, as indicated in established structural terms, which allow to formulate **27a** (but not **28a**) as a zwitterion, with the positive charge stabilized by a tropylium core, and the negative one by the phenylsulfonyloxy substituent.

In conclusion, heptaleno[1,2-*c*]furans behave in *Diels–Alder* type cycloaddition reactions like 3,4-disubstituted furans. The more-complex product pattern is due to the steric encumbrance and inherent chirality of the heptalene backbone. In addition, nonsymmetrically substituted dienophiles such as phenyl ethenesulfonate give rise to the formation of regioisomeric adducts. Whereas the stereoisomerism of the cycloadducts, except that of the heptalene core, is lost in the base- or acid-catalyzed rearrangement to benzo[*a*]heptalenes, their regioisomerism is preserved in the

---

[4]) The assignment of the relative configuration of all three pairs of isomers is more clearly recognizable by a comparison of their longest-wavelength HPLC–UV/VIS maxima (hexane/CH_2Cl_2/MeOH 800:99:1): 340 *vs.* 331 nm for *exo*-(*P**)/(*M**)-**25a**; 337 *vs.* 326 nm for *exo*-(*P**)/(*M**)-**26a**, and 340 *vs.* 329 nm for *endo*-(*P**)/(*M**)-**26a**.

Scheme 21



a) (*P**)/(*M**) Ratio of 83:17; yield of crystallized (*P**)-epimer: 30%. b) (*P**)/(*M**) Ratio of 82:18; yield of crystallized (*P**)-epimer: 23%. c) (*P**)/(*M**) Ratio of 83:17. d) The pure (*P**)-form was rearranged. e) Yield of recrystallized **27a**: 69%. f) Yield of recrystallized **28a**: 57%.

transformation to 2- or 3-substituted benzo[*a*]heptalenes. Generally speaking, we have developed a new efficient 4-step synthesis of benzo[*a*]heptalenes starting with heptalene-1,2- and/or -4,5-dicarboxylates.

We are grateful to Dr. *A. Linden* who skilfully performed the X-ray crystal-structure analyses and who also outlined the text of the X-ray section in the *Exper. Part*. We thank our NMR laboratory for specific NMR measurements and our MS laboratory for mass spectra. Financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. Reactions involving air- or moisture-sensitive reagents or intermediates were performed under N_2 or Ar in flame-dried glassware. If not otherwise stated, all commercially available compounds (*Fluka*, *Aldrich*) were used as received. Solvents for reactions were purchased in *puriss.* quality from *Fluka* or *Merck*. THF was freshly distilled over Na before use. Solvents for column-chromatography (CC) and workup procedures were purchased in technical quality, and were purified by distillation. TLC: Precoated silica gel *60* F_{254} aluminum sheets (*Merck*), visualization by UV light and/or dipping into phosphomolybdic acid soln. (phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot H_2O$ (10 g), conc. H_2SO_4 (60 ml), and H_2O (940 ml)), followed by heating to 120°. CC on Silica gel *60* (40–63 or 63–200 μm, *Chemie Uetikon AG* and *Merck*). If not otherwise mentioned, HPLC-analyses were performed on a *Spherisorb CN* (3 μm, 4 × 125 mm) column with a *JASCO MD-910* and PDA detector. Melting points (m.p.) were determined on a self-made microscope melting-point apparatus. UV/VIS Spectra were recorded on a *Perkin-Elmer* spectrophotometer, model *Lambda 19*, λ in nm (log ε). CD Spectra were recorded on a *JASCO 715* spectropolarimeter, λ in nm ($\Delta\varepsilon$ or mdeg, resp.). IR Spectra were recorded on a *Perkin-Elmer* FT-IR spectrophotometer, model *Spectrum ONE*; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra were recorded on *Bruker ARX-300* or *AV-300* [300 MHz (^1H), 75.5 MHz (^{13}C)], *Bruker DRX-500* [500 MHz (^1H), 125.8 MHz (^{13}C)], and *Bruker DRX-600* [600 MHz (^1H), 150.9 MHz (^{13}C)] spectrometers; chemical shifts δ in ppm), rel. to Me_4Si ($\delta = 0$ ppm) as internal standard, or rel. to $CDCl_3$ ($\delta(C) = 77.0$ ppm) coupling constants *J* in Hz. ^{13}C-NMR Spectra were proton broad-band-decoupled; assignments were confirmed by $^1H,^1H$-correlation data (DQF-COSY/ROESY, NOESY), one-bond $^1H,^{13}C$-correlation data (HSQC), and long-range $^1H,^{13}C$-correlation data (HMBC). EI-MS (*MAT 95* spectrometer, at 70 eV) and CI-MS measurements were performed by the MS-Servicelabor des Organisch-chemischen Institutes, Universität Zürich; in *m/z* (rel. %).

1. *Heptaleno[1,2-*c*]furans* **1** *and -furanones* **3**. 1.1. *8-Isopropyl-6,11-dimethylheptaleno[1,2-*c*]furan* (**1a**) *and 1,3-Dihydro-8-isopropyl-6,11-dimethylheptaleno[1,2-*c*]furan-3-one* (**3a**). *1.1.1. 9-Isopropyl-1,6-dimethylheptalene-4,5-dimethanol* (**2a**) [5]. To a cold soln. (0°) of dimethyl 7-isopropyl-5,10-dimethylheptalene-4,5-dicarboxylate (7.00 g, 20.56 mmol) in THF (350 ml), a *ca.* 1M (i-Bu)$_2$AlH soln. in hexane (65 ml) was added. The mixture was stirred for 30 min at 0°, then carefully quenched by addition of H_2O, and extracted with AcOEt. The org. phase was washed with brine, dried ($MgSO_4$), and the solvent was removed on a rotary evaporator. The residue was subjected to CC (SiO_2, 63–200 μm; *t*-BuOMe) to afford **2a** (4.91 g, 84%) as a yellow, viscous oil. From a hexane/AcOEt soln., 3.75 g (64%) of pure **2a** were obtained as fine, light-yellow crystals. The DBS isomer of **2a** was not isolated under these conditions. M.p. 106.1—106.8°. UV/VIS (hexane): λ_{max} 377 (sh, 2.74), 314 (sh, 3.52), 249 (4.33), 203 (439); λ_{min} 227 (4.08). IR (KBr): 3299*s*, 2957*s*, 1647*m*, 1606*m*, 1446*s*, 1378*m*, 1236*m*, 1139*m*, 1099*m*, 1032*s*, 1001*s*, 982*s*, 863*m*, 836*s*, 819*m*.

1.1.2. *Formation of* **1a** *and* **3a** [5]. To a suspension of basic MnO_2 (20 g; prepared according to [19]) and $TsOH \cdot H_2O$ (35 mg, 0.18 mmol) in AcOEt (200 ml) was added at once at 0° a soln. of **2a** (1.0 g, 3.52 mmol) in AcOEt (10 ml). The resulting mixture was stirred vigorously at 0° for 4 h. The MnO_2 was removed by filtration through a glass micro-fiber filter, and thoroughly washed with AcOEt. To the filtrate was added immediately a soln. of $TsOH \cdot H_2O$ (35 mg) in AcOEt (5 ml). After standing for 1 h at 5°, the soln. was washed with 5% aq. K_2CO_3 soln. and brine, dried ($MgSO_4$), filtered and evaporated. The oily residue was purified by CC (SiO_2; hexane/Et_2O 4:1) to afford 499 mg (54%) of **3a** as a light-yellow oil. Furan **3a** is not very stable and should be stored under N_2 at −20° and used within 2 d. For anal. data of **1a** and **3a**, see [5],

1.2. *6,7,9,11-Tetramethylheptaleno[1,2-*c*]furan* (**1b**) *and 1,3-Dihydro-6,7,9,11-tetramethylheptaleno[1,2-*c*]furan-3-one* (**3b**). See [5]. The reaction was performed in analogy to the formation of **1a** and **3a** (see above). Chromatographic separation gave **1b** (53%) and **3b** (27%) [5].

1.3. *9-Isopropyl-6-methylheptaleno[1,2-*c*]furan* (**1c**). 1.3.1. *8-Isopropyl-1-methylheptalene-4,5-dimethanol* (**2c**). To a cold soln. (0°) of dimethyl 8-isopropyl-5-methylheptalen-4,5-dicarboxylate (960 mg, 2.94 mmol; prepared from 6-isopropyl-1-methylazulene and ADM [20]) in THF (80 ml), a *ca.* 1M (i-Bu)$_2$AlH soln. in hexane (15 ml) was added. The mixture was stirred for 1 h at r.t., then carefully quenched by addition of H_2O at 0°, and extracted with AcOEt. The org. phase was washed with brine, dried ($MgSO_4$), and the solvent was removed. The residue was subjected to CC (SiO_2, 63–200 μm; *t*-BuOMe) to afford **2c** (575 mg, 72%) as an unstable, ochre-colored, viscous oil. R_f (*t*-BuOMe) 0.22. ^1H-NMR (300 MHz, $CDCl_3$): 6.35–6.15 (*m*, 3 H); 5.95–5.87 (*m*, 2 H); 5.77 (*d*, $^3J = 6.6$, 1 H); 4.47–4.23 (*m*, 2 HOCH_2–C(4,5)); 2.48 (*sept.*, $^3J = 6.9$, Me_2CH–C(8)); 2.05 (*s*, Me–C(1)); 1.11, 1.08 (2 *d*, $^3J = 6.9$, Me_2CH–C(8)).

1.3.2. *Formation of* **1c**. To a cold suspension (0°) of basic MnO_2 (11 g) in AcOEt (110 ml) was added $TsOH \cdot H_2O$ (15 mg). After stirring for 15 min, a soln. of **2c** (570 mg, 2.108 mmol) was added at once, and the resulting mixture was stirred vigorously at 0° for 1 h. The MnO_2 was removed by filtration through a glass micro-fiber

filter, and thoroughly washed with AcOEt. The filtrate, after adding a second portion of $TsOH \cdot H_2O$ (15 mg), was left at r.t. for 0.5 h. Subsequently, the soln. was washed with sat. aq. $NaHCO_3$ soln. (2×) and brine (1×), dried ($MgSO_4$), filtered, and evaporated at reduced pressure. The oily residue was purified by CC (SiO_2; *t*-BuOMe/hexane 4:1) to afford 249 mg (47%) of **1c** as an unstable, brownish-red oil. R_f (*t*-BuOMe) 0.42. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.282 (*d*, ^4J(1,3) = 1.5, H–C(3)); 7.211 (*q*-like *s*, H–C(1)); 6.430 (*d*, ^3J(4,5) = 11.7, H–C(4)); 6.15–6.10 (*m*, 2 H, H–C(7,10)); 5.952 (*d*, ^3J(10,11) = 7.2, H–C(11)); 5.872 (*d*, ^3J(4,5) = 11.6, H–C(5)); 5.820 (*d*, ^3J(7,8) = 11.3, H–C(8)); 2.446 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 1.767 (*s*, Me–C(6)); 1.105 (*d*, ^3J = 6.9, Me_2CH–C(9)). GC-MS: 250 (100, M^+), 235 (82), 192 (68), 165 (72), 152 (64).

1.4. *9-(*tert*-Butyl)-6-methylheptaleno[1,2-*c*]furan* (**1d**). 1.4.1. *8-(*tert*-Butyl)-1-methylheptalene-4,5-dimethanol* (**2d**). To a cold soln. (0°) of dimethyl 8-(*tert*-butyl)-1-methylheptalene-4,5-dicarboxylate (860 mg, 2.526 mmol; prepared in 30% yield by reaction of 6-(*tert*-butyl)-1-methylazulene with ADM in toluene at 130°; R_f (hexane/*t*-BuOMe) 0.32) in THF (70 ml), a *ca.* 1M (i-Bu)$_2$AlH soln. in hexane (13 ml) was added. The mixture was stirred for 30 min at 0°, and then for 30 min at r.t. Subsequently, the cooled mixture (0°) was carefully quenched by slow addition of H_2O, and extracted with AcOEt. The combined org. phase was washed with brine, dried ($MgSO_4$), and the solvent was removed. The solid residue was recrystallized from *t*-BuOMe to afford **2d** (365 mg, 51%) as light-yellow crystals. CC of the mother liquor (SiO_2; *t*-BuOMe, R_f 0.27) led to a dark yellow oil (157 mg; according to NMR-analysis identical with the crystalline material). Total yield: 522 mg (73%). M.p. 138.0–139.2°. UV/VIS (cyclohexane): λ_{max} 397 (sh, 2.67), 325 (3.67), 255 (4.41); λ_{min} 291 (3.47), 226 (4.07). IR (KBr): 3313*s*, 3013*m*, 2865*s*, 2958*s*, 1601*m*, 1458*s*, 1371*m*, 1219*m*, 1251*m*, 1018*s*, 1001*s*, 982*s*, 852*s*, 758*s*, 612*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.45–6.28 (*m*, H–C(3,7,9)); 5.94 (superimposed *d*, H–C(2,6)); 5.81 (*d*, ^3J(6,7) = 6.7, H–C(11)); 4.46–4.37, 4.33–4.22 (2 *m*, $HOCH_2$–C(4,5)); 2.055 (br. *s*, Me–C(1)); 1.773 (*s*, $HOCH_2$–C(4,5) + H_2O)); 1.144 (*s*, *t*-Bu–C(8)). EI-MS: 284 (70, M^+), 198 (100), 165 (58), 141 (38).

Formation of **1d**. To a cold suspension (0°) of basic MnO_2 (3 g) in AcOEt (60 ml) was added $TsOH \cdot H_2O$ (10 mg). After stirring for 15 min, a soln. of **2d** (328 mg, 1.153 mmol) was added at once, and the resulting mixture was stirred vigorously at 0° for 2 h. The MnO_2 was removed by filtration through a glass micro-fiber filter, and thoroughly washed with AcOEt. The filtrate was evaporated, and the oily residue was immediately purified by CC (SiO_2; *t*-BuOMe; R_f 0.40) to afford 249 mg (82%) of **1d** as an unstable, reddish-brown oil. IR ($CHCl_3$): 3009*m*, 2967*s*, 2909*m*, 2871*m*, 1753*s*, 1692*m*, 1603*m*, 1465*m*, 1372*m*, 1048*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.303 (*d*, ^4J(1,2) = 1.5, H–C(1)); 7.234 (br. *s*, H–C(3)); 6.439 (*d*, ^3J(4,5) = 11.6, H–C(4)); 6.329 (*dd*, ^3J(7,8) = 11.4, ^4J(8,10) = 1.7, H–C(8)); 6.250 (*dd*, ^3J(10,11) = 7.3, ^4J(8,10) = 1.5, H–C(10)); 5.984 (*d*, ^3J(10,11) = 7.3, H–C(11)); 5.878 (*d*, ^3J(5,6) = 11.7, H–C(5)); 5.839 (*d*, partially covered, ^3J(6,7) = 11.9, H–C(7)); 1.772 (br. *s*, Me–C(6)); 1.157 (*s*, *t*-Bu–C(9)). GC-MS: 264 (100, M^+), 249 (76), 234 (56), 181 (78).

1.5. *8-Isopropyl-3,6,11-trimethylheptaleno[1,2-c]furan* (**1e**). According to our earlier procedure [5], furanone **3a** was treated with *Tebbe* reagent to afford, after chromatographic purification (SiO_2) **1e** (49%) as a yellow oil. From a hexane soln., light-yellow crystals were obtained. For anal. data, see [5].

1.6. *3,6,7,9,11-Pentamethylheptaleno[1,2-c]furan* (**1f**). According to our earlier procedure [5], furanone **3b** was synthesized in an analogous manner to **1e**. Yield: 63%. For anal. data, see [5].

2. *Cycloaddition Reactions with* **1**. 2.1. *With Dimethyl Acetylenedicarboxylate* (ADM). 2.1.1. *Dimethyl (*P**,1*S**,4*R**)- and (*M**,1*S**,4*R**)-1,4-Dihydro-9-isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalene-2,3-dicarboxylate* ((*P**)- and (*M**)-**4a**). A soln. of **1a** (157 mg, 0.594 mmol) and ADM (125 mg, 0.880 mmol; *Acros*) in toluene (12 ml) was heated at reflux for 8 h. After removal of the solvent and the excess of ADM at 60°/1 mbar in a *Kugelrohr* apparatus, the residue was purified by CC (SiO_2; hexane/*t*-BuOMe 3:2). After drying *in vacuo*, an orange solid foam was obtained quantitatively, which, according to HPLC-analysis, was a mixture of the (*P**)- and (*M**)-cycloadducts **4a**. Crystallization from hexane/Et_2O gave orange crystals of (*P**)-**4a** (177 mg, 73%).

*Data of (*P**)-***4a***. M.p. 132.1–132.9°. R_f (hexane/*t*-BuOMe 3:2) 0.27. UV/VIS (hexane; *cf. Fig. 3*, *a*): λ_{max} 380 (sh, 3.45), 340 (sh, 3.68), 301 (sh, 3.81), 245 (4.35), 215 (4.41); λ_{min} 231 (4.31), 204 (4.37). IR (KBr): 3023*m*, 2958*s*, 2867*m*, 1758*s*, 1731*s*, 1610*m*, 1431*s*, 1311*s*, 1253*m*, 1208*s*, 1121*s*, 1038*m*, 986*m*, 928*m*, 855*w*, 793*w*, 760*w*, 744*w*, 717*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 6.243 (*d*, ^3J(5,6) = 6.6, H–C(5)); 6.124 (*dq*-like *dd*, ^3J(10,11) = 6.5, ^4J(11,Me–C(12)) = 1.4, H–C(11)); 5.986 (*d*, ^3J(10,11) = 6.5, H–C(10); 5.919 (*dq*-like *dd*, ^3J(5,6) = 6.6, ^4J(6,Me–C(7)) = 1.4, H–C(6)); 5.683 (*d*, ^4J(8,10) = 1.0, H–C(8)); 5.467 (br. *s*, H–C(1)); 5.457 (br. *s*, H–C(4)); 3.815 (*s*, MeO(O)C–C(3)); 3.790 (*s*, MeO(O)C–C(2)); 2.389 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 2.103 (*d*, ^4J(6,Me–C(7)) = 1.1, Me–C(7)); 1.996 (*s*, Me–C(12)); 1.071, 1.044 (2*d*, ^3J = 6.9, Me_2CH–C(9)); assignments were verified by ROESY. ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.89 (MeO(O)*C*–C(3)); 162.79 (MeO(O)*C*–C(2)); 149.78 (C(9)); 146.24 (C(2)); 144.43 (C(3)); 140.23 (C(7a)); 137.84 (C(7)); 133.13 (C(12b)); 132.94 (C(12a)); 132.85 (C(4a)); 130.29 (C(12)); 129.66 (C11)); 126.97 (C(8)); 126.46 (C(6)); 123.53 (C(10)); 122.46 (C(5)); 84.35 (C(4)); 83.38 (C(1)); 52.30 (*Me*O(O)C–C(3)); 52.23 (*Me*O(O)C–C(2)); 36.15

(Me_2CH−C(9)); 25.36 (*Me*−C(7)); 25.23 (*Me*−C(12)); 22.75, 22.60 (Me_2CH−C(9)); assignments were made *via* ^{1}H,^{13}C-correlation spectra. CI-MS (NH_3): 407 (100, $[M+H]^+$). The rel. (*P**)-configuration was established by an X-ray crystal-structure determination (see *Fig. 1* and *Table 4*).

*Data of (*M*)-**4a***. Mother liquor, light brown oil, enriched (*M**)/(*P**)-mixture. R_f (hexane/*t*-BuOMe 3:2) 0.30. UV/VIS (qual.): *cf. Fig. 3*, *a*. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.316 (*d*, $^3J(5,6)=6.6$, H−C(5)); 6.019 (*dq*-like *dd*, $^3J(10,11)=6.3$, $^4J(11,\text{Me}-\text{C}(12))=1.4$, H−C(11)); 5.938 (*dq*-like *dd*, $^3J(5,6)=6.6$, $^4J(6,\text{Me}-\text{C}(7))=1.4$, H−C(6)); 5.908 (*d*, $^3J(10,11)=6.3$, H−C(10)); 5.647 (*s*, H−C(1)); 5.595 (*s*, H−C(8)); 5.396 (*d*, $^4J(4,5)=1.2$, H−C(4)); 3.791 (*s*, MeO(O)C−C(3)); 3.698 (*s*, MeO(O)C−C(2)); 2.308 (*sept.*, $^3J=6.9$, $Me_2CH-C(9)$); 2.156 (*s*, Me−C(12)); 2.113 (*d*, $^4J(6,\text{Me}-\text{C}(7))=1.1$, Me−C(7)); 0.986, 0971 (2*d*, $^3J=6.9$, Me_2CH−C(9)).

