A New Alkylation Method for Heptalene-4,5-dicarboxylates and of One of Their Pseudoester Forms

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Dedicated to *Conrad Hans Eugster* on the occasion of his 90th birthday

Dimethyl heptalene-4,5-dicarboxylates[3]) undergo preferentially a *Michael* addition reaction at C(3) with α-lithiated alkyl phenyl sulfones at temperatures below $-50°$, leading to corresponding *cis*-configured 3,4-dihydroheptalene-4,5-dicarboxylates (*cf. Table 1*, *Schemes 3* and *4*). The corresponding heptalenofuran-1-one-type pseudoesters of dimethyl heptalene-4,5-dicarboxylates (*Scheme 5*) react with [(phenylsulfonyl)methyl]lithium almost exclusively at C(1) of the furanone group (*Scheme 6*). In contrast to this expected behavior, the uptake of 1-[phenylsulfonyl)ethyl]lithium occurs at C(5) of the heptalenofuran-1-ones as long as they carry a Me group at C(11) (*Schemes 6* and *7*). The 1,4- as well as the 1,6-addition products eliminate, on treatment with MeONa/MeOH in