Table 4. *Crystallographic Data of (*P*)-**4a**, *(*M*)-**4f**, *and (*M*,*1*R*,*2*R*)-**16b***

	(*P**)-**4a**	(*M**)-**4f**	(*M**,1*R**,2*R**)-**16b**
Crystallized from	CH_2Cl_2/hexane	CH_2Cl_2/hexane	CH_2Cl_2/hexane
Empirical formula	$C_{25}H_{26}O_5$	$C_{25}H_{26}O_5$	$C_{24.67}H_{27.34}Cl_{1.34}O_5$
Formula weight [g/mol]	406.48	406.48	451.37
Crystal color, habit	orange, prism	yellow, prism	yellow, plate
Crystal dimensions [mm]	$0.15\times0.30\times0.40$	$0.16\times0.20\times0.25$	$0.05\times0.15\times0.20$
Temperature [K]	173(1)	160(1)	160(1)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)
Z	4	2	4
Refl. for cell determination	20	5948	53270
2θ Range for cell determin. [°]	11–20	4–60	4–50
Unit cell parameters a [Å]	22.541(3)	9.2717(1)	12.4998(3)
b [Å]	9.828(4)	10.9626(1)	8.1850(2)
c [Å]	9.480(2)	11.3030(1)	23.4410(5)
α [°]	90	73.6281(5)	90
β [°]	93.14(2)	71.0008(5)	101.813(1)
γ [°]	90	74.1178(6)	90
V [Å^3]	2097.0(9)	1021.06(2)	2347.5(1)
$F(000)$	864	432	952.56
D_x [g cm^{-3}]	1.287	1.322	1.277
$\mu(\text{Mo}K_\alpha)$ [mm^{-1}]	0.0888	0.0912	0.233
Scan type	ω /2θ	ϕ and ω	ϕ and ω
$2\theta_{max}$ [°]	55	60	50
Transmission factors (min; max)	–	–	0.865; 0.987
Total refl. measured	5400	44541	45672
Symmetry independent refl.	4819	5956	4143
R_{int}	0.087	0.043	0.074
Refl. used [$I>2\sigma(I)$]	2013	4570	3129
Refl. used in refinement	–	–	4143
Parameters refined; restraints	289	272	327; 37
Reflection/parameter ratio	6.97	16.8	
Final $R(F)$ [$I>2\sigma(I)$ refl.]	0.0669	0.0503	0.0495
$wR(F^2)$ (all data)	0.0519	0.0511	0.1256
Weights: p in $w=[\sigma^2(F_o)+(pF_o)^2]^{-1}$	0.005	0.005	[a])
Goodness-of-fit	1.769	3.122	1.164
Secondary extinction coeff.		$2.6(6)\times10^{-6}$	0.011(1)
Final Δ_{max}/σ	0.001	0.0004	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.35; −0.30	0.32; −0.29	0.28; −0.28
$\sigma(d_{(C-C)})$ [Å]	0.006–0.02	0.002	0.003–0.004

[a]) $w=[\sigma^2(F_o^2)+(0.0319P)^2+1.9119P]^{-1}$, where $P=(F_o^2+2F_c^2)/3$.

Heating of (*P**)-**4a** in toluene (100°, 2 h) gave a thermal equilibrium mixture of 56% of (*P**)-**4a** and 44% of (*M**)-**4a** (see *Table 1*).

2.1.1.1. *Dimethyl (*P**,1*S**,4*R**)- and (*M**,1*S**,4*R**)-1,4-Dihydro-9-isopropyl-7,12-dimethyl-1,4-epoxy-[1,4-$^2H_2$]benzo[*d*]heptalene-2,3-dicarboxylate* ((*P**)- and (*M**)-[1,4-$^2H_2$]-**4a**). Dimethyl 9-isopropyl-1,6-dimethylheptalene-4,5-dicarboxylate was reduced with LiAl[$^2H_4$] in the usual manner (*cf.* [5]), and then transformed by MnO_2 into [1,3-$^2H_2$]-**1a**. A soln. of the latter (70.7 mg, 0.265 mmol) and ADM (60 mg, 0.422 mmol) in toluene (4 ml) was heated in a *Schlenk* tube at 130° for 2 h. After removal of the solvent and the excess ADM at 60°/1 mbar in a *Kugelrohr* apparatus, the residue was purified by CC (SiO_2; *t*-BuOMe/hexane 3:2). From hexane/Et_2O, orange crystals of (*P**)-[1,4-$^2H_2$]-**4a** (48.0 mg, 44%) were obtained. After evaporation of the solvents, the mother liquor afforded a light-red oil (54.5 mg, 50%) consisting of an enriched (*M**)/(*P**)-mixture of [1,4-$^2H_2$]-**4a**.

Data of (P*)*-[1,4-$^2H_2$]-***4a**. M.p. 128.3–129.3°. ^{1}H-NMR (300 MHz, $CDCl_3$): No signals detected at 5.467 (H–C(1)) and 5.457 (H–C(4)).

*Data of (*M*)*-[1,4-$^2H_2$]-***4a**. ^{1}H-NMR (300 MHz, $CDCl_3$): No signals detected at 5.647 (H–C(1)) and 5.396 (H–C(4)).

2.1.2. *Dimethyl (*P**,1*S**,4*R**)- and (*M**,1*S**,4*R**)-1,4-Dihydro-7,8,10,12-tetramethyl-1,4-epoxybenzo[*d*]heptalene-2,3-dicarboxylate* ((*P**)- and (*M**)-**4b**). Under an atmosphere of Ar, a *Schlenk* tube was charged with **1b** (50.0 mg, 0.200 mmol), ADM (45 mg, 0.316 mmol), and toluene (1.5 ml). The tube was sealed, and heated in an oil bath (80°) during 4 h. Workup as described above yielded, after purification of the resulting crude product by CC (SiO_2, Et_2O/hexane 1:1), a mixture of (*P**)- and (*M**)-**4b** (71 mg, 90%). Recrystallization from Et_2O/hexane furnished dark-yellow crystals of pure (*M**)-**4b** (63.7 mg, 81%).

*Data of (*M*)*-***4b**. M.p. 156.3–158.8°. R_f (hexane/Et_2O 1:1) 0.29. HPLC (hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1; 0.7 ml/min): 6.43 min. UV/VIS (hexane): λ_{max} 368 (sh, 3.33), 297 (sh, 3.81), 245 (4.39), 215 (4.36), 201 (4.38); λ_{min} 229 (4.30), 208 (4.35). IR (KBr): 2952*m*, 2912*m*, 2855*w*, 1732*s*, 1709*s*, 1630*m*, 1435*s*, 1372*m*, 1340*m*, 1294*s*, 1280*s*, 1223*m*, 1116*m*, 1070*m*, 964*m*, 921*m*, 844*s*, 789*m*, 650*m*, 636*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 6.443 (*d*, ^3J(5,6) = 6.3, H–C(5)); 6.094 (*dq*-like *dd*, ^3J(5,6) = 6.3, ^4J(6,Me–C(7) = 1.5, H–C(6)); 5.960 (br. *s*, H–C(9)); 5.943 (*t*-like *s*, H–C(11)); 5.675 (*q*-like *s*, H–C(1)); 5.426 (*d*, ^4J(4,5) = 1.1, H–C(4)); 3.792 (*s*, MeO(O)C–C(3)); 3.754 (*s*, MeO(O)C–C(2)); 2.128 (*d*, ^4J(11,Me–C(12) = 1.3, Me–C(12)); 1.997 (*d*, ^4J(6,Me–C(7) = 1.0, Me–C(7)); 1.905 (*d*, ^4J(9,Me–C(10) = 1.2, Me–C(10)); 1.664 (*s*, Me–C(8)); assignments were verified by ROESY. CI-MS (NH_3): 393 (100, $[M+H]^+$), 361 (9, $[M-MeO]^+$).

*Data of (*P*)*-***4b**. HPLC (hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1; 0.7 ml/min): 5.45 min. UV/VIS (qual.): λ_{max} 358 (sh, 0.14), 298 (sh, 0.33), 245 (1.0). ^{1}H-NMR (300 MHz, $CDCl_3$, beside 85% (*M**)-**4b**): 6.37 (*dq*-like *dd*, ^3J(5,6) = 6.2, ^4J(4,5) = 0.5, H–C(5)); 6.08 (superimposed, H–C(9)); 6.07 (partially covered *dd*, H–C(6)); 6.04 (*t*, ^4J(11,Me–C(12)) = 1.3, H–C(11)); 5.51 (*q*-like *s*, H–C(1)); 5.48 (*d*-like br. *s*, H–C(4)); 3.84, 3.83 (2*s*, MeOCO–C(2,3)); *ca.* 2.00 (covered), 1.98 and 1.97 (2*d*, ^4J = 1.3, Me–C(7,10,12)); 1.72 (*s*, Me–C(8)).

2.1.3. *Dimethyl (*P**,1*S**,4*R**)-10-(*tert*-Butyl)-1,4-dihydro-7-methyl-1,4-epoxybenzo[*d*]heptalene-2,3-dicarboxylate* ((*P**)-**4d**). Under an atmosphere of Ar, a *Schlenk* tube was charged with **1d** (62 mg, 0.235 mmol), ADM (60 mg, 0.42 mmol), and toluene (4 ml). The tube was sealed, and heated in an oil bath (100°) during 50 min. After evaporation of the solvent, the crude product was purified by CC (SiO_2, hexane/*t*-BuOMe 3:2): 47.6 mg (50%) of (*P**)-**4d** as a reddish-brown oil.

*Data of (*P*)*-***4d**. R_f (hexane/Et_2O 1:1) 0.24. UV/VIS (hexane): λ_{max} 417 (sh, 3.32), 347 (3.67), 249 (4.33), 207 (4.30); λ_{min} 314 (3.58), 225 (4.26). IR ($CHCl_3$): 3030*m*, 3009*w*, 2957*m*, 1737*s*, 1630*w*, 1438*m*, 1331*m*, 1297*m*, 1258*m*, 1119*m*, 909*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.333 (*dd*, ^3J(11,12) = 11.4, ^4J(9,11) = 1.8, H–C(11)); 6.184 (*dd*, ^3J(8,9) = 7.6, ^4J(9,11) = 1.6, H–C(9)); 6.019 (*d*, ^3J(5,6) = 6.9, H–C(5)); 5.746 (*dd*, ^3J(5,6) ≈ 7.0, ^4J(6,Me–C(7)) = 1.4, H–C(6)); 5.744 (*d*, ^3J(11,12) ≈ 11.1, H–C(12)); 5.683 (*d*, ^3J(8,9) = 7.6, H–C(8)); 5.438 (*s*, H–C(1)); 5.423 (*s*, H–C(4)); 3.829, 3.807 (2*s*, MeO(O)C–C(2,3)); 2.053 (*d*, ^4J(6,Me–C(7)) = 1.0, Me–C(7)); 1.113 (*s*, *t*-Bu); assignments were verified by ROESY. ^{13}C-NMR (150.9 MHz, $CDCl_3$): 162.84, 162.48 (2 MeO(O)*C*–C(2,1)); 152.19 (C(10)); 144.30 (C(3)); 143.27 (C(2)); 140.19 (C(7a)); 135.73 (C(11)); 134.38 (C(7)); 133.08 (C(12b)); 129.98 (C(12a)); 127.67 (C(6)); 126.84 (C(8)); 126.21 (C(9)); 125.98 (C(12)); 122.56 (C(5)); 84.85 (C(4)); 83.04 (C(1)); 52.42, 52.34 (*Me*O(O)C–C(2,3)); 29.73 (*Me*$_3$C–C(10)); 25.91 (Me–C(7)); assignments were made *via* ^{1}H,^{13}C-correlation spectra. GC-MS: 406 (100, M^+), 374 (66, $[M-MeOH]^+$).

The mother liquor of the crystallization of (*P**)-**4d** was not further analyzed. However, according to our calculations (see *Table 1*), it must have contained (*M**)-**4d**.

2.1.4. *Dimethyl (*P**,1*S**,4*R**)- and (*M**,1*S**,4*R**)-1,4-Dihydro-9-isopropyl-4,7,12-trimethyl-1,4-epoxybenzo[*d*]heptalene-2,3-dicarboxylate* ((*P**)- and (*M**)-**4e**). Under an atmosphere of Ar, a *Schlenk* tube was charged with **1e** (116 mg, 0.417 mmol), ADM (80 mg, 0.56 mmol), and toluene (8 ml). The tube was sealed, and heated

in an oil bath first for 3 h at 120°, then during 3 h at 130°. After evaporation of the solvent, the resulting mixture was purified by CC (SiO_2, hexane/Et_2O 3:2 → 2:3), whereby 17.7 mg (15%) of starting material was recovered, together with 137 mg (78%) of an orange-colored oil, composed of (*P**)- and (*M**)-**4e**. From a hexane soln., 73.5 mg (42%) of (*P**)-**4e** could be isolated as yellow crystals. The mother liquor gave a mixture enriched in (*M**)-**4e** (orange-colored oil).

*Data of (*P**)-***4e***. M.p. 120.6–121.6°. R_f (Et_2O/hexane 3:2) 0.37. UV/VIS (hexane): λ_{max} 335 (sh, 3.77), 300 (sh, 3.89), 244 (4.37), 215 (4.44), 193 (4.44); λ_{min} 232 (4.35), 204 (4.40). IR (KBr): 2959*m*, 1736*s*, 1708*s*, 1632*w*, 1438*s*, 1393*m*, 1331*m*, 1269*s*, 1237*s*, 1215*s*, 1133*s*, 1099*m*, 1051*m*, 927*m*, 855*m*, 732*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.144 (*d*, ^3J(5,6) = 6.7, H–C(5)); 6.118 (*dq*-like *dd*, ^3J(10,11) = 6.5, ^4J(11,Me–C(12)) = 1.4, H–C(11)); 5.981 (*d*, ^3J(10,11) = 6.5, H–C(10)); 5.962 (*dq*-like *dd*, ^3J(5,6) = 6.5, ^4J(6,Me–C(7)) = 1.4, H–C(6)); 5.674 (*d*, ^4J(8,10) = 1.0, H–C(8)); 5.391 (br. *s*, H–C(1)); 3.818, 3.751 (2*s*, MeO(O)C–C(2,3)); 2.391 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 2.110 (*d*, ^4J(6,Me–C(7)) = 1.1, Me–C(7)); 2.018 (br. *s*, Me–C(12)); 1.716 (*s*, Me–C(4)); 1.075, 1.046 (2*d*, ^3J = 6.9, Me_2CH–C(9)). CI-MS (NH_3): 421 (100, $[M+H]^+$), 389 (10, $[M-MeO]^+$).

*Data of (*M**)-***4e*** (mixture of 13% (*P**)- and 87% (*M**)-**4e**): R_f (Et_2O/hexane 3:2) 0.37. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.162 (*d*, ^3J(5,6) = 6.6, H–C(5)); 6.012 (*dq*-like *dd*, ^3J(10,11) = 6.3, ^4J(11,Me–C(12)) = 1.4, H–C(11)); 5.950 (*dq*-like *dd*, ^3J(5,6) = 6.7, ^4J(6,Me–C(7)) = 1.4, H–C(6)); 5.895 (*d*, ^3J(10,11) = 6.3, H–C(10)); 5.576 (br. *s*, 2 H, H–C(1,8)); 3.777, 3.675 (2*s*, MeO(O)C–C(2,3)); 2.300 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 2.154 (br. *s*, Me–C(12)); 2.112 (*d*, ^4J(6,Me–C(7)) = 1.1, Me–C(7)); 1.718 (*s*, Me–C(4)); 0.955, 0.969 (2*d*, ^3J = 6.9, Me_2CH–C(9)).

Heating of (*P**)-**4e** in toluene at 120° for 2 h furnished an equilibrium mixture of 58% of the (*P**)- and 42% of the (*M**)-epimer (*cf. Table 1*).

2.1.5. *Dimethyl (*P**,1*S**,4*R**)- and (*M**,1*S**,4*R**)-1,4-Dihydro-4,7,8,10,12-pentamethyl-1,4-epoxybenzo[*d*]-heptalene-2,3-dicarboxylate* ((*P**)- and (*M**)-**4f**). Under an atmosphere of Ar, a *Schlenk* tube was charged with **1f** (185 mg, 0.700 mmol), ADM (150 mg, 1.055 mmol), and toluene (6 ml). The tube was sealed, and heated in an oil bath (80°) for 4 h. After evaporation of the solvent, the residue was purified by CC (SiO_2, hexane/Et_2O 1:1) to afford (*M**)-**4f** contaminated with the (*P**)-epimer. From an Et_2O/hexane soln., 163 mg (57%) of dark-yellow crystals were formed. This material contained, according to NMR analysis, **4f** and *ca.* 5% of an unidentified product. Recrystallization from CH_2Cl_2/hexane yielded the pure product.

*Data of (*M**)-***4f***. M.p. 144.5–146.5°. R_f (Et_2O/hexane 1:1) 0.30. HPLC (hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1; 0.7 ml/min): 4.32 min. UV/VIS (qual.): λ_{max} 361 (sh, 0.10), 297 (sh, 0.31), 245 (1.0). UV/VIS (hexane; *cf. Fig. 3*, *b*): λ_{max} 365 (sh, 3.38), 299 (sh, 3.85), 244 (4.37), 216 (4.39), 198 (sh, 4.34); λ_{min} 231 (4.33), 209 (4.38). IR (KBr): 2947*m*, 2913*m*, 1733*s*, 1712*s*, 1633*s*, 1432*s*, 1395*m*, 1373*w*, 1329*m*, 1264*s*, 1242*s*, 1207*s*, 1124*m*, 1050*m*, 969*m*, 835*m*, 818*m*, 784*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.287 (*d*, ^3J(5,6) = 6.4, H–C(5)); 6.093 (*dq*-like *dd*, ^3J(5,6) = 6.4, ^4J(6,Me–C(7)) = 1.3, H–C(6)); 5.946 (br. *s*, H–C(9)); 5.936 (br. *s*, H–C(11)); 5.598 (*s*, H–C(1)); 3.786 (*s*, MeO(O)C–C(3)); 3.718 (*s*, MeO(O)C–C(2)); 2.125 (*d*, ^4J(11,Me–C(12)) = 0.8, Me–C(12)); 1.996 (*d*, ^4J(6,Me–C(7)) = 1.0, Me–C(7)); 1.894 (*d*, ^4J(9,Me–C(10)) = 0.8, Me–C(10)); 1.735 (*s*, Me–C(4)); 1.660 (*s*, Me–C(8)); assignments were verified by ROESY. ^{13}C-NMR (150.9 MHz, $CDCl_3$): 164.30 (MeO(O)*C*–C(3)); 161.53 (MeO(O)*C*–C(2)); 147.30 (C(3)); 144.68 (C(2)); 142.70 (C(4a)); 137.56 (10)); 135.01 (C(12b)); 132.14 (C(12)); 131.88 (C(7)); 131.57 (C(9)); 131.08 (C(11)); 130.88 (C(7a)); 130.65 (C(12a)); 125.61 (C(6)); 120.85 (C(5)); 91.24 (C(4)); 79.92 (C(1)); 52.14 (*Me*O(O)C–C(3)); 52.06 (*Me*O(O)C–C(2)); 24.94 (Me–C(10)); 23.56 (Me–C(7)); 23.47 (Me–C(12)); 18.72 (Me–C(8)); 14.18 (Me–C(4)); assignments were made *via* ^{1}H,^{13}C-correlation spectra. CI-MS (NH_3): 424 (19, $[M+NH_4]^+$), 407 (84, $[M+H]^+$), 375 (31, $[M-MeO]^+$), 281 (100). The rel. (*M**)-configuration was established by an X-ray crystal-structure determination (see *Fig. 2* and *Table 4*).

*Data of (*P**)-***4f***. HPLC (hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1; 0.7 ml/min): 3.70 min: UV/VIS (qual.; *cf. Fig. 3*, *b*): λ_{max} 301 (0.39), 240 (1.0); λ_{min} 290 (0.38).

2.2. *With Dimethyl Maleate (DM)*. 2.2.1. *Dimethyl (*P**,1*S**,2*R**,3*S**,4*R**)-, (*M**,1*S**, *2*R**,3*S**,4*R**)-, (*P**,1*S**,2*S**,3*R**,4*R**)-, and (*M**,1*S**,2*S**,3*R**,4*R**)-1,4-Epoxy-1,2,3,4-tetrahydro-9-isopropyl-7,12-dimethylbenzo[*d*]heptalene-2,3-dicarboxylate* (2,3-*exo*-(*P**)- and 2,3-*exo*-(*M**)-**14a** and 2,3-*endo*-(*P**)- and 2,3-*endo*-(*M**)-**14a**). A soln. of **1a** (100 mg, 0.378 mmol) and DM (*Fluka pract.*; freshly distilled over K_2CO_3; 250 mg, 1.73 mmol) in toluene (2.5 ml) was heated at 120° in a sealed *Schlenk* tube during 23 h. Then, the solvent was evaporated, and most of the remaining DM residue was removed by distillation in a *Kugelrohr* apparatus at 90°/2 mbar. The residue was purified by CC (SiO_2; *t*-BuOMe/hexane 3:2) to yield 33.9 mg (18%) of a 3:1 mixture of (*P**)/(*M**)-2,3-*endo*-**14a** as a dark yellow oil, and 91.2 mg (59%) of 2,3-*exo*-**14a** as orange platelets after recrystallization from Et_2O/hexane.

Data of 2,3-endo-*(*M**)*-**14a**. R_f (*t*-BuOMe/hexane 7:3) 0.36. HPLC (hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1; 1 ml/min): 5.99 min. UV/VIS (qual.; hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1): λ_{max} 335 (0.22), 259 (1.0); λ_{min} 309 (0.21). ^{1}H-NMR (300 MHz, $CDCl_3$; mixture with 75% of 2,3-*endo*-(*P**)-**14a**): 6.10 (*d*, ^3J(10,11) = 7.3, H–C(10)); 6.00 (*dq*-like, ^3J(5,6) = 6.8, ^4J(6,Me–C(7) = 1.2, H–C(6)); 5.91 (*d*, ^3J(10,11) = 6.6, H–C(11)); 5.89 (*d*, ^3J(5,6) = 6.3, H–C(5)); 5.55 (*s*, H–C(8)); 5.27 (*d*, ^3J(1,2) = 4.6, H–C(1)); 4.79 (*d*, ^3J(3,4) = 5.1, H–C(4)); 3.58, 3.54 (2 *s*, MeO(O)C–C(2,3)); 3.53 (*dd*, ^3J(2,3) = 11.5, ^3J(1,2 or 3,4) = 5.2, H–C(2 or 3)); 3.32 (*dd*, ^3J(2,3) = 11, ^3J(1,2 or 3,4) = 4.9, H–C(2 or 3)); 2.37 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 2.12 (*d*, Me–C(12)); 2.09 (*d*, ^4J(Me–C(7),6) = 1.1, Me–C(7)); 1.08, 1.07 (2*d*, ^3J = 6.9, Me_2CH–C(9)).

Data of 2,3-endo-(P*)-**14a**. R_f (*t*-BuOMe/hexane 7:3) 0.36. HPLC (hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1; 1 ml/min): 5.57 min. UV/VIS (qual.; hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1): λ_{max} 338 (0.30), 258 (1.0), 250 (sh, 0.98); λ_{min} 299 (0.20). ^{1}H-NMR (300 MHz, $CDCl_3$; mixture with 25% of 2,3-*endo*-(*M**)-**14a**): 6.28 (*d*, ^3J(10,11) = 6.6, H–C(10)); 6.08–6.04 (*m*, H–C(5,6)); 5.91 (*d*, ^3J(10,11) = 6.6, H–C(11)); 5.62 (*d*, ^4J = 1.2, H–C(8)); 5.13 (*d*, ^3J(1,2) = 4.8, H–C(1)); 4.94 (*dd*, ^3J(3,4) = 5, H–C(4)); 3.62, 3.54 (2*s*, MeO(O)C–C(2,3)); 3.52 (*dd*, ^3J(2,3) = 11.1, ^3J(1,2 or 3,4) = 4.8, H–C(2 or 3)); 3.39 (*dd*, ^3J(2,3) = 11.1, ^3J(1,2 or 3,4) = 4.6, H–C(2 or 3)); 2.37 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 2.12 (*s*, Me–C(12)); 1.82 (*s*, Me–C(7)); 1.06, 1.03 (2*d*, ^3J = 6.9, Me_2CH–C(9)).

Data of 2,3-exo-(P*)-**14a**. M.p. 133.5—135.9°. UV/VIS (hexane): λ_{max} 409 (sh, 2.96), 336 (3.72), 252 (4.34), 214 (4.38), 197 (4.40); λ_{min} 302 (3.60), 232 (4.21), 207 (4.37). IR (KBr): 2996*m*, 2957*s*, 2871*m*, 1749*s*, 1729*s*, 1606*w*, 1433*s*, 1351*s*, 1321*m*, 1266*s*, 1159*s*, 1057*m*, 998*m*, 819*m*, 603*m*. ^{1}H-NMR (600 MHz, C_6D_6): 5.916 (*dd*, ^3J(10.11) = 6.6, ^4J(11,Me–C(12)) = 0.9, H–C(11)); 5.886 (*d*, ^3J(10,11) = 6.6, H–C(10)); 5.752 (*dd*, ^3J(5,6) = 6.8, ^4J(6,Me–C(7) = 1.7, H–C(6)); 5.685 (*s*, H–C(8)); 5.536 (*d*, ^3J(5,6) = 6.8, H–C(5)); 5.349 (*s*, H–C(1)); 5.232 (*s*, H–C(4)); 3.353 (*s*, MeO(O)C–C(3)); 3.332 (*s*, MeO(O)C–C(2)); 2.963 (*d*, ^3J(2,3) = 9.4, H–C(2)); 2.852 (*d*, ^3J(2,3) = 9.4, H–C(3)); 2.182 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 1.995 (br. *s*, Me–C(7)); 1.858 (br. *s*, Me–C(12)); 0.925, 0.910 (2*d*, ^3J = 6.9, Me_2CH–C(9)); assignments were verified by NOE. EI-MS: 408 (44, M^+), 377 (5, $[M - MeO]^+$), 331 (7), 264 (100), 249 (23), 224 (18), 196 (20).

On heating at 120° in toluene, 2,3-*exo*-(*P**)-**14a** underwent epimerization at the chiral axis, which led, after 5.5 h, to a thermal equilibrium mixture of 75% of 2,3-*exo*-(*P**)-**14a** and 25% of 2,3-*exo*-(*M**)-**14a**.

Data of 2,3-exo-(M*)-**14a**. ^{1}H-NMR (600 MHz, C_6D_6; mixture with 75% of 2,3-*exo*-(*P**)-**14a**): 5.848 (*d*, ^3J(5.6) = 6.3, H–C(5)); 5.803 (*dq*-like, ^3J(5,6) = 6.4, ^4J(6,Me–C(7)) = 1.2, H–C(6)); 5.728 (*d*, ^3J(10,11) = 6.5, H–C(10)); 5.668 (*dq*-like, ^3J(10,11) = 6.5, ^4J(11,Me–C(12)) = 1.4, H–C(11)); 5.624 (*s*, H–C(8)); 5.547 (*d*-like, ^4J(4,5) ≈ 1, H–C(4)); 5.170 (*s*, H–C(1)); 3.366, 3.292 (2*s*, MeO(O)C–C(2,3)); 3.162, 3.146 (*AB*, $^3J_{AB}$ = 9.4, H–C(2,3)); 2.176 (*sept.*, ^3J = 6.8, Me_2CH–C(9)); 1.903 (*s*, Me–C(12)); 1.848 (*s*, Me–C(7)); 0.937, 0.905 (2*d*, ^3J = 6.8, Me_2CH–C(9)).

2.2.2. *Dimethyl (*P**,1*S**,2*R**,3*S**,4*R**)- and (*M**,1*S**,2*R**,3*S**,4*R**)-1,2,3,4-Tetrahydro-7,8,10,12-tetramethyl-1,4-epoxybenzo[*d*]heptalene-2,3-dicarboxylate* (2,3-*exo*-(*P**)- and 2,3-*exo*-(*M**)-**14b**). A soln. of **1b** (50 mg, 0.200 mmol) and DM (1 ml) in toluene (3 ml) was heated at 120° in a sealed *Schlenk* tube during 3 d. Subsequently, the solvent was evaporated, and most of the remaining DM residue was removed from the product mixture by distillation at 90°/2 mbar in a *Kugelrohr* apparatus. The residue was purified by CC (SiO_2; *t*-BuOMe/hexane 3:2). The TLC-uniform product fraction was recrystallized from Et_2O/hexane: yellow crystals (73.0 mg, 93%) composed of a mixture of 2,3-*exo*-(*P**)- and 2,3-*exo*-(*M**)-**14b**.

Data of the 2,3-exo-(P*)*/*(M*)*-Mixture.* M.p. 147–180°. R_f (*t*-BuOMe/hexane 3:2) 0.19. IR (KBr): 2951*m*, 2930*m*, 2911*m*, 2852*w*, 1755*s*, 1739*s*, 1435*s*, 1356*m*, 1330*s*, 1242*s*, 1887*s*, 1160*s*, 1050*m*, 986*m*, 977*m*, 901*m*, 840*s*, 747*w*.

Data of 2,3-exo-(M*)-**14b**. HPLC (hexane/i-PrOH 95:5; 0.8 ml/min): 7.6 min. UV/VIS (qual.): λ_{max} 311 (0.23), 253 (1.0), 217 (0.95); λ_{min} 297 (0.23), 233 (0.72). ^{1}H-NMR (500 MHz, C_6D_6; mixture with 43% of 2,3-*exo*-(*P**)-**14b**): 5.957 (br. *s*, H–C(9)); 5.908 (*d*, ^3J(5,6) = 6.1, H–C(5)); 5.875 (*dq*-like, ^3J(5,6) = 6.1, ^4J(6,Me–C(7)) = 1.3, H–C(6)); 5.704 (br. *s*, H–C(11)); 5.575 (br. *s*, H–C(1)); 5.246 (br. *s*, H–C(4)); 3.340 (*s*, MeO(O)C–C(3)); 3.316 (*s*, MeO(O)C–C(2)); 3.098 (*d*, ^3J(2,3) = 9.4, H–C(2)); 3.021 (*d*, ^3J(2,3) = 9.4, H–C(3)); 1.867 (*d*, ^4J(6,Me–C(7)) = 0.9, Me–C(7)); 1.799 (*d*, ^4J(9,Me–C(10)) = 1.0, Me–C(10)); 1.780 (*d*, ^4J(11,Me–C(12)) = 1.0, Me–C(12)); 1.571 (*s*, Me–C(8)).

Data of 2,3-exo-(P*)-**14b**. HPLC (hexane/i-PrOH 95:5; 0.8 ml/min): 9.4 min. UV/VIS (qual.): λ_{max} 319 (0.21), 257 (1.0), 217 (0.75); λ_{min} 297 (0.17), 229 (0.64). ^{1}H-NMR (500 MHz, C_6D_6; mixture with 57% of 2,3-*exo*-(*M**)-**14b**): 5.964 (superimposed *dd*, H–C(6)); 5.927 (br. *s*, H–C(9)); 5.802 (br. *s*, H–C(11)); 5.733 (*d*, ^3J(5,6) = 6.5, H–C(5)); 5.436 (*s*, H–C(1)); 5.266 (br. *s*, H–C(4)); 3.374 (*s*, MeO(O)C–C(3)); 3.364 (*s*, MeO(O)C–C(2)); 2.928 (*d*, ^3J(2,3) = 9.4, H–C(3)); 2.901 (*d*, ^3J(2,3) = 9.4, H–C(2)); 1.998 (*d*, ^4J(6,Me–C(7)) = 0.9, Me–C(7)); 1.823 (*d*, ^4J(11,Me–C(12)) = 0.9, Me–C(12)); 1.732 (*d*, ^4J(9,Me–C(10)) =

1.0, Me–C(10)); 1.626 (*s*, Me–C(8)); assignments were verified by NOESY. EI-MS: 394 (66, M^+), 363 (9, [M – MeO]$^+$), 250 (85), 235 (100), 220 (13), 210 (57), 196 (29), 113 (71).

Heating of the mixture at 120° in toluene furnished an equilibrium mixture consisting of 65% 2,3-*exo*-(*P**)- and 35% 2,3-*exo*-(*M**)-**14b**.

2.2.3. *Dimethyl (*P**,1*S**,2*R**,3*S**,4*R**)- and (*P**,1*S**,2*S**,3*R**,4*R**)-1,2,3,4-Tetrahydro-8-isopropyl-5-methyl-1,4-epoxybenzo[*d*]heptalene-2,3-dicarboxylate* (2,3-*exo*-(*P**)- and 2,3-*endo*-(*P**)-**14c**). A soln. of **1c** (90 mg, 0.3595 mmol) and DM (132 mg, 0.916 mmol) in toluene (3 ml) was heated at 120° in a sealed *Schlenk* tube. After 22.5 h, another portion of DM (80 mg) was added. After a total time of 48 h, the solvent was evaporated, and the excess DM was removed by distillation in a *Kugelrohr* apparatus at 60°/1 mbar. The residue was purified by CC (SiO_2; hexane/Et_2O 3:2 → 1:4): 60.6 mg (50%) of 2,3-*exo*-(*P**)-**14c** and 11.9 mg (8.5%) of 2,3-*endo*-(*P**)-**14c**.

Data of 2,3-exo-*(*P**)*-**14c**. Unstable, red oil. R_f (hexane/Et_2O 1:1) 0.10. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.10–6.04 (*m*, H–C(9,11)); 5.790 (*d*, ^3J(5,6) = 7.1, H–C(5)); 5.750 (*dq*-like *dd*, ^3J(5,6) = 7.1, ^4J(6,Me–C(7)) = 0.9, H–C(6)); 5.530 (*d*, ^3J(8,9) = 7.3, H–C(8)); 5.475 (*d*, ^3J(11,12) = 11.4, H–C(12)); 5.114, 5.102 (2 br. *s*, H–C(1,4)); 3.683, 3.681 (2*s*, MeO(O)C–C(2,3)); 3.090, 3.016 (2*d*, ^3J(2,3) = 9.5, H–C(2,3)); 2.348 (*sept.*, ^3J = 6.9, Me_2CH–C(10)); 2.046 (*d*, ^4J(6,Me–C(7)) = 1.0, Me–C(7)); 1.056, 1.051 (2*d*, ^3J = 6.9, Me_2CH–C(10)). ^{1}H-NMR (300 MHz, C_6D_6): 5.900 (*dquint.*-like *d*, ^3J(8,9) = 7.4, H–C(9)); 5.762 (*dd*, ^3J(11,12) = 11.0, ^4J(9,11) = 1.6, H–C(11)); 5.530 (*dq*-like *dd*, ^3J(5,6) = 7.0, ^4J(6,Me–C(7)) = 1.3, H–C(6)); 5.410 (*d*, ^3J(8,9) = 7.6, H–C(8)); 5.382 (*d*, ^3J(5,6) = 7.1, H–C(5)); 5.324, 5.110 (2 br. *s*, H–C(1,4)); 5.245 (*d*, ^3J(11,12) = 11.0, H–C(12)); 3.369, 3.349 (2*s*, MeO(O)C–C(2,3)); 2.920, 2.849 (2*d*, ^3J(2,3) = 9.4, H–C(2,3)); 2.080 (*sept.*, ^3J = 6.9, Me_2CH–C(10)); 1.897 (*d*, ^4J(6,Me–C(7)) = 1.1, Me–C(7)); 0.892, 0.883 (2*d*, ^3J = 6.9, Me_2CH–C(10)).

Data of 2,3-endo-*(*P**)*-**14c**. Unstable, brown oil. R_f (hexane/Et_2O 1:1) 0.22. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.12–6.05 (*m*, 2 H, H–C(6,11)); 5.778 (*t*-like *AB*, $^3J \approx 7.1$, 2 H, H–C(8,9)); 5.671 (*d*, ^3J(11,12) = 11.2, H–C(12)); 5.558 (*d*, ^3J(5,6) = 7.7, H–C(5)); 5.044 (*dd*, ^3J(1,2) = 4.9, ^4J(1,3) = 1.0, H–C(1 or 4)); 4.864 (*dd*, ^3J(3,4) = 4.8, ^4J(2,4) = 1.0, H–C(4 or 1)); 3.661, 3.606 (2*s*, MeO(O)C–C(2,3)); 3.435 (*dd*, ^3J(2,3) = 10.5, ^3J(1,2) = 5.0, H–C(2 or 3)); 3.342 (*dd*, ^3J(2,3) = 11.0, ^3J(3,4) = 4.8, H–C(3 or 2)); 2.343 (*sept.*, ^3J = 6.9, Me_2CH–C(10)); 2.052 (br. *s*, Me–C(7)); 1.064, 1.041 (2*d*, ^3J = 6.9, Me_2CH–C(10)).

2.3. *With Fumaronitrile* (FN). 2.3.1. *(*P**,1*R**,2*S**,3*S**,4*S**)-, (*M**,1*R**,2*S**,3*S**,4*S**)-, (*P**,1*R**,2*R**,3*R**,4*S**)-, and (*M**,1*R**,2*R**,3*R**,4*S**)-1,2,3,4-Tetrahydro-9-isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalene-2,3-dicarbonitrile* (2-*exo*,3-*endo*-(*P**)- and 2-*exo*,3-*endo*-(*M**)-**17a**, and 2-*endo*,3-*exo*-(*P**)- and 2-*endo*,3-*exo*-(*M**)-**17a**, resp.). A soln. of **1a** (80 mg, 0.303 mmol) and FN (freshly sublimed at 80°/2 mbar; 64 mg, 0.820 mmol) in toluene (2 ml) was heated at 90° (oil bath temp.) in a sealed *Schlenk* tube during 1 h, which led to complete consumption of **1a**. The solvent was evaporated, and the excess of FN was removed by sublimation at 90°/16 mbar in a *Kugelrohr* apparatus. The residue was purified by CC (basic *Alox* IV; CH_2Cl_2). From an Et_2O/hexane soln. of the resulting oil, a yellow-colored powder precipitated (90.3 mg, 86%), according to NMR analysis consisting of a mixture of 44% of 2-*exo*,3-*endo*-(*P**)-, 17% of 2-*exo*,3-*endo*-(*M**)-, 29% of 2-*endo*,3-*exo*-(*P**)- and 10% of 2-*endo*,3-*exo*-(*M**)-**17a**.

Data of **17a**. M.p. 107.8–108.9°. R_f (*t*-BuOMe/hexane 3:2) 0.36. IR (KBr): 2959*s*, 2871*m*, 2247*m*, 1613*m*, 1434*m*, 1381*w*, 1362*w*, 1310*m*, 1016*m*, 962*m*, 919*m*, 866*m*, 818*s*, 610*m*. EI-MS: 342 (30, M^+), 264 (100, [M – $(CHCN)_2$]$^+$), 249 (44, [M – $(CHCN)_2$ – Me]$^+$), 221 (37), 209 (26), 195 (48), 165 (43), 152 (28).

Data of 2-exo,*3*-endo-*(*P**)*-**17a**. UV/VIS (hexane/i-PrOH 95:5; qual.): λ_{max} 339 (0.25), 249 (1.0), 217 (0.92); λ_{min} 305 (0.19), 231 (0.74). ^{1}H-NMR (300 MHz, $CDCl_3$, isomer mixture): 6.30–5.90 (H–C(5,6,10,11)); 5.688 (*d*, ^4J = 1.2, H–C(8)); 5.251 (*d*, ^3J(3,4) = 4.6, H–C(4)); 5.035 (*s*, H–C(1)); 3.319 (*t*-like, $^3J(3,4) \approx {}^3J(2,3) \approx 5.0$, H–C(3)); 2.935 (*d*, ^3J(2,3) = 5.2, H–C(2)); 2.14 (*d*, Me–C(7 or 12)); 2.019 (*s*, Me–C(12 or 7)); 2.39, 1.08–1.03 (Me_2CH).

Data of 2-exo,*3*-endo-*(*M**)*-**17a**. ^{1}H-NMR (300 MHz, $CDCl_3$, isomer mixture): 6.30–5.90 (H–C(5,6,10,11)); 5.639 (*d*, ^4J = 1.0, H–C(8)); 5.035 (*s*, H–C(1)); 5.110 (*d*, ^3J(3,4) = 5.4, H–C(4)); 3.334 (*dd*, ^3J(3,4) = 5.0, ^3J(2,3) = 4.1, H–C(3)); 2.715 (*d*, ^3J(2,3) = 4.0, H–C(2)); 2.14 (*d*, Me–C(7,12)); 2.39, 1.08–1.03 (Me_2CH).

Data of 2-endo,*3*-exo-*(*P**)*-**17a**. ^{1}H-NMR (300 MHz, $CDCl_3$, isomer mixture 6.30–5.90 (H–C(5,6,10,11)); 5.682 (*d*, $^4J \approx 1.2$, H–C(8)); 5.299 (*s*, H–C(4)); 5.144 (*d*, ^3J(1,2) = 5.0, H–C(1)); 3.371 (*dd*, ^3J(1,2) = 5.0, ^3J(2,3) = 3.9, H–C(2)); 2.975 (*d*, ^3J(2,3) = 3.9, H–C(3)); 2.159 (*s*, Me–C(7 or 12)); 2.14 (*s*, Me–C(12 or 7)); 2.39, 1.08–1.03 (Me_2CH).

Data of 2-endo,*3*-exo-*(*M**)*-**17a**. ^{1}H-NMR (300 MHz, $CDCl_3$, isomer mixture): 6.30–5.90 (H–C(5,6,10,11)); 5.627 (*d*, $^4J \approx 1$, H–C(8)); 5.291 (*d*, $^3J(1,2) \approx 5$, H–C(1)); 5.017 (*s*, H–C(4)); 3.297 (*dd*,

$^3J(1,2) = 5.4$, $^3J(2,3) = 5.9$, H–C(2)); 3.154 (*d*, $^3J(2,3) = 5.9$, H–C(3)); 2.14 (*s*, Me–C(7,12)); 2.39, 1.08–1.03 (Me_2CH).

2.3.2. *(*P*,1*R*,2*S*,3*S*,4*S*)-, (*M*,1*R*,2*S*,3*S*,4*S*)-, (*P*,1*R*,2*R*,3*R*,4*S*)-, and (*M*,1*R*,2*R*,3*R*,4*S*)-1,2,3,4-Tetrahydro-7,8,10,12-tetramethyl-1,4-epoxybenzo[*d*]heptalene-2,3-dicarbonitrile* (2-*exo*,3-*endo*-(*P**)-, 2-*exo*,3-*endo*-(*M**)-, 2-*endo*,3-*exo*-(*P**)-, and 2-*endo*,3-*exo*-(*M**)-**17b**). A soln. of **1b** (80.5 mg, 0.322 mmol) and FN (64 mg, 0.820 mmol) in toluene (2 ml) was heated at 90° in a sealed *Schlenk* tube during 15 h. Subsequently, the solvent was evaporated, and excess FN was removed by sublimation at 80°/2 mbar in a *Kugelrohr* apparatus. The residue was purified by CC (basic *Alox* IV; CH_2Cl_2), and the resulting solid material was recrystallized from Et_2O/pentane: 99.0 mg (94%) of orange crystals. The $CDCl_3$ soln. contained, after standing for several days, 14% of the 2-*exo*,3-*endo*-(*P**)-form, and 80% of the 2-*exo*,3-*endo*-(*M**)-form, 2.5 and 3.5% of the 2-*endo*,3-*exo*-(*P**)- and (*M**)-forms, resp.

Data of 2-exo,3-endo-*(*M**)*-**17b**. M.p. 182.0–182.8°. R_f (hexane/*t*-BuOMe 3:2) 0.22. UV/VIS (EtOH): λ_{max} 390 (sh, 2.86), 308 (sh, 3.64), 257 (4.23), 247 (4.23), 214 (sh, 4.27), 200 (4.40); λ_{min} 252 (4.22), 230 (4.09). HPLC (hexane/i-PrOH 95:5; 1.0 ml/min): 9.0 min. UV/VIS (hexane/i-PrOH 95:5): λ_{max} 309 (sh, 0.15), 263 (1.0), 219 (0.64); λ_{min} 235 (0.41). IR (KBr): 3008*m*, 2973*s*, 2943*s*, 2911*s*, 2854*m*, 2242*m*, 1657*m*, 1626*w*, 1576*m*, 1440*s*, 1372*m*, 1303*m*, 1107*m*, 1029*m*, 1004*m*, 955*m*, 924*s*, 832*s*, 652*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.391 (*d*, $^3J(5,6) = 6.0$, H–C(5)); 6.14 (superimposed *dd*, $^4J(6,Me–C(7)) = 1.4$, H–C(6)); 6.120 (br. *s*, H–C(9)); 6.020 (br. *s*, H–C(11)); 5.339 (*s*, H–C(1)); 5.163 (*d*, $^3J(3,4) = 4.9$, H–C(4)); 3.342 (*dd*, $^3J(3,4) = 4.9$, $^3J(2,3) = 4.0$, H–C(3)); 2.631 (*d*, $^3J(2,3) = 3.9$, H–C(2)); 2.092 (*d*, $^4J(11,Me–C(12)) = 1.1$, Me–C(12)); 2.021 (*d*, $^4J(6,Me–C(7)) = 1.0$, Me–C(7)); 1.987 (*d*, $^4J(9,Me–C(10)) = 1.0$, Me–C(10)); 1.678 (*s*, Me–C(8)); assignments were verified by NOESY. ^{13}C-NMR (150.9 MHz, $CDCl_3$): 139.28 (C(4a)); 137.21 (C(10)); 134.33 (C(7)); 133.57 (C(12b)); 132.33 (C(12a); 132.25 (C(9)), 132.22 (C(11)); 131.07 (C(8)); 130.80 (C(12)); 130.05 (C(7a)); 125.22 (C(6)); 124.07 (C(5)); 118.45 (N*C*–C(2)); 116.16 (N*C*–C(3)); 82.67 (C(4)); 82.11 (C(1)); 40.74 (C(2)); 37.13 (C(3)); 25.16 (*Me*–C(10)); 23.38 (*Me*–C(7)); 22.75 (*Me*–C(12)); 17.86 (*Me*–C(8)); assignments were made *via* ^{1}H,^{13}C-correlation spectra. EI-MS: 328 (43, M^+), 250 (66, $[M - NC–CH{=}CH–CN]^+$), 220 (14, $[M - (CHCN)_2 - Me]^+$), 210 (49), 196 (25), 165 (18).

Data of 2-exo,3-endo-*(*P**)*-**17b**. HPLC (hexane/i-PrOH 95:5; 1.0 ml/min): 8.3 min; UV/VIS (qual.; hexane/i-PrOH 95:5): λ_{max} 303 (0.27), 257 (0.99), 247 (1.0), 215 (0.96); λ_{min} 209 (0.26), 253 (0.98), 229 (0.73). ^{1}H-NMR (600 MHz, $CDCl_3$, isomer mixture): 6.381 (*d*, $^3J(5,6) = 6.0$, H–C(5); partially covered by *d* of H–C(5) of 2-*exo*,3-*endo*-(*M**)-form); 6.293 (*dq*-like, $^3J(5,6) = 6.4$, $^4J(6,Me–C(7)) = 1.2$, H–C(6)); signals of H–C(9,11) are superimposed by the partially covered dominant signals of H–C(6) and H–C(9) of the 2-*exo*,3-*endo*-(*M**)-form); 5.282 (*d*, $^3J(3,4) = 4.7$, H–C(4)); 5.132 (*s*, H–C(1)); 3.366 (*t*-like, $\Sigma(^3J(2,3) + ^3J(3,4)) = 10.0$, H–C(3)); 2.903 (*d*, $^3J(2,3) = 5.2$, H–C(2)); 2.007 (*d*, $^4J(6,Me–C(7)) = 1.1$, Me–C(7)); signals of Me–C(10,12) are covered by the signal of Me–C(8) of the 2-*exo*,3-*endo*-(*M**)-form; 1.724 (*s*, Me–C(8)). ^{13}C-NMR (150.9 MHz, $CDCl_3$, isomer mixture): 138.09 (C(12a)); 136.26 (C(4a)); 134.64 (C(12b)); 133.08 (C(11)); 132.46 (C(9)); 131.29 (C(8)); 131.01 (C(7)); 130.85 (C(10)); 130.38 (C(12)); 129.19 (C(7a)); 127.18 (C(6)); 123.37 (C(5)); 118.15 (N*C*–C(2)); 116.34 (N*C*–C(3)); 81.96 (C(1)); 81.30 (C(4)); 38.74 (C(3)); 36.87 (C(2)); 25.31 (*Me*–C(10)); 25.09 (*Me*–C(12)); 23.47 (*Me*–C(7)); 18.61 (*Me*–C(8)).

2.3.3. *(*P*,1*R**,2*S**,3*S**,4*R**)- and (*P**,1*R**,2*R**,3*R**,4*R**)-1,4-Epoxy-1,2,3,4-tetrahydro-10-isopropyl-7-methylbenzo[*d*]heptalene-2,3-dicarbonitrile* (2-*exo*,3-*endo*-(*P**)- and 2-*endo*,3-*exo*-(*P**)-**17c**). A soln. of **1c** (90 mg, 0.359 mmol) and FN (69 mg, 0.884 mmol) in toluene (2 ml) was heated at 90° (oil-bath temp.) in a sealed *Schlenk* tube during 3.5 h. Afterwards, the solvent was evaporated, and excess of reagent was removed by sublimation at 70–80°/10 mbar in a *Kugelrohr* apparatus. The residue was purified by CC (basic *Alox* IV; CH_2Cl_2). From an Et_2O/pentane soln. of the resulting brown-red oil, small brownish-red crystals precipitated: 52.7 mg of **17c**. A second crop (31.4 mg) of **17c** (total yield: 71%) could be isolated from the mother liquor. In an NMR sample, 7% of 2-*endo*,3-*exo*-(*P**)-**17c** were detected.

Data of 2-exo,3-endo-*(*P**)*-**17c**. M.p. 147–152°. R_f (*t*-BuOMe/hexane 7:3) 0.42. UV/VIS (EtOH): λ_{max} 441 (sh, 2.51), 348 (3.66), 261 (4.29), 206 (sh, 4.29); λ_{min} 303 (3.45), 233 (4.14). IR (KBr): 2964*s*, 2873*m*, 2240*m*, 1658*w*, 1608*m*, 1466*m*, 1449*m*, 1308*m*, 1187*m*, 1012*m*, 957*m*, 913*m*, 861*m*, 839*s*, 811*s*, 601*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.199 (superimposed *dd*, $^3J(11,12) = 11.1$, $^4J(9,11) = 1.6$, H–C(11)); 6.163 (superimposed br. *d*, H–C(9)); 5.967 (*d*, $^3J(5,6) = 7.0$, H–C(5)); 5.874 (br. *dd*, $^3J(5,6) = 7.0$, $^4J(6,Me–C(7)) = 1.3$, H–C(6)); 5.632 (*d*, $^3J(8,9) = 7.4$, H–C(8)); 5.458 (*d*, $^3J(11,12) = 11.0$, H–C(12)); 5.140 (*d*, $^3J(3,4) = 5.2$, H–C(4)); 5.104 (*s*, H–C(1)); 3.292 (*t*-like, $\Sigma((^3J(3,4) + ^3J(2,3)) = 9.6$, H–C(3)); 2.923 (*d*, $^3J(2,3) = 4.8$, H–C(2)); 2.391 (*sept.*, $^3J = 6.9$, $Me_2CH–C(10)$); 2.066 (*d*, $^4J(6,Me–C(7)) = 1.2$, Me–C(7)); 1.085, 1.072 (2*d*, $^3J = 6.9$, $Me_2CH–C(10)$). EI-MS: 328 (7, M^+), 250 (100, $[M - (CHCN)_2]^+$), 235 (23, $[M - (CHCN)_2 - Me]^+$), 182 (26), 165 (11).

Data of 2-endo,*3*-exo-*(*P**)*-**17c**. ^{1}H-NMR (300 MHz, $CDCl_3$; isomer mixture, selected signals): 5.297 (*s*, H–C(4)); 5.158 (*d*, $^3J(1,2) \approx 5$, H–C(1)); 3.290 (*t*-like, Σ ($^3J(2,3) + {}^3J(1,2)$) = 9.0, H–C(2)); 2.973 (*d*, $^3J(2,3)$ = 4.4, H–C(3)); 2.066 (Me–C(7), signal fully superimposed by that of the main isomer); 1.075, 1.063 (2*d*, mainly covered by the signals of the main isomer, $^3J = 7$, Me_2CH).

2.3.4. *(*P**,1*R**,2*S**,3*S**,4*S**)-, (*M**,1*R**,2*S**,3*S**,4*S**)-, (*P**,1*R**,2*R**,3*R**,4*S**)-, (*M**,1*R**,2*R**,3*R**,4*S**)-1,4-Epoxy-1,2,3,4-tetrahydro-9-isopropyl-4,7,12-trimethylbenzo[*d*]heptalene-2,3-dicarbonitrile* (2-*exo*,3-*endo*-(*P**)-, 2-*exo*,3-*endo*-(*M**)-,2-*endo*,3-*exo*-(*P**)-, and 2-*endo*,3-*exo*-(*M**)-**17e**). A soln. of **1e** (138 mg, 0.496 mmol) and FN (101 mg, 1.29 mmol) in toluene (4 ml) was heated at 90° (oil-bath temperature) in a sealed *Schlenk* tube during 2.5 h. Subsequently, the solvent was evaporated, and excess of reagent was removed by sublimation at 80°/2 mbar in a *Kugelrohr* apparatus. The residue was purified by CC (basic *Alox* IV; CH_2Cl_2) to afford 162 mg (quant.) of product as an orange solid foam, consisting of 42% of 2-*exo*,3-*endo*-(*P**)-, 19% of 2-*exo*,3-*endo*-(*M**)-, 29% of 2-*endo*,3-*exo*-(*P**)-, and 10% of 2-*endo*,3-*exo*-(*M**)-**17e**. R_f (hexane/Et_2O 7:3) 0.25 and 0.18.

Data of 2-exo,*3*-endo-*(*P**)*-**17e**. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.2–5.9 (H–C(5,6,10,11)); 5.681 (*d*, $^4J = 1.5$, H–C(8)); 4.957 (*s*, H–C(1)); 3.020, 2.974 (*AB*, $^3J_{AB} = 5.5$, H–C(2,3)); *ca.* 2.14 (*d*, Me–C(7 or 12)); 2.013 (*d*-like, Me–C(12 or 7)); 1.791 (*s*, Me–C(4)); 2.39/2.40 and 1.1–1.0 (i-Pr).

Data of 2-exo,*3*-endo-*(*M**)*-**17e**. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.2–5.9 (H–C(5,6,10, 11)); 5.637 (*d*, ^4J = 1.1, H–C(8)); 5.258 (*s*, H–C(1)); 3.055, 2.760 (*AB*, $^3J_{AB} = 4.1$, H–C(2,3)); *ca.* 2.14 (*d*, Me–C(7,12)); 1.748 (*s*, Me–C(4)); 2.39/2.40 and 1.1–1.0 (i-Pr).

Data of 2-endo,*3*-exo-*(*P**)*-**17e**. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.2–5.9 (H–C(5,6,10,11)); 5.676 (*d*, $^4J = 1.6$, H–C(8)); 5.049 (*d*, $^3J(1,2) = 5.1$, H–C(1)); 3.453 (*dd*, $^3J(1,2) = 5.1$, $^3J(2,3) = 4.2$, H–C(2)); 2.933 (*d*, $^3J(2,3)$ = 4.2, H–C(3)); 2.16 (*d*-like, Me–C(7 or 12)); *ca.* 2.14 (*d*, Me–C(7 or 12)); 1.820 (*s*, Me–C(4)); 2.39/2.40 and 1.1–1.0 (i-Pr).

Data of 2-endo,*3*-exo-*(*M**)*-**17e**. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.2–5.9 (H–C(5,6,10, 11)); 5.620 (*d*-like, H–C(8)); 5.203 (*d*, $^3J(1,2) = 4.9$, H–C(1)); 3.370 (*dd*, $^3J(1,2) = 5.0$, $^3J(2,3) = 5.9$, H–C(2)); 3.157 (*d*, $^3J(2,3)$ = 5.9, H–C(3)); *ca.* 2.14 (*d*, Me–C(7,12)); 1.742 (*s*, Me–C(4)); 2.39/2.40 and 1.1–1.0 (i-Pr).

2.4. *With Hex-3-yne-2,5-dione.* 2.4.1. *(*P**,1*S**,4*R**)- and (*M**,1*S**,4*R**)-2,3-Diacetyl-1,4-dihydro-9-isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalene* ((*P**)- and (*M**)-**19a**). In a *Schlenk* tube, a soln. of **1a** (123 mg, 0.465 mmol) and hex-3-yne-2,5-dione (73 mg, 0.663 mmol) [17] in toluene (5 ml) was stirred at r.t. overnight. Then, the solvent was evaporated, and the residue was purified by CC (SiO_2; Et_2O/hexane 3:2) to yield 173 mg (99%) of a mixture of 87% (*M**)- and 13% (*P**)-**19a** as a dark-red viscous oil. R_f (Et_2O/hexane 3:2) 0.10. IR ($CHCl_3$): 2965*m*, 2874*w*, 1687*s*, 1603*m*, 1364*s*, 1308*m*, 836*m*. CI-MS (NH_3): 375 (100, $[M+H]^+$), 333 (6), 264 (7), 237 (7), 172 (21).

*Data of (*P**)-***19a**. R_t HPLC (hexane/i-PrOH 98:2; 0.8 ml/min): 5.75 min. UV/VIS (qual.; hexane/i-PrOH 98:2): λ_{max} 381 (sh, 0.12), 317 (sh, 0.27), 247 (1), 219 (0.91); λ_{min} 231 (0.85). ^{1}H-NMR (300 MHz, $CDCl_3$; isomer mixture, selected signals): 6.22 (*d*, $^3J(5,6) = 6.2$, H–C(5)); 6.13 (*dq*-like, $^3J(10,11) = 6.8$, $^4J(11,Me–C(12) \approx 1.3$, H–C(11)); 5.98 (*dq*-like, $^3J(5,6) = 6.8$, $^4J(6,Me–C(7)) \approx 1.3$, H–C(6)); 5.68 (*d*, $^4J \approx 1.1$, H–C(8)); 5.49, 5.47 (2*d*, $^4J \approx 1.5$, H–C(1,4)); 2.40, 2.35 (2*s*, Ac–C(2,3)); 2.10, 1.96 (2 br. *s*, Me–C(7,12)); 1.08, 1.05 (2 *t*-like *d*, ^3J = 6.9, Me_2CH–C(9)).

*Data of (*M**)-***19a**. HPLC (hexane/i-PrOH 98:2; 0.8 ml/min): 6.07 min. UV/VIS (qual.; hexane/i-PrOH 98:2): λ_{max} 379 (sh, 0.09), 303 (sh, 0.30), 247 (1), 219 (0.87); λ_{min} 226 (0.82). ^{1}H-NMR (300 MHz, $CDCl_3$; isomer mixture): 6.329 (*d*, $^3J(5,6) = 6.6$, H–C(5)); 6.058 (*dq*-like, $^3J(10,11) = 6.3$, $^4J(11,Me–C(12)) = 1.4$, H–C(11)); 5.949 (*dq*-like, $^3J(5,6) = 6.7$, $^4J(6,Me–C(7)) = 1.4$, H–C(6)); 5.909 (*d*, $^3J(10,11) = 6.3$, H–C(10)); 5.637 (br. *s*, H–C(8)); 5.609 (*d*-like, H–C(1)); 5.389 (*d*, $^5J = 1.3$, H–C(4)); 2.329 (*sept.*, $^3J = 6.9$, $Me_2CH–C(9)$); 2.308, 2.267 (2*s*, Ac–C(2,3)); 2.180, (br. *s*, Me–C(12)); 2.117 (*d*, $^4J(6,Me–C(7)) = 1.2$, Me–C(7)); 0.986, 0.971 (2*d*, $^3J = 6.9$, Me_2CH–C(9)).

2.5. *With (*E*)/(*Z*)-Hex-3-ene-2,5-dione.* 2.5.1. *(*P**,1*S**,2*S**,3*S**,4*R**)-, (*M**,1*S**,2*S**,3*S**,4*R**)-, (*P**,1*S**,2*R**,3*R**,4*R**)-, and (*P**,1*S**,2*R**,3*S**,4*R**)-2,3-Diacetyl-1,2,3,4-tetrahydro-9-isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalene* (2-*endo*,3-exo-(*P**)-, 2-*endo*,3-*exo*-(*M**)-, 2-*exo*,3-*endo*-(*P**)-, and 2-*exo*,3-*exo*-(*P**)-**22a**). A soln. of **1a** (200 mg, 0.756 mmol) and (*E*)/(*Z*)-hex-3-ene-2,5-dione (490 mg, 4.37 mmol) [18] in toluene (6 ml) was heated at 120° in a sealed *Schlenk* tube during 63 h. Subsequently, the solvent was evaporated, and excess of reagent was removed from the product mixture by sublimation at 90°/2 mbar in a *Kugelrohr* apparatus. This furnished a crude product mixture, which was separated by CC (SiO_2; *t*-BuOMe/hexane 3:2): *Fraction 1* afforded 138 mg (48%) of a brownish-yellow oil, representing a 55:45 mixture of 2-*exo*,3-*endo*-(*P**)- and 2-*endo*,3-*exo*-(*M**)-**22a**; *Fraction 2* gave 117.8 mg of a dark-yellow crystalline material. Recrystallization from *t*-BuOMe/hexane yielded 78.5 mg (28%) of 2-*endo*,3-*exo*-(*P**)-**22a** as fluffy orange

needles contaminated with dark-red cubes (*ca.* 2%) of 2-*exo*,3-*exo*-(*P**)-**22a**, which could be separated mechanically.

Data of 2-endo,*3*-exo-*(*M**)*-**22a**. Light-red oil. R_f (*t*-BuOMe/hexane 7:3) 0.28. HPLC (hexane/i-PrOH 97:3; 1 ml/min): 7.2 min. UV/VIS (qual.; hexane/i-PrOH 97:3): λ_{max} 321 (sh, 0.24), 257 (1.0), 219 (0.94); λ_{min} 233 (0.66). ^{1}H-NMR (300 MHz, C_6D_6; isomer mixture): 5.985 (*d*, $^3J(5,6) = 6.3$, H–C(5)); 5.883 (*dq*-like, $^3J(5,6) = 6.3$, $^4J(6,Me–C(7)) = 1.5$, H–C(6)); 5.73–5.68 (covered, H–C(6,10,11)); 5.558 (*d*, $^4J(8,10) = 1.2$, H–C(8)); 5.316 (*s*, H–C(4)); 4.696 (*d*, $^3J(1,2) = 5.4$, H–C(1)); 3.72–3.67 (superimposed *m*, H–C(2)); 3.361 (*d*, $^3J(2,3) = 4.5$, H–C(3)); 2.328 (covered, $Me_2CH–C(9)$); 1.956 (*d*, $^4J(11,Me–C(12)) = 1.0$, Me–C(12)); 1.896 (br. *s*, Me–C(7)); 1.751, 1.644 (2*s*, Ac–C(2,3)); 1.15 (partially covered *d*, $^3J = 6.9$, $Me_2CH–C(9)$). ^{1}H-NMR (300 MHz, $CDCl_3$; isomer mixture): 6.11–5.98 (superimposed *m*, H–C(5,6,10,11)); 5.543 (*s*, H–C(8)); 5.226 (*s*, H–C(4)); 5.019 (*d*, $^3J(1,2) = 5.4$, H–C(1)); 3.68–3.63 (superimposed *t*-like, H–C(2)); 3.139 (*d*, $^3J(2,3) = 4.5$, H–C(3)); 2.41 (covered, $Me_2CH–C(9)$); 2.19 (superimposed *d*, Me–C(12)); 2.15 (br. *s*, Me–C(7)); 2.12, 2.11 (2*s*, Ac–C(2,3)); 1.08 (partially covered *t*, $Me_2CH–C(9)$).

Data of 2-exo,*3*-endo-*(*P**)*-**22a**. HPLC (hexane/i-PrOH 97:3; 1 ml/min): 10.8 min. UV/VIS (qual.; hexane/i-PrOH 97:3): λ_{max} 337 (0.24), 254 (1.0), 219 (0.97); λ_{min} 304 (0.17), 233 (0.71). ^{1}H-NMR (300 MHz, C_6D_6, isomer mixture): 5.816 (*d*, $^3J(5,6) = 6.3$, H–C(5)); 5.741 (*s*-like *AB*, H–C(10,11)); *ca.* 5.71 (covered, H–C(6)); 5.575 (*s*, H–C(8)); 5.135 (*d*, $^3J(3,4) \approx 4.7$, H–C(4)); 4.761 (*s*, H–C(1)); 3.72–3.67 (superimposed *m*, H–C(3)); 3.579 (*d*, $^3J(2,3) = 5.5$, H–C(4)); 2.307 (covered, $Me_2CH–C(9)$); 1.950 (*s*, Me–C(12)); 1.847 (*t*-like, Me–C(7)); 1.765, 1.702 (2*s*, Ac–C(2,3)); 1.15 (partially covered *d*, $^3J = 6.9$, $Me_2CH–C(9)$). ^{1}H-NMR (300 MHz, $CDCl_3$, isomer mixture): 6.11–5.98 (superimposed *m*, H–C(5,6,10,11)); 5.543 (*s*, H–C(8)); 5.349 (*d*, $^3J(3,4) = 5.2$, H–C(4)); 4.897 (*s*, H–C(1)); 3.68–3.63 (superimposed *t*-like, H–C(3)); 3.558 (*d*, $^3J(2,3) = 5.4$, H–C(2)); 2.40 (covered, $Me_2CH–C(9)$); 2.19 (superimposed *d*, Me–C(12)); 2.12, 2.11 (2*s*, Ac–C(2,3)); 2.08 (*d*, $^4J(6,Me–C(7)) = 1.2$, Me–C(7)); 1.10 (partially covered *t*, $Me_2CH–C(9)$).

Data of 2-endo,*3*-exo-*(*P**)*-**22a**. Dark-yellow crystals from Et_2O/hexane. M.p. 141–144°. R_f (*t*-BuOMe/hexane 7:3) 0.19. UV/VIS (hexane): λ_{max} 336 (3.69), 252 (4.32), 214 (4.36); λ_{min} 302 (3.57), 232 (4.18), 206 (4.34). IR (KBr): 3001*w*, 2958*s*, 1704*s*, 1618*w*, 1431*m*, 1360*s*, 1316*m*, 1179*m*, 994*w*, 865*m*, 815*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.143 (*dq*-like, $^3J(10,11) = 6.6$, $^4J(11,Me–C(12)) = 1.4$, H–C(11)); 5.954 (*d*, $^3J(10,11) = 6.5$, H–C(10)); 5.854 (*dq*-like, $^3J(5,6) = 6.8$, $^4J(6,Me–C(7)) = 1.3$, H–C(6)); 5.785 (*d*, $^3J(5,6) = 6.8$, H–C(5)); 5.620 (*d*, $^4J(8,10) = 1.1$, H–C(8)); 5.271 (*d*, $^3J(3,4) = 5.2$, H–C(1)); 4.934 (*s*, H–C(4)); 3.691 (*t*-like, $\Sigma(^3J(1,2) + {}^3J(2,3)) = 10.3$, H–C(2)); 3.296 (*d*, $^3J(3,4) = 5.2$, H–C(3)); 2.359 (*sept.*, $^3J = 6.9$, $Me_2CH–C(9)$); 2.232, 2.221 (2*s*, Ac–C(2,3)); 2.095 (*d*, $^4J(11,Me–C(12)) = 1.2$, Me–C(12)); 2.085 (*t*-like, Me–C(7)); 1.055, 1.028 (2*d*, $^3J = 6.9$, $Me_2CH–C(9)$). EI-MS: 376 (27, M^+), 264 (100, $[M - Ac–CH{=}CH–Ac]^{+\cdot}$), 249 (29), 196 (27), 165 (17), 152 (10).

Data of 2-exo,*3*-exo-*(*P**)*-**22a**. Dark-red crystals from Et_2O/hexane. M.p. 164.7–165.7°. R_f (*t*-BuOMe/hexane 7:3) 0.19. UV/VIS (hexane): λ_{max} 405 (sh, 2.62), 338 (3.589), 252 (4.23), 215 (4.29); λ_{min} 304 (3.47), 232 (4.08). ^{1}H-NMR (300 MHz, C_6D_6): 5.928 (br. *s*, with satellites at 5.952 and 5.902, $^3J(10,11) \approx 7.5$, H–C(10,11)); 5.843 (*dq*-like, $^3J(5,6) = 6.9$, $^4J(6,Me–C(7)) = 1.5$, H–C(6)); 5.708 (*s*, H–C(8)); 5.557 (*d*, $^3J(5,6) = 6.7$, H–C(5)); 5.148 (*d*-like, H–C(1 or 4)); 4.876 (*s*, H–C(4 or 1)); 2.695, 2.645 (*AB*, $^3J_{AB} = 9.6$, H–C(2,3)); 2.206 (*sept.*, $^3J = 6.9$, $Me_2CH–C(9)$); 2.038 (*d*, $^4J(11,Me–C(12)) = 1.2$, Me–C(12)); 1.833, 1.807 (2*s*, Ac–C(2,3)); 1.751 (*s*, Me–C(7)); 0.949, 0.935 (2*d*, $^3J = 6.9$, $Me_2CH–C(9)$).

2.5.2. *(*P**,1*S**,2*S**,3*S**,4*R**)- and (*M**,1*S**,2*S**,3*S**,4*R**)-, (*P**,1*S**,2*R**,3*R**,4*R**)-, (*M**,1*S**,2*R**,3*R**,4*R**)-, (*P**,1*S**,2*R**,3*S**,4*R**)-, and (*M**,1*S**,2*R**,3*S**,4*R**)-2,3-Diacetyl-1,2,3,4-tetrahydro-7,8,10,12-tetramethyl-1,4-epoxybenzo[*d*]heptalene* (2-*endo*,3-*exo*-(*P**)-, 2-*endo*,3-*exo*-(*M**)-, 2-*exo*,3-*endo*-(*P**)-, 2-*exo*,3-*endo*-(*M**)-, 2-*exo*,3-*exo*-(*P**)- and 2-*exo*,3-*exo*-(*M**)-**22b**). A soln. of **1b** (73.5 mg, 0.294 mmol) and (*E*)/(*Z*)-hex-3-en-2,5-dione (190 mg, 1.69 mmol) in toluene (2 ml) was heated at 120° in a sealed *Schlenk* tube during 63 h. Workup as describe for **22a** furnished a semicrystalline residue, which was treated with a small amount of Et_2O. The solvent was then decanted from the bright-yellow crystalline precipitate of 2-*endo*,3-*exo*-(*P**)-**22b** (19.3 mg, 18%). The filtrate was purified by CC (SiO_2; *t*-BuOMe/hexane 7:3). The first fraction consisted of **1b** (10.9 mg, 15%). The second fraction represented a yellow oil (33.1 mg), from which, by dissolution in an Et_2O/hexane mixture, dark-yellow crystals of 2-*exo*,3-*endo*-(*M**)-**22b** (25.2 mg, 24%) were obtained, which still contained 4% of 2-*endo*,3-*exo*-(*M**)-**22b**. The fourth fraction, a yellow oil (22.7 mg), gave, on treatment with Et_2O/pentane, a small amount of crystalline material (5.2 mg), identified as 2-*endo*,3-*exo*-(*P**)- and 2-*exo*,3-*exo*-**22b** (presumably (*P**)-configured) in a ratio of 2:1.

Data of 2-exo,*3*-endo-*(*M**)-**22b**. M.p. 144–158°. R_f (*t*-BuOMe/hexane 7:3) 0.25. UV/VIS (hexane): λ_{max} 388 (sh, 2.89), 303 (3.66), 255 (4.27), 202 (4.41); λ_{min} 300 (3.66), 232 (4.14), 195 (4.40). IR (KBr): 2967*m*, 2940*m*, 2912*m*, 1706*s*, 1627*w*, 1442*m*, 1359*s*, 1311*m*, 1278*m*, 1172*s*, 1026*m*, 987*m*, 869*m*, 824*s*. ^{1}H-NMR (600 MHz,

$CDCl_3$): 6.199 (*d*, $^3J(5,6) = 6.1$, H–C(5)); 6.097 (br. *s*, H–C(9)); 6.044 (*dq*-like, $^3J(5,6) = 6.1$, $^4J(6,Me–C(7)) = 1.3$, H–C(6)); 6.012 (br. *s*, H–C(11)); 5.206 (*s*, H–C(1)); 5.081 (*d*, $^3J(3,4) = 5.4$, H–C(4)); 3.653 (*t*-like, $\Sigma(^3J(2,3) + ^3J(3,4)) = 9.9$, H–C(3)); 3.077 (*d*, $^3J(2,3) = 4.5$, H–C(2)); 2.204 (*s*, Ac–C(2)); 2.107 (*d*, $^4J(11,Me–C(12)) = 0.9$, Me–C(12)); 2.052 (*s*, Ac–C(3)); 2.001 (br. *s*, 6 H, Me–C(7,10)); 1.640 (*s*, Me–C(8)); assignments were verified by ROESY. EI-MS: 362 (42, $M^{+\cdot}$), 319 (7, $[M - C(O)Me]^+$), 250 (78, $[M - Ac–CH=CH–Ac]^+$), 235 (100), 210 (57), 196 (30), 165 (22).

Data of 2-endo,*3*-exo-*(M*)*-**22b**. ^{1}H-NMR (600 MHz, $CDCl_3$; isomer mixture): 6.240 (*d*, $^3J(5,6) = 6.4$, H–C(5)); 6.152 (br. *s*, H–C(9)); 6.082 (*dq*-like, partially covered, $^3J(5,6) = 6.3$, $^4J(6,Me–C(7)) = 1.5$, H–C(6)); 5.930 (br. *s*, H–C(11)); 5.393 (*d*, $^3J(3,4) = 5.4$, H–C(1)); 4.938 (*s*, H–C(4)); 3.675 (*t*-like, $\Sigma(^3J(1,2) + ^3J(2,3)) \approx 11$, H–C(2)); 3.477 (*d*, $^3J(2,3) = 5.4$, H–C(3)); 2.191 (*s*, Ac–C(3)); 2.121 (*s*, Ac–C(2)); 2.098 (*d*, $^4J(11,Me–C(12)) = 1.0$, Me–C(12)); 1.983 (br. *s*, Me–C(10)); 1.952 (*d*, $^4J(6,Me–C(7)) = 0.9$, Me–C(7)); 1.668 (*s*, Me–C(8)); assignments of the signals were verified by ROESY.

Data of 2-endo,*3*-exo-*(P*)*-**22b**. Subl. point ≈ 245°. UV/VIS (EtOH): λ_{max} 319 (3.59), 256 (4.23), 200 (4.29); λ_{min} 298 (3.56), 230 (4.08). IR (KBr): 2971*m*, 2945*m*, 2905*m*, 1705*s*, 1436*m*, 1363*s*, 1187*s*, 1016*w*, 978*m*, 846*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.071 (br. *s*, H–C(9,11)); 6.054 (*dd*-like, partially covered, $^3J(5,6) \approx 6$, $^4J(6,Me–C(7)) = 1.4$, H–C(6)); 5.971 (*d*, $^3J(5,6) = 6.4$, H–C(5)); 5.303 (*d*, $^3J(1,2) = 5.5$, H–C(1)); 5.010 (*s*, H–C(4)); 3.731 (*t*-like, $\Sigma(^3J(1,2) + ^3J(2,3)) \approx 10.4$, H–C(2)); 3.253 (*d*, $^3J(2,3) = 5.2$, H–C(3)); 2.239, 2.253 (2*s*, Ac–C(2,3)); 2.048 (br. *s*, Me–C(12)); 1.967, 1.963 (2 br. *s*, 6 H, Me–C(7,10)); 1.692 (*s*, Me–C(8)). EI-MS: 362 (46, M^+), 319 (7, $[M - C(O)Me]^+$), 250 (85, $[M - Ac–CH=CH–Ac]^{+\cdot}$), 235 (100), 210 (51), 196 (26), 165 (17).

Data of 2-exo,*3*-exo-*(P*)*-**22b**. Mixture of 65% 2-*endo*,3-*exo*-(*P**)- and 35% 2-*exo*,3-*exo*-**22b**. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.151 (*s*, H–C(9)); 6.12–6.05 (H–C(5,6,11)); 5.217 (*d*-like, $^4J(1,4) \approx 1.2$, H–C(1 or 4)); 5.108 (*d*-like, $^4J(4,1) \approx 1.2$, H–C(4 or 1)); 3.131, 3.063 (*AB*, $^3J_{AB} = 9.3$, H–C(2,3)); 2.208, 2.172 (2*s*, Ac–C(2,3)); *ca.* 1.96 (Me–C(10), covered); 1.933 (*d*, $^4J(6,Me–C(7)) = 1.2$, Me–C(7)); 1.704 (*s*, Me–C(8)).

2.6. *With Phenyl Ethenesulfonate.* 2.6.1. *Phenyl (*P**,1*S**,2*R**,4*S**)- and (*M**,1*S**,2*R**,4*S**)-9-Isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalene-2-sulfonate* (*exo-(P**)- and *exo-(M**)-**25a**), *as well as Phenyl (*P**,1*R**,3*S**,4*R**)-, (*M**,1*R**,3*R**,4*R**)-, (P*,1R*,3R*,4R*)-, and (*M**,1*R**,3*R**,4*R**)-9-Isopropyl-7,12-dimethyl-1,4-epoxybenzo[d]heptalene-3-sulfonate* (*exo-*(*P**)-, *exo-*(*M**)-, *endo-*(*P**)-, and *endo-*(*M**)-**26a**). A soln. of **1a** (120 mg, 0.454 mmol) and phenyl ethenesulfonate (102 mg, 0.554 mmol; *Fluka purum*) in toluene (3.5 ml) was heated at 120° in a sealed *Schlenk* tube during 23 h. Subsequently, the solvent was evaporated, and the residue was purified by CC (SiO_2; hexane/AcOEt 7:3): orange-colored foam (208 mg) consisting of a mixture of three stereo- and regioisomers in a ratio of 43.0:38.5:18.5, whereby all three consisted of their (*P**)- and (*M**)-epimers in ratios of 83:17, which represents the thermal equilibrium ratio (*cf. Scheme 21*). Further purification by prep. HPLC (*Spherisorb CN*, 5 μm, 20 × 250 mm, hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1; 14 ml/min) furnished two main fractions. Recrystallization of the solid material of each of these fractions from Et_2O/hexane yielded *exo-*(*P**)-**25a** (61 mg, 30%) as light-red crystals, and *exo-*(*P**)-**26a** (46.7 mg, 23%) as light-yellow crystals.

Data of exo-(P*)-**25a**. M.p. ≈ 147–153°. R_f (hexane/AcOEt 7:3) 0.34. UV/VIS (hexane): λ_{max} 404 (sh, 2.64), 336 (3.45), 273 (sh, 3.93), 251 (4.10), 213 (sh, 4.23), 200 (4.27); λ_{min} 303 (3.34), 232 (3.96). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.42–7.26 (*m*, 5 arom. H); 6.150 (br. *d*, $^3J(10,11) = 6.6$, H–C(11)); 5.971 (superimposed *d*, H–C(10)); 5.959 (*s*-like *AB*, H–C(5,6)); 5.656 (*s*, H–C(8)); 5.262 (*s*, H–C(1)); 5.167 (*d*, $^3J(4,3) = 4.8$, H–C(1)); 3.614 (*q*, $^3J(2,3) = 5.4$, 8.6, H–C(2)); 2.496 (*dt*-like, $^2J(3,3) = 12.4$, $^3J(2,3) = 5.4$, H–C(3)); 2.374 (*sept.*, $^3J \approx 7.3$, $Me_2CH–C(9)$); 2.124, 2.059 (2*s*, Me–C(7,12)); 2.007 (*q*, $^2J(3,3) = 12.3$, $^3J(2,3) = 8.7$, H–C(3)); 1.064, 1.039 (2*d*, $^3J \approx 7.3$, $Me_2CH–C(9)$). CI-MS (NH_3): 466 (54, $[M + NH_4]^+$), 449 (100, $[M + H]^+$), 412 (16, $[M + NH_4 - MeC{\equiv}CMe]^+$), 293 (75, $[M + H - SO_3–C_6H_4]^+$), 275 (37, $[M + H - SO_3–C_6H_4 - H_2O]^+$), 258 (54, $[M + H - CH_2{=}CH–SO_3Ph]^+$), 213 (30).

Data of exo-(P*)-**26a**. M.p. ≈ 138–148°. R_f (hexane/AcOEt 7:3) 0.34. UV/VIS (hexane): λ_{max} 406 (sh, 2.88), 336 (3.69), 274 (sh, 4.17), 251 (4.34), 213 (sh, 4.46), 198 (4.51); λ_{min} 303 (3.58), 231 (4.20), 197 (4.50). IR (KBr): 2957*s*, 2869*m*, 1657*w*, 1612*w*, 1587*w*, 1489*m*, 1446*m*, 1360*s*, 1301*m*, 1192*s*, 1167*s*, 1145*s*, 910*m*, 882*s*, 774*s*, 587*m*, 528*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.44–7.26 (*m*, 5 arom. H); 6.127 (br. *d*, $^3J(10,11) = 6.6$, H–C(11)); 6.013 (*d*, $^3J = 6.8$, H–C(5)); 6.0–5.9 (*m*, 2 H, H–C(6,10)); 5.630 (*s*, H–C(8)); 5.445 (*s*, H–C(4)); 4.927 (*d*, $^3J(1,2) = 5.0$, H–C(1)); 3.495 (*dd*, $^3J(2_{endo},3) = 8.7$, $^3J(2_{exo},3) = 4.6$, H–C(3)); 2.536 (*dt*, $^2J(2,2) = 12.8$, $^3J(1,2) = 5.0$, $^3J(2_{exo},3) = 4.6$, $H_{exo}–C(2)$); 2.371 (*sept.*, $^3J = 7.1$, $Me_2CH–C(9)$); *ca.* 2.12 (*dd*, $^2J(2,2) = 12.8$, $^3J(2_{endo},3) = 8.7$, $H_{endo}–C(2)$); 2.127, 1.986 (2*s*, Me–C(7,12)); 1.063, 1.036 (2*d*, $^3J = 7.1$, $Me_2CH–C(9)$). CI-MS (NH_3): 466 (81, $[M + NH_4]^+$), 449 (100, $[M + H]^+$), 391(11, $[M + H - MeC{\equiv}CH - H_2O]^+$), 293 (67, $[M + H - SO_3–C_6H_4]^+$), 275 (45, $[M + H - SO_3–C_6H_4 - H_2O]^+$), 265 (50, $[M + H - CH_2{=}CH–SO_3Ph]^+$), 202 (17).

3. *Rearrangements.* – 3.1. *Acid-Catalyzed Transformation of* **4**. 3.1.1. *Formation of Dimethyl 4-Hydroxy-9-isopropyl-7,12-dimethylbenzo[*a*]heptalene-2,3-dicarboxylate* (**5a**) *and Dimethyl 9-Isopropyl-7-methyl-12-[(tri-*

fluoroacetoxy)methyl]benzo[a]heptalene-2,3-dicarboxylate (**6a**). *Method A*. To a soln. of crystalline (*P**)-**4a** (170.5 mg, 0.419 mmol) in $CHCl_3$ (4 ml), trifluoroacetic acid (TFA) (100 µl, 148 mg, 1.30 mmol) was added, and the mixture was heated at reflux for 3 h. A further amount of TFA (50 µl) was added, and the mixture was heated at reflux for another 1 h. Subsequently, the soln. was allowed to cool to ambient temp., diluted with Et_2O (50 ml) washed with sat. aq. $NaHCO_3$ soln. (2 × 30 ml) and brine (1 × 30 ml), dried ($MgSO_4$), filtered, and evaporated at reduced pressure. The resulting orange oily residue was purified by CC (SiO_2, hexane/AcOEt 7:1) to afford a 78:22 mixture of **5a** and **6a** (141.6 mg, 83%). From a hexane soln., **5a** was obtained as orange crystals (79.1 mg). A second amount of **5a** was isolated from the mother liquor by prep. HPLC (*Spherisorb CN*, 5 µm, 20 × 250 mm, 1.5% i-PrOH in hexane).

Method B. Only **5a** was formed when (*P**)-**4a** (29.5 mg, 0.072 mmol) was heated at reflux in MeOH (2 ml) in the presence of conc. aq. HCl soln. (60 µl) for 48 h. Workup yielded semicrystalline **5a** (22.2 mg, 75%), which was recrystallized from hexane (15.6 mg, 53%).

Method C. **5a** was formed as the sole product, when a soln. of (*P**)-**4a** (28.1 mg, 0.069 mmol) in cyclohexane (1 ml) was heated in a sealed *Schlenk* tube in the presence of *Amberlyst 15* (36 mg; *Fluka*, H^+-form; 20–50 mesh) at 80° for 19 h. Workup gave crude **5a** (18.0 mg, 64%), which was recrystallized from hexane (13.6 mg, 48%).

Data of **5a**. M.p. 159–161°. R_f (hexane/AcOEt 7:3) 0.40. UV/VIS (hexane): λ_{max} 383 (sh, with tailing up to 500 nm, 3.33), 319 (4.11), 274 (4.32), 254 (4.34), 220 (sh, 4.48), 207 (4.49); λ_{min} 301 (4.03), 264 (4.30), 241 (4.32). IR (KBr): 3126*w* (OH···O=C), 3019*m*, 2953*s*, 2865*m*, 1735*s*, 1677*s*, 1595*m*, 1552*m*, 1530*m*, 1435*s*, 1332*s*, 1297*s*, 1265*s*, 1206*s*, 1155*s*, 1021*s*, 979*m*, 802*s*, 785*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 11.145 (*s*, HO–C(4)); 7.183 (*d*, ^3J(5,6) = 12.0, H–C(5)); 6.621 (*s*, H–C(1)); 6.419 (*d*, ^3J(10,11) = 11.9, H–C(11)); 6.411 (*d*, ^3J(5,6) = 12.0, H–C(6)); 6.379 (*d*, ^3J(10,11) = 11.9, H–C(10)); 5.699 (br. *s*, H–C(8)); 3.918 (*s*, MeO(O)C–C(3)); 3.861 (*s*, MeO(O)C–C(2)); 2.551 (*sept.*, ^3J = 7.0, Me_2CH–C(9)); 1.705 (br. *s*, Me–C(7)); 1.639 (*s*, Me–C(12)); 1.148, 1.134 (2*d*, ^3J = 7.0, Me_2CH–C(9)); assignments of the signals were verified by NOESY. ^{13}C-NMR (125.8 MHz, $CDCl_3$): 170.04 (MeO(O)*C*–C(3)); 169.61 (MeO(O)*C*–C(2)); 158.99 (C(4)); 147.83 (C(9)); 142.46 (C(7)); 135.83 (C(11)); 135.47 (C(2)); 135.19 (C(6)); 134.48 (C(7a)); 133.77 (C(12a)); 132.32 (C(10)); 128.97 (C(4a)); 128.85 (C(12b)); 125.06 (C(5)); 122.55 (C(8)); 120.28 (C(1)); 107.67 (C(3)); 53.07 (*Me*O(O)C–C(2)); 52.76 (*Me*O(O)C–C(3)); 34.80 (Me_2*C*H–C(10)); 22.96, 22.90 (Me_2CH–C(10)); 19.41 (*Me*–C(12)); 17.22 (*Me*–C(7)); assignments were made *via* ^{1}H,^{13}C-correlation spectra. EI-MS: 406 (100, M^+), 374 (37, [*M* – MeOH]$^+$), 334 (44), 306 (28), 229 (18), 215 (31), 202 (42).

Data of **6a**. Yellow oil. R_f (hexane/AcOEt 7:3) 0.40. UV/VIS (hexane): λ_{max} *ca.* 400 (sh, with long tailing up to 500 nm, 3.10), 336 (3.83), 296 (sh, 4.15), 261 (4.59), 224 (4.58); λ_{min} 324 (3.82), 240 (4.46), 215 (4.56). IR ($CHCl_3$): 2962*m*, 2872*w*, 1782*s*, 1727*s*, 1601*w*, 1460*m*, 1437*s*, 1338*m*, 1293*s*, 1175*s*, 1144*s*, 1054*m*, 970*w*, 919*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.620 (*s*, H–C(4)); 7.462 (*s*, H–C(1)); 6.880 (*d*, ^3J(5,6) = 11.8, H–C(5)); 6.583 (*dd*, ^3J(10,11) = 11.9, ^4J(8,10) = 1.2, H–C(10)); 6.480 (*d*, ^3J(10,11) = 11.9, H–C(11)); 6.415 (*d*, ^3J(5,6) = 11.8, H–C(6)); 5.681 (br. *s*, H–C(8)); 4.788, 4.363 (2*d*, ^2J = 11.6, F_3CC(O)OCH_2–C(12)); 3.929 (*s*, MeO(O)C–C(3)); 3.878 (*s*, MeO(O)C–C(2)); 2.599 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 1.760 (*s*, Me–C(7)); 1.174, 1.154 (2*d*, ^3J = 6.9, Me_2CH–C(9)); assignments of the signals were verified by ROESY. ^{13}C-NMR (125.8 MHz, $CDCl_3$): 168.03 (MeO(O)*C*–C(3)); 167.24 (MeO(O)*C*–C(2)); 157.02 (*d*, $^1J \approx 46$, F_3CC(O)OCH$_2$–C(12)); 148.62 (C(9)); 140.67 (C(4a)); 139.56 (C(12a)); 135.90 (C(12b)); 135.61 (C(6)); 134.70 (C(10)); 132.51 (C(7a)); 131.79 (C(3)); 131.72 (C(2,11)); 130.42 (C(5)); 129.74 (C(7)); 129.42 (C(1)); 128.93 (C(4)); 128.89 (C(12)); 122.28 (C(8)); 67.53 (F_3CC(O)O*C*H$_2$–C(12)); 52.81 (*Me*O(O)C–C(3)); 52.64 (*Me*O(O)C–C(2)); 34.66 (Me_2*C*H–C(10)); 22.64, 22.50 (Me_2CH–C(10)); 17.24 (*Me*–C(7)); assignments were made *via* ^{1}H,^{13}C-correlation spectra. EI-MS: 502 (100, M^+), 462 (14, [*M* – H–C≡C–Me]$^+$), 389 (10, [*M* – OC(O)CF_3]$^+$), 329 (15, [*M* – OC(O)CF_3–C(O)OCH_3) + H]$^+$), 226 (11).

3.1.1.1. *Rearrangement of (*P**)-[1,4-$^2H_2$]-***4a*** (Method C)*. A soln. of (*P**)-[1,4-$^2H_2$]-**4a** (14.5 mg, 0.036 mmol) in cyclohexane (0.5 ml) was heated in the presence of *Amberlyst 15* (16 mg) at 80° for 18 h. Yield of crude **5a**: 9.3 mg (64%); after recrystallization from hexane: 7.3 mg (50%), orange crystals.

*Data of of (*P**)-[1,4-$^2H_2$]-***5a***.* M.p. 161.9–162.5°. IR (KBr): 3128*w*, 3017*w*, 2956*m*, 2866*w*, 1735*s*, 1676*s*, 1588*m*, 1549*w*, 1528*m*, 1443*s*, 1375*s*, 1360*s*, 1330*s*, 1295*s*, 1225*s*, 1153*s*, 1021*m*, 794*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): No signal at 6.621 (H–C(1)). EI-MS: 407 (100, M^+), 375 (45 [*M* – MeOH]$^+$), 360 (16), 335 (34), 307 (16), 289 (10).

3.1.1.2. *Rearrangement of (*P**)-[1,4-$^2H_2$]-***4a*** (Method A)*. A soln. of (*P**)-[1,4-$^2H_2$]-**4a** (17.3 mg, 0.042 mmol) and TFA (30 µl) in $CHCl_3$ (0.5 ml) was heated for 5.5 h. The crude product mixture of [1-^{2}H]-**5a** and [1,4-$^2H_2$]-**6a** was purified by CC (SiO_2): 13.2 mg of a 4:1 mixture of **5a**/**6a**.

^{1}H-NMR (300 MHz, $CDCl_3$): No signals at 7.620 (H–C(4) of **6a**) and 7.462 (H–C(1) of **6a**). Also no signal was observed at 5.457 (H–C(1) of **5a**).

3.1.2. *Formation of Dimethyl 4-Hydroxy-7,8,10,12-tetramethylbenzo[*a*]heptalene-2,3-dicarboxylate* (**5b**), *Dimethyl 7,8,10-Trimethyl-12-[(trifluoroacetoxy)methyl]benzo[*a*]heptalene-2,3-dicarboxylate* (**6b**), *and Dimethyl 7,10,12-Trimethyl-8-[(trilfuoroacetoxy)methyl]benzo[*a*]heptalene-2,3-dicarboxylate* (**13b**). To a soln. of (*M**)-**4b** (46.2 mg, 0.118 mmol) in $CHCl_3$ (2 ml), TFA (30 µl, 148 mg, 1.30 mmol) was added, and the mixture was heated at reflux for 2.5 h. A second portion of TFA (30 µl) was added, and the mixture was heated at reflux for another 3 h. Workup as described for **5a** afforded a light-yellow oil, which was purified by CC (SiO_2, hexane/Et_2O 1:1): 41.4 mg of **5b**/**6b**/**13b** in a ratio of *ca.* 1:1:1. From hexane/Et_2O, light yellow crystals of **6b** (11.3 mg, 20%) were formed. **13b** (10.3 mg, 18%) was separated as a yellow oil from the mother liquor by prep. HPLC (*Spherisorb CN*, 5 µm, 20 × 250 mm, 1.5% i-PrOH in hexane). Compound **5b** decomposed during HPLC separation on the *Spherisorb CN* column.

In a second experiment, starting from **4b** (82.5 mg, 0.210 mmol) and 2 × 50 µl TFA, compound **5b** (28.4 mg, 34%) could be isolated by prep. HPLC on a *Spherisorb* NH_2 column (5 µm, 20 × 250 mm, 1.5% i-PrOH in hexane). From hexane/Et_2O, light yellow crystals of **5b** (21.8 mg, 26%) were obtained.

Data of **5b**. M.p. 157.6–158.5°. R_f (hexane/Et_2O 1:1) 0.25. UV/VIS (hexane): λ_{max} 378 (sh, with long tailing up to 500 nm, 3.41), 341 (sh, 3.92), 314 (4.16), 275 (sh, 4.38), 252 (sh, 4.38), 245 (4.38), 223 (4.49); λ_{min} 297 (4.11), 265 (4.24), 240 (4.37), 210 (4.43). IR (KBr): 3113*w* (OH···O=C), 2591*m*, 2915*m*, 1730*s*, 1675*s*, 1441*s*, 1373*s*, 1331*s*, 1259*s*, 1234*s*, 1199*s*, 1152*s*, 1022*s*, 848*m*, 782*s*, 720*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 11.133 (*s*, HO–C(4)); 7.215 (*d*, ^3J(5,6) = 12.0, H–C(5)); 6.605 (*s*, H–C(1)); 6.409 (*d*, ^3J(5,6) = 12.0, H–C(6)); 6.157 (br. *s*, H–C(11)); 6.011 (br. *s*, H–C(9)); 3.914, 3.853 (2*s*, MeO(O)C–C(2,3)); 2.015 (*d*, ^4J(Me–C(10),11) = 1.2, Me–C(10)); 1.918 (*d*, ^4J(Me–C(8),9) = 1.3, Me–C(8)); 1.735 (*s*, Me–C(7)); 1.621 (*s*, Me–C(12)). EI-MS: 392 (100, M^+), 360 (21, $[M - MeOH]^+$), 345 (66, $[M - MeOH - Me]^+$), 320 (44), 306 (28), 274 (17), 215 (10).

Data of **6b**. M.p. 179–182°. R_f (hexane/Et_2O 1:1) 0.29. UV/VIS (hexane): λ_{max} 376 (sh, 3.07), 332 (3.59), 299 (sh, 4.12), 254 (4.42), 227 (4.45); λ_{min} 326 (3.59), 239 (4.33), 206 (4.37). IR (KBr): 3014*w*, 2954*m*, 2911*w*, 1785*s*, 1742*s*, 1722*s*, 1537*w*, 1434*s*, 1343*s*, 1297*s*, 1257*s*, 1212*s*, 1153*s*, 1057*m*, 922*m*, 792*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.647 (*s*, H–C(4)); 7.423 (*s*, H–C(1)); 6.904 (*d*, ^3J(5,6) = 11.8, H–C(5)); 6.411 (*d*, ^3J(5,6) = 11.8, H–C(6)); 6.212 (br. *s*, H–C(11)); 6.153 (br. *s*, H–C(9)); 4.737, 4.360 (2*d*, ^2J = 11.6, $F_3CC(O)OCH_2$–C(12)); 3.927, 3.869 (2*s*, MeO(O)C–C(2,3)); 2.076 (*d*, ^4J(Me–C(10),11) = 0.8, Me–C(10)); 1.943 (*d*, ^4J(Me–C(8),9) = 0.8, Me–C(8)); 1.786 (*s*, Me–C(7)); assignments were verified by ROESY. EI-MS: 488 (100, M^+), 448 (30, $[M - Me - C{\equiv}CH]^+$), 392 (51, $[M - C(O)CF_3]^+$), 375 (23, $[M - OC(O)CF_3]^+$), 345 (37), 322 (30), 301 (22), 242 (26), 226 (40), 202 (32), 189 (23), 164 (18).

Data of **13b**. R_f (hexane/Et_2O 1:1) 0.29. UV/VIS (hexane): λ_{max} 385 (sh, 2.82), 330 (sh, 3.47), 292 (sh, 4.19), 249 (4.32), 226 (4.46); λ_{min} 243 (4.31), 208 (4.34). IR ($CHCl_3$): 3030*w*, 3004*w*, 2954*w*, 2919*w*, 1783*s*, 1725*s*, 1602*w*, 1437*m*, 1377*m*, 1323*m*, 1289*s*, 1175*s*, 1143*s*, 1057*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.640 (*s*, H–C(4)); 7.369 (*s*, H–C(1)); 6.913 (*d*, ^3J(5,6) = 11.8, H–C(5)); 6.364 (*d*, ^3J(5,6) = 11.8, H–C(6)); 6.325 (br. *s*, H–C(9)); 6.316 (br. *s*, H–C(11)); 4.954, 4.744 (2*d*, ^2J = 12.6, $F_3CC(O)OCH_2$–C(8)); 3.920 (*s*, MeO(O)C–C(3)); 3.875 (*s*, MeO(O)C–C(2)); 2.078 (*d*, ^4J(Me–C(10),11) = 1.1, Me–C(10)); 1.778 (*s*, Me–C(7)); 1.625 (*s*, Me–C(12)); assignments were verified by ROESY.

3.1.3. *Formation of Dimethyl 10-(*tert*-Butyl)-4-hydroxy-7-methylbenzo[*a*]heptalene-2,3-dicarboxylate* (**5d**). To a soln. of (*P**)-**4d** (60 mg, 0.148 mmol) in $CHCl_3$ (3 ml), TFA (50 µl) was added, and the mixture was heated at reflux for 1 h. Then, a second portion of TFA (50 µl) was added, and the mixture was heated at reflux for another 3.5 h. Workup as described for **5a** afforded a brown oil, which was purified by CC (SiO_2, hexane/AcOEt 7:3). After drying *in vacuo*, 33.8 mg of a mixture of **5d** and starting material in a ratio of 3:2 (73% yield with respect to reacted starting material) was obtained. Product **5d** could be separated from **4d** by prep. HPLC (*Spherisorb CN*, 5 µm, 20 × 250 mm, 1% i-PrOH in hexane).

Data of **5d**. Dark yellow foam. R_f (hexane/Et_2O 1:1) 0.29. UV/VIS (hexane): λ_{max} 415 (sh, 2.98), 326 (4.20), 272 (sh, 4.34), 259 (4.36), 219 (4.43); λ_{min} 298 (3.94), 235 (4.23), 210 (4.42). IR ($CHCl_3$): 2957*m*, 2871*w*, 1731*s*, 1676*s*, 1598*w*, 1555*w*, 1442*m*, 1371*m*, 1332*s*, 1270*s*, 1241*m*, 1160*m*, 1024*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 11.092 (*s*, HO–C(4)); 7.090 (*d*, ^3J(5,6) = 12.1, H–C(5)); 6.674 (*s*, H–C(1)); 6.433 (*dd*, ^3J(11,12) = 6.8, ^4J(9,11) = 1.2, H–C(11)); 6.356 (*dd*, ^3J(8,9) = 11.1, ^4J(9,11) = 1.5, H–C(9)); 6.351 (*d*, ^3J(5,6) = 12.2, H–C(6)); 5.802 (*d*, ^3J(8,9) = 11.1, H–C(8)); 5.767 (*d*, ^3J(11,12) = 6.8, H–C(12)); 3.908, 3.846 (2*s*, MeO(O)C–C(2,3)); 1.729 (*s*, Me–C(7)); 1.164 (*s*, *t*-Bu); assignments of the signals were verified by ROESY. ^{13}C-NMR (150.9 MHz, $CDCl_3$): 169.79, 169.16 (MeO(O)*C*–C(2,1)); 158.06 (C(4)); 152.74 (C(10)); 145.58 (C(12b)); 137.05 (C(12a)); 136.06 (C(2)); 135.60 (C(6)); 133.50 (C(7a)); 130.35 (C(9)); 129.45 (C(12)); 129.38 (C(7)); 128.60 (C(4a)); 126.53 (C(8)); 125.35 (C(5)); 124.55 (C(11)); 119.77 (C(1)); 108.19 (C(3)); 52.91, 52.54 (*Me*O(O)C–C(2,1)); 36.11

(Me_3C–C(10)); 29.91 (Me_3C–C(10)); 17.54 (Me–C(7)); assignments were made *via* ^{1}H,^{13}C-correlation spectra. EI-MS: 406 (100, M^+), 374 (39, $[M - MeOH]^+$), 291 (11), 202 (12), 188 (13).

3.1.4. *Formation of Dimethyl 9-Isopropyl-4,7-dimethyl-12-[(trilfuoroacetoxy)methyl]benzo[*a*]heptalene-2,3-dicarboxylate* (**6e**). A soln. of (*P**)-**4e** (7.3 mg, 0.017 mmol) and TFA (15 µl) in $CHCl_3$ (0.5 ml) was heated at reflux for 2 h. Usual workup afforded after chromatographic purification a mixture (2 mg) of at least four products. One of the products (20%) showed, on HPLC analysis, a UV/VIS spectrum similar to that of **6a**. The ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) showed the expected two *d* for $F_3CC(O)OCH_2$–C(12)) of **6e** at 4.80 and 4.40 ppm, with $^2J = 11.6$ Hz, accompanied by signals at 3.97 and 3.86 ppm (2*s*, MeO(O)C–C(2,3), and a separated *s* at 7.55 ppm (H–C(1)) of **6e**. The presence of **6e** in the product mixture was also supported by HPLC/MS measurements, which showed for the peak, supposed to be responsible for **6e**, the expected fragmentation pattern.

Treatment of (*P**)-**4e** with *Amberlyst 15* in cyclohexane according to *Method C* led to the destruction of **4e** without significant product formation (see **9e** in *Scheme 10*).

3.2. *Acid-Catalyzed Transformation of 2,3-Diacetyl-1,4-epoxy-1,4-dihydro-9-isopropyl-7,12-dimethylbenzo[*d*]heptalene* (**19a**). A soln of (*P**)- and (*M**)-**19a** (73 mg, 0.195 mmol) in toluene (2 ml) was heated at 90° in the presence of *Amberlyst 15* (50 mg) for 16 h. Filtration through a short column of SiO_2 with hexane/Et_2O 3:2 afforded a yellow oil (12.5 mg). The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of the product mixture exhibited, beside a number of unidentified signals, two sets of signals that could be attributed to compounds **20a** (5%) and **21a** (6%).

Data of **20a**. ^{1}H-NMR (selected signals): 12.06 (*s*, HO–C(4)); 6.62 (*s*, H–C(1)).

Data of **21a**. ^{1}H-NMR (selected signals): 11.54 (*s*, HO–C(1)); 6.62 (*s*, H–C(4)).

3.3. *Base-Catalyzed Transformation of* **4**. 3.3.1. *Formation of Dimethyl 9-Isopropyl-7,12-dimethylbenzo[*a*]heptalene-2,3-dicarboxylate* (**15a**). In analogy to [21], a soln. of diisopropylamine (75 mg, 0.740 mmol) in THF (1 ml) was cooled to −70° and treated with a soln. of BuLi (0.24 ml of a *ca*. 2.5M soln. in hexane, 0.60 mmol). After 10 min, a soln. of (*P**)-**14a** (60.0 mg, 0.147 mmol) in THF (1 ml) was added drop by drop. The resulting dark-red soln. was stirred at −70° for 1 h, and then diluted with Et_2O (3 ml), and H_2O (0.3 ml) was added. The resulting mixture was allowed to warm to r.t., diluted further with Et_2O (40 ml), and washed with half-sat. aq. NaCl soln. and brine. Drying ($MgSO_4$) and solvent removal afforded an oily residue, which was purified by CC (SiO_2, *t*-BuOMe/hexane 7:3) to yield 51.7 mg (90%) of the title compound as a yellow oil. From cold hexane (−20°), light-red crystals (37 mg) were formed.

Data of **15a**. M.p. 124.9–125.7°. R_f (*t*-BuOMe/hexane 3:2) 0.38. UV/VIS (hexane): λ_{max} 413 (sh, 2.96), 338 (3.61), 293 (sh, 4.19), 257 (4.41), 224 (4.49); λ_{min} 330 (3.60), 241 (4.34), 208 (4.43). IR (KBr): 3013*w*, 2960*m*, 2924*w*, 2867*w*, 1736*s*, 1719*s*, 1525*w*, 1436*m*, 1289*s*, 1274*s*, 1248*s*, 1127*m*, 1051*m*, 906*m*, 787*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.598 (*s*, H–C(4)); 7.369 (*s*, H–C(1)); 6.819 (*d*, $^3J(5,6) = 11.7$, H–C(5)); 6.441 (*d*, $^3J(10,11) = 11.9$, H–C(11)); 6.401 (*dd*, $^3J(10,11) = 11.9$, $^3J(8,10) = 1.2$, H–C(10)); 6.361 (*d*, $^3J(5,6) = 11.7$, H–C(6)); 5.717 (*s*, H–C(8)); 3.911, 3.885 (2*s*, MeO(O)C–C(2,3)); 2.562 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 1.714 (br. *s*, Me–C(7)); 1.612 (*s*, Me–C(12)); 1.166, 1.151 (2*d*, $^3J = 6.9$, Me_2CH–C(9)); assignments of the signals were verified by NOESY. ^{13}C-NMR (150.9 MHz, $CDCl_3$): 168.20, 167.85 (MeO(O)*C*–C(2,3)); 147.70 (C(9)); 140.83 (C(4a)); 138.54 (C(12b); 135.83 (C(6)); 135.70 (C(11)); 134.86 (C(7a)); 133.45 (C(12a)); 132.68 (C(12)); 132.04 (C(10)); 131.67 (C(2)); 130.50 (C(3)); 130.36 (C(1)); 130.14 (C(5)); 128.93 (C(4)); 128.11 (C(7)); 122.34 (C(8)); 52.64, 52.58 (2 *Me*O(O)C–C(2,3)); 34.63, (Me_2*C*H–C(9)); 22.78, 22.74 (Me_2CH–C(9)); 19.23 (*Me*–C(12)); 17.30 (*Me*–C(7)); assignments were made *via* ^{1}H,^{13}C-correlation spectra. CI-MS (NH_3): 391 (100, $[M + H]^+$).

3.3.2. *Formation of Dimethyl 7,8,10,12-Tetramethylbenzo[*a*]heptalene-2,3-dicarboxylate* (**15b**) *and Dimethyl (*M**,1*R**,2*R**)-1,2-Dihydro-1-hydroxy-7,8,10,12-tetramethylbenzo[*a*]heptalene-2,3-dicarboxylate* ((*M**,1*R**,2*R**)-**16b**). A soln. of diisopropylamine (38 mg, 0.375 mmol) in THF (0.5 ml) was cooled to −70°, and treated with a soln. of BuLi (0.12 ml of a *ca*. 2.5M soln. in hexane, 0.30 mmol). After 10 min, a soln. of the starting material (*P**/*M**)-**14b** (28.2 mg, 0.071 mmol) in THF (1.5 ml) was slowly added. The resulting dark-red soln. was stirred at −75° for 1 h and then diluted with Et_2O (2 ml), and H_2O (0.2 ml) was added. The mixture was allowed to warm to r.t., diluted further with Et_2O, (40 ml) and washed once with half-sat. aq. NaCl soln. and once with brine. Drying ($MgSO_4$) and solvent removal afforded an oily residue, which was purified by CC (SiO_2, *t*-BuOMe/hexane 3:2) to yield 16.7 mg (62%) of a yellow oil, which was crystallized from hexane to afford 12.2 mg of **15b** (yellow crystals), and 8.4 mg (30%) of **16b**, which was recrystallized from *t*-BuOMe to yielded 3.3 mg of orange crystals.

Data of **15b**. M.p. 125–126°. R_f (*t*-BuOMe/hexane 3:2) 0.47. UV/VIS (hexane): λ_{max} 392 (sh, 3.09), 332 (sh, 3.59), 293 (4.26), 249 (4.41), 225 (4.53); λ_{min} 279 (4.25), 241 (4.41), 207 (4.41). IR (KBr): 2950*m*, 2914*w*, 1736*s*, 1727*s*, 1436*m*, 1305*m*, 1283*s*, 1255*s*, 1231*m*, 1129*s*, 1057*m*, 794*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.628 (*s*, H–C(4));

7.372 (*s*, H–C(1)); 6.852 (*d*, ^3J(5,6) = 11.7, H–C(5)); 6.370 (*d*, ^3J(5,6) = 11.7, H–C(6)); 6.182 (br. *s*, H–C(11)); 6.053 (br. *s*, H–C(9)); 3.918 (*s*, MeO(O)C–C(3)); 3.878 (*s*, MeO(O)C–C(2)); 2.033 (*d*, ^4J(Me–C(10),11) = 1.1, Me–C(10)); 1.925 (*d*, ^4J(Me–C(8),9) = 1.2, Me–C(8)); 1.745 (*s*, Me–C(7)); 1.598 (*s*, Me–C(12)); assignments were verified by NOESY. EI-MS: 376 (100, M^+), 361 (77, $[M - Me]^+$), 336 (67, $[M - Me - C{\equiv}CH]^+$), 322 (24), 302 (11), 243 (13), 202 (11).

Data of **16b**. M.p. 207–216°. R_f (*t*-BuOMe/hexane 3:2) 0.20. UV/VIS (hexane): λ_{max} 376 (3.41), 301 (4.36), 264 (4.26), 219 (4.27); λ_{min} 361 (3.40), 280 (4.24), 239 (4.05), 208 (4.25). IR (KBr): 3450*s*, 2954*m*, 2910*m*, 2852*w*, 1747*s*, 1707*s*, 1613*m*, 1435*s*, 1406*m*, 1375*m*, 1278*s*, 1228*s*, 1192*s*, 1167*s*, 1108*m*, 1098*m*, 1048*m*, 1028*m*, 844*m*, 782*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.269 (*d*, ^4J(2,4) = 3.0, H–C(4)); 6.607 (*d*, ^3J(5,6) = 6.0, H–C(5)); 6.276 (*dq*-like, ^3J(5,6) = 6.0, ^4J(6,Me–C(7)) = 1.5, H–C(6)); 6.074, 6.034 (2 br. *s*, H–C(9,11)); 4.806 (*q*, ^3J(1,HO–C(1)) = 4.8, ^3J(1,2) = 3.3, H–C(1)); 3.800, 3.726 (2*s*, MeO(O)C–C(2,3)); 3.489 (*t*-like, $^3J \approx 3.2$, H–C(2)); 2.577 (*d*, ^3J(1,HO–C(1)) = 4.8, HO–C(1)); 2.136, 1.993 (2*d*, ^4J = 1.3, Me–C(7,12)); 2.029 (br. *s*, Me–C(10)); 1.722 (*s*, Me–C(8)). EI-MS: 394 (8, M^+), 362 (100, $[M - MeOH]^+$), 334 (44, $[M - MeO(O)C - H]^+$), 319 (76, $[M - MeO(O)C - Me - H]^+$), 303 (37), 287 (16), 260 (16), 229 (16), 217 (19), 202 (23). The final structure of (*M**,1*R**,2*R**)-**16b** was established by an X-ray crystal-structure analysis (see *Tables 2* and *4* and *Figs. 6* and *7*).

3.3.3. *Formation of Dimethyl 10-Isopropyl-7-methylbenzo[*a*]heptalene-2,3-dicarboxylate* (**15c**). To a soln. of (*P**)-**14c** (60.6 mg, 0.1536 mmol) in 1,2-dimethoxyethane (DME; 3 ml) was added Cs_2CO_3 (120 mg, 0.368 mmol), and the mixture was stirred at 80° for 3.5 h (TLC control). The resulting mixture was diluted with Et_2O, and washed with H_2O and brine; the org. phase was dried ($MgSO_4$) and evaporated. The residue was purified by CC (SiO_2; *t*-BuOMe/hexane 3:2) to yield a reddish-brown oil (40.2 mg). The expected product **15c** and the *trans*-isomers **14c** could be separated by prep. HPLC (*Spherisorb CN*, 5 μm, 20 × 250 mm, 2% i-PrOH in hexane): 7.2 mg (12.5%) of **15c** as a yellow oil, 12.7 mg (21%) of 2-*endo*,3-*exo*-**14c** as a brownish-red oil, and 10.1 mg (17%) of 2-*exo*,3-*endo*-**14c** as reddish-black crystals from Et_2O/hexane.

Data of **15c**. R_f (Et_2O/hexane 7:3) 0.40. UV/VIS (hexane): λ_{max} 428 (sh, 2.85), 349 (3.69), 294 (sh, 4.21), 258 (4.43), 222 (4.45); λ_{min} 330 (3.64), 238 (4.28), 204 (4.39). IR ($CHCl_3$): 2962*m*, 1725*s*, 1599*w*, 1436*m*, 1296*s*, 1259*m*, 1134*m*, 1072*w*, 972*w*, 910*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.431, 7.389 (2*s*, H–C(1,4)); 6.690 (*d*, ^3J(5,6) = 11.9, H–C(5)); 6.367 (br. *d*, ^3J(11,12) = 6.8, H–C(11)); 6.296 (*d*, ^3J(5,6) = 11.9, H–C(6)); 6.201 (*dd*, ^3J(8,9) = 11.0, ^4J(9,11) = 1.3, H–C(9)); 5.812 (*d*, ^3J(8,9) = 11.0, H–C(8)); 5.695 (*d*, ^3J(11,12) = 6.8, H–C(12)); 3.894, 3.869 (2*s*, MeO(O)C–C(2,3)); 2.492 (*sept.*, ^3J = 6.9, Me_2CH–C(10)); 1.745 (br. *s*, Me–C(7)); 1.142, 1.113 (2*d*, ^3J = 6.9, Me_2CH–C(10)). GC-MS: 376 (100, M^+), 336 (91), 308 (26), 202 (25).

*Data of Dimethyl (*P**,1*R**,2*S**,3*S**,4*S**)-1,2,3,4-Tetrahydro-10-isopropyl-7-methyl-1,4-epoxybenzo[*d*]heptalene-2,3-dicarboxylate* (2-*endo*,3-*exo*-**14c**). R_f (Et_2O/hexane 7:3) 0.40. UV/VIS (hexane): λ_{max} 349 (3.73), 260 (4.36), 207 (sh, 4.28), 197 (4.28); λ_{min} 302 (3.45), 227 (4.14). IR ($CHCl_3$): 3029*w*, 2961*m*, 1737*s*, 1607*w*, 1438*m*, 1318*w*, 1262*m*, 1180*m*, 1089*w*, 1027*w*. ^{1}H-NMR (300 MHz, C_6D_6): 5.929 (*d*, ^3J(8,9) ≈ 7.5, H–C(9)); 5.896 (*dd*, partially covered, ^3J(11,12) = 11.4, ^4J(9,11) = 1.5, H–C(11)); 5.674 (*d*, ^3J(11,12) = 11.4, H–C(12)); 5.571 (*dq*-like *dd*, ^3J(5,6) = 6.9, ^4J(6,Me–C(7)) = 1.5, H–C(6)); 5.521 (*d*, ^3J(5,6) = 6.9, H–C(5)); 5.445 (*d*, ^3J(8,9) = 7.5, H–C(8)); 5.225 (*s*, H–C(4)); 5.142 (*d*, ^3J(1,2) = 5.4, H–C(1)); 3.969 (*dd*, ^3J(1,2) = 5.4, ^3J(2,3) = 4.2, H–C(2)); 3.336 (*d*, ^3J(2,3) = 4.2, H–C(3)); 3.270, 3.262 (2 *s*, MeO(O)C–C(2,3)); 2.106 (*sept.*, ^3J = 6.9, Me_2CH–*C*(10)); 1.859 (*d*, ^4J(6,Me–C(7)) = 1.0, Me–C(7)); 0.908, 0.893 (2*d*, ^3J = 6.9, Me_2CH–C(10)).

*Data of Dimethyl (*P**,1*R**,2*R**,3*R**,4*S**)-1,2,3,4-Tetrahydro-10-isopropyl-7-methyl-1,4-epoxybenzo[*d*]heptalene-2,3-dicarboxylate* (2-*exo*,3-*endo*-**14c**). M.p. 141.5–142.2° R_f (Et_2O/hexane 7:3) 0.40. UV/VIS (hexane): λ_{max} 349 (3.77), 261 (4.39), 205 (sh, 4.31), 194 (4.33); λ_{min} 301 (3.43), 227 (4.17). IR (KBr): 2956*s*, 2868*w*, 1735*s*, 1655*w*, 1604*w*, 1435*m*, 1324*s*, 1288*s*, 1210*s*, 1182*s*, 1036*m*, 989*m*, 870*m*, 844*m*, 821*m*, 785*m*. ^{1}H-NMR (600 MHz, C_6D_6): 5.916 (*d*, ^3J(8,9) ≈ 7.5, H–C(9)); 5.775 (*dd*, ^3J(11,12) = 11.0, ^4J(9,11) = 1.5, H–C(11)); 5.568 (*dq*-like *dd*, ^3J(5,6) = 7.1, ^4J(6,Me–C(7)) = 1.1, H–C(6)); 5.538 (*d*, ^3J(5,6) = 7.1, H–C(5)); 5.424 (*d*, ^3J(8,9) = 7.2, H–C(8)); 5.420 (*d*, ^3J(11,12) = 11.4, H–C(12)); 5.371 (*s*, H–C(1)); 4.977 (*d*, ^3J(4,3) = 5.4, H–C(4)); 3.954 (*t*-like, $\Sigma(^3J(3,4) + {}^3J(2,3)) = 10.1$, H–C(3)); 3.504 (*d*, ^3J(2,3) = 4.7, H–C(2)); 3.239, 3.226 (2*s*, MeO(O)C–C(2,3)); 2.088 (*sept.*, ^3J = 6.9, Me_2CH–*C*(10)); 1.864 (*d*, ^4J(6,Me–C(7)) = 0.7, Me–C(7)); 0.889, 0.879 (2*d*, ^3J = 6.9, Me_2CH–C(10)). EI-MS: 394 (12, M^+), 250 (100, $[M - C_6H_8O_4\,(DM)]^+$), 235 (19), 192 (11), 182 (25), 165 (13).

3.4. *Base-Catalyzed Transformation of* **17**. *General Procedure*. To a soln. of **17** (0.1 mmol) in DME (2.5 ml), $CsCO_3$ (0.3 mmol) was added. The mixture was stirred at 80–85° (oil-bath temperature) during 1–18 h. The cold product mixture was diluted with *t*-BuOMe and washed twice with half-sat. aq. NaCl soln. Drying ($MgSO_4$) and solvent removal afforded the crude dinitriles **18**, which were purified by recrystallization or CC, followed by recrystallization.

3.4.1. *9-Isopropyl-7,12-dimethylbenzo[*a*]heptalene-2,3-dicarbonitrile* (**18a**). The pure 2-*exo*,3-*endo*-(*P**)-epimer (0.263 mmol) was used; reaction time 2 h; yield of pure **18a**: 65%. Red crystals, M.p. 206.8–207.9°

(AcOEt). R_f (*t*-BuOMe/hexane 3:2) 0.49. UV/VIS (hexane; see also *Table 3*): λ_{max} 355 (3.55), 303 (4.17), 260 (4.45), 226 (4.54), 203 (sh, 4.40); λ_{min} 333 (3.46), 290 (4.15), 242 (4.36). IR (KBr): 3023*w*, 2963*m*, 2924*m*, 2863*m*, 2229*s*, 1641*m*, 1521*m*, 1485*m*, 1462*m*, 1439*m*, 1382*m*, 1235*m*, 912*s*, 788*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.659 (*s*, H–C(4)); 7.372 (*s*, H–C(1)); 6.783 (*d*, ^3J(5,6) = 11.7, H–C(5)); 6.481 (*d*, ^3J(5,6) = 11.9, H–C(6)); 6.454 (superimposed *s*-like *AB*, H–C(10,11)); 5.754 (br. *s*, H–C(8)); 2.574 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 1.726 (*d*, ^4J(6,Me–C(7)) = 0.7, Me–C(7)); 1.589 (*s*, Me–C(12)); 1.170, 1.156 (2*d*, ^3J = 6.9, Me_2CH–C(9)). ^{1}H-NMR (300 MHz, C_6D_6): 6.691, 6.673 (2*s*, H–C(1,4)); 6.257 (*dd*, ^3J(10,11) = 11.9, ^4J(8,10) = 1.3, H–C(10)); 6.182 (*d*, ^3J(10,11) = 11.7, H–C(11)); 6.151 (*d*, ^3J(5,6) = 11.8, H–C(5)); 6.038 (*d*, ^3J(5,6) = 11.8, H–C(6)); 5.649 (br. *s*, H–C(8)); 2.381 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 1.502 (*d*, ^4J(6,Me–C(7)) = 0.8, Me–C(7)); 1.136 (*s*, Me–C(12)); 1.073, 1.059 (2 *d*, ^3J = 6.9, Me_2CH–C(9)). EI-MS: 324 (100, M^+), 309 (50, $[M - Me]^+$), 284 (38, $[M - Me - C{\equiv}CH]^+$), 265 (35), 256 (22), 215 (13), 139 (20), 133 (25).

3.4.2. *7,8,10,12-Tetramethylbenzo[*a*]heptalene-2,3-dicarbonitrile* (**18b**). The pure 2-*exo*,3-*endo*-(*P**)-epimer (0.117 mmol) was used; reaction time 1 h; yield of pure **18b**: 86%. Orange crystals. M.p. 189.3–190.3° (Et_2O/hexane). R_f (*t*-BuOMe/hexane 7:3) 0.40. UV/VIS (hexane; *cf. Table 3*): λ_{max} 401 (sh, 3.21), 350 (3.55), 309 (4.28), 298 (sh, 4.21), 252 (4.46), 228 (4.59); λ_{min} 335 (3.52), 282 (4.15), 244 (4.44), 205 (4.43). IR (KBr): 3066*m*, 3014*m*, 2941*s*, 2913*s*, 2855*m*, 2228*s*, 1646*m*, 1613*m*, 1586*s*, 1517*s*, 1484*s*, 1438*s*, 1375*m*, 1238*s*, 1198*m*, 1027*m*, 904*s*, 833*m*, 787*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.719 (*s*, H–C(4)); 7.350 (*s*, H–C(1)); 6.818 (*d*, ^3J(5,6) = 11.8, H–C(5)); 6.490 (*d*, ^3J(5,6) = 11.8, H–C(6)); 6.181 (br. *s*, H–C(11)); 6.072 (br. *s*, H–C(9)); 2.04 (*d*, ^4J(Me–C(10),11) = 1.2, Me–C(10)); 1.938 (*d*, ^4J(Me–C(8),9) = 1.3, Me–C(8)); 1.759 (*s*, Me–C(7)); 1.566 (*s*, Me–C(12)). EI-MS: 310 (94, M^+), 295 (100, $[M - Me]^+$), 280 (35, $[M - 2\ Me]^+$), 270 (52, $[M - Me - C{\equiv}CH]^+$), 265 (38, $[M - 3\ Me]^+$), 256 (23, $[M - CHCN - Me]^+$), 239 (12), 123 (28).

3.4.3. *10-Isopropyl-7-methylbenzo[*a*]heptalene-2,3-dicarbonitrile* (**18c**). The pure 2-*exo*,3-*endo*-(*P**)-epimer (0.102 mmol) was used; reaction time 18 h; yield of pure **18c**: 44%. Reddish-black crystals. M.p. 185–187° (Et_2O/pentane). R_f (Et_2O/hexane 1:1) 0.23. UV/VIS (hexane, *cf. Table 3*): λ_{max} 441 (sh, 2.98), 362 (3.69), 304 (4.28), 261 (4.50), 226 (4.53), 196 (4.41); λ_{min} 336 (3.59), 287 (4.19), 241 (4.32), 206 (4.37). IR (KBr): 3019*w*, 2955*s*, 2868*m*, 2225*s*, 1585*m*, 1526*m*, 1487*m*, 1462*m*, 1372*m*, 1240*m*, 902*s*, 846*s*, 779*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.475 (*s*, H–C(4)); 7.349 (*s*, H–C(1)); 6.643 (*d*, ^3J(5,6) = 11.9, H–C(5)); 6.410 (*d*, ^3J(5,6) = 11.7, H–C(6)); 6.407 (superimposed *dquint*-like, ^3J(11,12) ≈ 6.8, H–C(11)); 6.240 (*dd*, ^3J(8,9) = 11.1, ^4J(9,11) = 1.5, H–C(9)); 5.843 (br. *d*, ^3J(8,9) = 11.0, H–C(8)); 5.633 (*d*, ^3J(11,12) = 6.8, H–C(12)); 2.506 (*sept.*, ^3J = 6.9, Me_2CH–C(10)); 1.753 (*d*, ^4J(6,Me–C(7)) = 0.8, Me–C(7)); 1.148, 1.118 (2*d*, ^3J = 6.9, Me_2CH–C(10)). EI-MS: 310 (100, M^+), 295 (25, $[M - Me]^+$), 277 (35), 270 (66, $[M - Me - C{\equiv}CH]^+$), 265 (22), 255 (19), 242 (17).

3.4.4. *9-Isopropyl-4,7,12-trimethylbenzo[*a*]heptalene-2,3-dicarbonitrile* (**18e**). The mixture of all four *trans*-isomers (0.129 mmol) was used; reaction time 2.5 h; yield of pure **18e**: 93%. Red glittering crystals. M.p. 236.8–237.8° (AcOEt/hexane). R_f (hexane/Et_2O 7:3) 0.33. UV/VIS (hexane; *cf. Table 3*): λ_{max} 394 (sh, 3.26), 346 (3.54), 304 (4.13), 274 (sh, 4.23), 257 (4.39), 251 (sh, 4.34), 228 (4.50), 202 (4.42); λ_{min} 337 (3.53), 291 (4.11), 243 (4.36), 209 (4.41). IR (KBr): 3017*m*, 2963*s*, 2926*s*, 2868*m*, 2229*s*, 1641*m*, 1573*w*, 1524*s*, 1462*s*, 1384*m*, 1277*m*, 1035*m*, 898*s*, 798*s*, 788*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.224 (*s*, H–C(1)); 6.914 (*d*, ^3J(5,6) = 12.0, H–C(5)); 6.523 (*d*, ^3J(5,6) = 12.0, H–C(6)); 6.461, 6.419 (*s*-like *AB*, ^3J ≈ 11, H–C(10,11)); 5.763 (br. *s*, H–C(8)); 2.659 (*s*, Me–C(4)); 2.567 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 1.713 (br. *s*, Me–C(7)); 1.596 (*s*, Me–C(12)); 1.167, 1.153 (2 *d*, ^3J = 6.9, Me_2CH–C(9)). EI-MS: 338 (100, M^+), 309 (63, $[M - Me]^+$), 298 (34, $[M - Me - C{\equiv}CH]^+$), 254 (53), 159 (24).

3.5. *Base-Catalyzed Transformation of* **22**. 3.5.1. *(*P**,10*R**)- and (*M**,10*R**)-11,12-Dihydro-12-hydroxy-4-isopropyl-1,6,12-trimethyl-10*H*-indeno[5,6-*a*]heptalen-10-one* ((*P**)- and (*M**)-**24a**). In a *Schlenk* tube, a mixture of **22a** (14.5 mg, 0.0385 mmol) and Cs_2CO_3 (62 mg, 0.190 mmol) in DMF (1 ml) was stirred at r.t. overnight. The cold product mixture was diluted with *t*-BuOMe and washed with half-sat. aq. NaCl soln. (2×). After drying ($MgSO_4$) and solvent removal, the crude product mixture was separated by prep. TLC (SiO_2 *60*; Et_2O/hexane 19:1) to yield 6.3 mg (*ca.* 45%) of a brownish yellow oil (see below), and 7.3 mg (53%) of a 4:3 mixture of (*P**)- and (*M**)-**24a** as a bright-yellow oil.

*Data of (*P**)- and (*M**)-*-**24a**. R_f (Et_2O/hexane 19:1) 0.18. IR (4:3 mixture; $CHCl_3$): 2967*s*, 2933*m*, 2871*m*, 1708*s*, 1601*m*, 1464*m*, 1447*m*, 1389*m*, 1376*m*, 1366*m*, 1344*m*, 1238*m*, 1190*m*, 1079*m*. ^{1}H-NMR (600 MHz, C_6D_6; main epimer): 7.659 (*s*, H–C(13)); 7.348 (*s*, H–C(9)); 6.758 (*d*, ^3J(8,7) = 11.8, H–C(8)); 6.34–6.28 (superimposed *AB*, H–C(2,3)); 6.189 (*d*, ^3J(7,8) = 11.7, H–C(7)); 5.696 (br. *s*, H–C(5)); 2.531 (*s*, CH_2(11)); 2.400 (superimposed *sept.*, Me_2CH–C(4)); 1.602 (br. *s*, Me–C(6)); 1.518 (*s*, Me–C(1)); 1.279 (br. *s*, HO–C(10)); 1.238 (*s*, Me–C(10)); 1.09–1.04 (superimposed, Me_2CH–C(4)). ^{1}H-NMR (600 MHz, C_6D_6; minor epimer): 7.649 (*s*, H–C(13)); 7.317 (*s*, H–C(9)); 6.738 (*d*, ^3J(8,7) = 11.9, H–C(8)); 6.34–6.28 (superimposed *AB*, H–C(2,3)); 6.195 (*d*, ^3J(7,8) = 11.7, H–C(7)); 5.756 (br. *s*, H–C(5)); 2.561 (*s*, CH_2(11));

2.418 (superimposed *sept.*, $Me_2CH-C(4)$); 1.639 (br. *s*, Me–C(6)); 1.471 (*s*, Me–C(1)); 1.308 (*s*, Me–C(10)); 1.254 (br. *s*, HO–C(10)); 1.09–1.04 (superimposed, $Me_2CH-C(4)$); assignments were verified by NOESY.

The brownish-yellow oil represented, according to its ^{1}H-NMR spectrum in C_6D_6, mainly a 7:3 mixture of the other two possible epimers, *i.e.*, *(*P**,12*R**)- and (*M**,12*R**)-11,12-Dihydro-10-hydroxy-4-isopropyl-1,6,10-trimethyl-10*H*-indeno[5,6-*a*]heptalene*-12-one ((*P**)- and (*M**)-**24′a**, not shown).

*Data of (*P**)- and (*M**)-**24′a***. R_f (Et_2O/hexane 19:1) 0.27. ^{1}H-NMR (600 MHz, C_6D_6; main epimer): 7.725 (*s*, H–C(9)); *ca*. 7.16 (*s*, H–C(13), covered by the signal of C_6D_5H; the signal *s* of H–C(13) appears in $CDCl_3$ at 7.301); 6.697 (*d*, $^3J(8,7) = 11.7$, H–C(8)); 6.39–6.30 (superimposed *AB*, H–C(2,3)); 6.105 (*d*, $^3J(7,8) = 11.7$, H–C(7)); 5.753 (br. *s*, H–C(5)); 2.57, 2.54 (*AB* system, $^2J_{AB} = 18.5$, CH_2(11)); 2.43 (superimposed *sept.*, $Me_2CH-C(4)$); 1.614 (br. *s*, Me–C(6)); 1.518 (*s*, Me–C(1)); 1.16 (*s*, Me–C(12)); 1.10–1.06 (superimposed, $Me_2CH-C(4)$). ^{1}H-NMR (600 MHz, C_6D_6; minor epimer): 7.753 (*s*, H–C(9)); 7.268 (*s*, H–C(13)); 6.717 (*d*, $^3J(8,7) = 11.7$, H–C(8)); 6.39–6.30 (superimposed *AB*, H–C(2,3)); 6.100 (*d*, $^3J(7,8) = 11.7$, H–C(7)); 5.696 (br. *s*, H–C(5)); 2.514 (*s*, CH_2(11)); 2.418 (superimposed *sept.*, $Me_2CH-C(4)$); 1.58 (br. *s*, Me–C(1,6)); 1.16 (*s*, Me–C(12)); 1.10–1.06 (superimposed, $Me_2CH-C(4)$).

3.6. *Base-Catalyzed Transformation of* **25a** *and* **26a**. 3.6.1. *Formation of Phenyl 9-Isopropyl-7,12-dimethylbenzo[*a*]heptalene-2-sulfonate* (**27a**). To a soln. of *exo*-(*P**)-**25a** (31.8 mg, 0.071 mmol) in DME (1 ml), Cs_2CO_3 (72 mg, 0.22 mmol) was added. The mixture was stirred at 90° (oil-bath temp.) during 3.5 h. The cold product mixture was diluted with Et_2O, and washed with H_2O and brine. Drying ($MgSO_4$) and solvent removal afforded a crude product, which was purified by CC (SiO_2, hexane/Et_2O 7:3) to yield **27a** (29.2 mg, 96%) as a yellow oil. Recrystallization from Et_2O/pentane furnished orange crystals (21.2 mg, 69%) of **27a**. M.p. 136.5–137.1°. R_f (hexane/Et_2O 3:2) 0.40. UV/VIS (hexane): λ_{max} 344 (3.60), 286 (sh, 4.15), 258 (4.39), 220 (4.48), 197 (4.54); λ_{min} 322 (3.52), 237 (4.34), 217 (4.48). IR (KBr): 3060*w*, 3018*w*, 2960*m*, 2925*m*, 2866*w*, 1586*m*, 1489*m*, 1370*s*, 1204*s*, 1176*s*, 1150*s*, 1084*m*, 1026*w*, 914*m*, 859*s*, 834*m*, 774*s*, 726*m*, 688*m*, 655*m*, 612*m*, 534*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.736 (*dd*, $^3J(3,4) = 8.3$, $^4J(1,3) = 2.0$, H–C(3)); 7.393 (*d*, $^3J(3,4) \approx 7.8$, H–C(4)); 7.387 (*d*, $^3J(1,3) \approx 2.3$, H–C(1)); 7.29–7.20 (*m*, H_m and H_p of Ph); 7.03–7.00 (*d*-like, H_o of Ph); 6.827 (*d*, $^3J(5,6) = 11.8$, H–C(5)); 6.396 (*d*, $^3J(5,6) = 11.6$, H–C(6)); 6.389 (*d*-like *AB*, $J_{AB} \approx 12$, H–C(10,11)); 5.705 (br. *s*, H–C(8)); 2.553 (*sept.*, $^3J = 6.8$, $Me_2CH-C(9)$); 1.723 (*d*, $^4J(6,Me-C(7)) = 0.8$, Me–C(7)); 1.382 (*s*, Me–C(12)); 1.159, 1.148 (2*d*, $^3J = 6.8$, $Me_2CH-C(9)$); assignments were verified by NOE. CI-MS (NH_3): 448 (100, $[M + NH_4]^+$), 431 (43, $[M + H]^+$), 307 (6), 275 (12).

3.6.2. *Formation of Phenyl 9-Isopropyl-7,12-dimethylbenzo[*a*]heptalene-3-sulfonate* (**28a**). Heating of *exo*-(*P**)-**26a** (32.8 mg, 0.073 mmol) in DME (1 ml) at reflux with Cs_2CO_3 (80 mg, 0.245 mmol) during 3.5 h furnished, after the same workup procedure as described for **27a**, a crude product mixture, which was purified by filtration through a short column of SiO_2. From a pentane soln., crystalline starting material (2.6 mg) could be separated. By keeping a hexane soln. of the yellow oily mother liquor (17.8 mg, 57%) at −20° overnight, light-red crystals of **28a** (12.1 mg, 38%) were formed. M.p. 130–140°. R_f (hexane/Et_2O 3:2) 0.28. UV/VIS (hexane): λ_{max} 334 (3.67), 282 (sh, 4.17), 254 (4.39), 221 (4.49), 196 (4.51); λ_{min} 313 (3.60), 238 (4.30), 212 (4.47). ^{1}H-NMR (500 MHz, C_6D_6): 7.864 (*d*, $^2J(2,4) = 1.9$, H–C(4)); 7.711 (*dd*, $^3J(1,2) = 8.1$, $^4J(2,4) = 2.0$, H–C(2)); 6.95–6.91 (*m*, 2 H of Ph); 6.78–6.72 (*m*, 3 H of Ph); 6.678 (*d*, $^3J(1,2) = 8.1$, H–C(1)); 6.370 (*d*, $^3J(5,6) = 11.7$, H–C(5)); 6.274 (*s*-like, $^3J(10,11) \approx 12$, H–C(10,11)); 6.029 (*d*, $^3J(5,6) = 11.7$, H–C(6)); 5.587 (br. *s*, H–C(8)); 2.353 (*sept.*, $^3J = 7.1$, $Me_2CH-C(9)$); 1.504 (br. *s*, Me–C(7)); 1.382 (*s*, Me–C(12)); 1.046, 1.031 (2*d*, $^3J = 7.1$, $Me_2CH-C(9)$); assignments were verified by NOE.

4. *Crystal-Structure Determinations*[5]). 4.1. *Dimethyl (*P**,1*S**,4*R**)-1,4-Dihydro-9-isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalene-2,3-dicarboxylate* ((*P**)-**4a**). A crystal of $C_{25}H_{26}O_5$, obtained from hexane/CH_2Cl_2, was mounted on a glass fibre and used for a low-temperature X-ray structure determination. All measurements were made on a *Rigaku AFC5R* diffractometer using graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å) and a 12-kW rotating anode generator. The unit-cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of 20 carefully centered reflections in the range $11° < 2\theta < 20°$. The $\omega/2\theta$ scan mode was employed for data collection, where the ω scan width was $(1.42 + 0.35 \tan\theta)°$, and the ω scan speed was 8°/min. The weaker reflections [$I < 10\sigma(I)$] were rescanned up to a maximum of 4 scans, and the counts were accumulated. Stationary background counts were recorded on each

---

[5]) CCDC-259510–259512 contain the supplementary crystallographic data for this paper. These data can be obtained, free of charge, *via* www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: data_request@ccdc.cam.ac.uk).

side of the reflection, with a peak / background counting time ratio of 2 : 1 (*cf. Table 4*). The structure was solved and refined successfully (*cf. Fig. 1*). Since the space group is centrosymmetric, the crystals are racemic. The crystal was quite small and weakly diffracting, which reduced the accuracy of the atomic and geometric parameters, although the overall structure was clearly defined. The i-Pr substituent is disordered over two conformations. The secondary C-atom and one Me group occupy two equally occupied sites, while the other Me group occupies the same site in both conformations.

4.2. *Dimethyl (*M**,1*S**,4*R**)-1,4-Epoxy-1,4-dihydro-4,7,8,10,12-pentamethylbenzo[*d*]heptalene-2,3-dicarboxylate* ((*M**)-**4f**). A crystal of $C_{25}H_{26}O_5$, obtained from CH_2Cl_2/hexane, was mounted on a glass fibre and used for a low-temperature X-ray structure determination. All measurements were made on a *Nonius KappaCCD* diffractometer using graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) and an *Oxford Cryosystems Cryostream-700* cooler. The unit-cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of 5948 reflections in the range $4^\circ < 2\theta < 60^\circ$. The mosaicity was $0.461(1)^\circ$. A total of 618 frames were collected using ϕ and ω scans with κ offsets, 40-s exposure time, and a rotation angle of 2.0° per frame, and a crystal-detector distance of 30.0 mm (*cf. Table 4*). The structure was solved and refined successfully, with no unusual features. Since the space group is centrosymmetric, the crystals are racemic. As expected, the Me substituent on the six-membered ring lies *cis* to the ether bridge, and this bridge lies on the opposite side of the molecule as the concave curvature of the heptalene rings (*cf. Fig. 2*).

4.3. *Dimethyl (*M**,1*R**,2*R**)-1,2-Dihydro-1-hydroxy-7,8,10,12-tetramethyl-benzo[*a*]heptalene-2,3-dicarboxylate* ((*M**,1*R**,2*R**)-**16b**). A crystal of $C_{24}H_{26}O_5 \cdot 0.67\ CH_2Cl_2$, obtained from CH_2Cl_2/hexane, was mounted on a glass fibre and used for a low-temperature X-ray structure determination. All measurements were made on a *Nonius KappaCCD* area-detector diffractometer using graphite-monochromated MoK_α radiation ($\lambda =$ 0.71073 Å) and an *Oxford Cryosystems Cryostream-700* cooler. The unit-cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of 53270 reflections in the range $4^\circ < 2\theta < 50^\circ$. The mosaicity was $0.771(1)^\circ$. A total of 467 frames were collected, using ϕ and ω scans with κ offsets, 105-s exposure time, a rotation angle of 1.5° per frame, and a crystal-detector distance of 34.9 mm (*cf. Table 4*). Data reduction was performed with *HKL Denzo* and *Scalepack*. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method was applied. The space group was uniquely determined by the systematic absences. Equivalent reflections were merged. Data collection and refinement parameters are given in *Table 4*. A view of the molecule is shown in *Fig.* 6.

The structure was solved and refined successfully. Since the space group is centrosymmetric, the compound in the crystal is racemic. The asymmetric unit includes a site for a CH_2Cl_2 molecule, which is only approximately 67% occupied and is additionally disordered over two unequally occupied orientations. That the crystal has a propensity to lose some of its solvent of crystallization is evident from the remaining crystals becoming opaque after being left to stand for several hours. The OH group is on the opposite side of the six-membered ring, and *cis* to its adjacent ester substituent. The OH group forms an intermolecular H-bond with a carbonyl O-atom of an adjacent centrosymmetrically-related molecule and, thereby, links pairs of molecules into dimers (*cf. Fig. 7*).

REFERENCES

[1] C. O. Kappe, S. S. Murphree, A. Padwa, *Tetrahedron* **1997**, *53*, 14179.
[2] N. Chronakis, M. Orfanopoulos, *Org. Lett.* **2001**, *3*, 545; S. H. Sutherland, K. C. Higgs, N. Taylor, R. Rodrigo, *Tetrahedron* **2001**, *57*, 309.
[3] M. Shoji, J. Yamaguchi, H. Kakeya, H. Osada, Y. Hayashi, *Angew. Chem.* **2002**, *114*, 3324; *Angew. Chem., Int. Ed.* **2002**, *41*, 3192.
[4] M. Meyer, K. Abou-Hadeed, H.-J. Hansen, *Helv. Chim. Acta* **2000**, *83*, 2383.
[5] P. Uebelhart, P. Mohler, R.-A. Fallahpour, H.-J. Hansen, *Helv. Chim. Acta* **1995**, *78*, 1437.
[6] C. Hörndler, H.-J. Hansen, *Helv. Chim. Acta* **1997**, *80*, 2520.
[7] R.-A. Fallahpour, H.-J. Hansen, *Helv. Chim. Acta* **1994**, *77*, 2297.
[8] W. Bernhard, P. Brügger, J. J. Daly, P. Schönholzer, R. H. Weber, H.-J. Hansen, *Helv. Chim. Acta* **1985**, *68*, 415.
[9] K. Abou-Hadeed, H.-J. Hansen, *Helv. Chim. Acta* **1997**, *80*, 2535.
[10] D. B. Dess, J. C. Martin, *J. Am. Chem. Soc.* **1991**, *113*, 7277; R. K. Boeckman, P. Shao, J. J. Mullins, K. P. Minbiole, A. B. Smith III, *Org. Synth.* **2004**, *Coll. Vol. X*, 696.

[11] W. Bernhard, P. Brügger, P. Schönholzer, R. H. Weber, H.-J. Hansen, *Helv. Chim. Acta* **1985**, *68*, 429.
[12] K. Hafner, G. L. Knaup, H. J. Lindner, H.-C. Flöter, *Angew. Chem., Int. Ed.* **1985**, *24*, 212; K. Hafner, G. L. Knaup, *Tetrahedron Lett.* **1986**, *27*, 1665.
[13] R. H. Weber, P. Brügger, T. A. Jenny, H.-J. Hansen, *Helv. Chim. Acta* **1987**, *70*, 742; R. H. Weber, P. Brügger, W. Arnold, P. Schönholzer, H.-J. Hansen, *Helv. Chim. Acta* **1987**, *70*, 1439.
[14] A. V. Willi, 'Isotopeneffekte bei chemischen Reaktionen', Georg Thieme Verlag, Stuttgart, 1983.
[15] A. P. Marchand, 'Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems', Verlag Chemie International, Deerfield Beach, 1982.
[16] a) P. Kouroupis, H.-J. Hansen, *Helv. Chim. Acta* **1995**, *78*, 1247; b) A. A. S. Briquet, P. Uebelhart, H.-J. Hansen, *Helv. Chim. Acta* **1996**, *79*, 2282.
[17] P. J. Dunn, C. W. Rees, *J. Chem. Soc., Perkins Trans. 1* **1987**, 1579.
[18] P. D. Williams, E. LeGoff, *J. Org. Chem.* **1981**, *46*, 4143.
[19] 'Vogel's Textbook of Practical Organic Chemistry', 4th edn., Longman Scientific & Technical, Essex, 1987, p. 302.
[20] G. Singh, A. Linden, K. Abou-Hadeed, H.-J. Hansen, *Helv. Chim. Acta* **2002**, *85*, 27.
[21] P. Magnus, S. A. Eisenbeis, N. A. Magnus, *J. Chem. Soc., Chem. Commun*. **1994**, 1545.

Received December 22, 2004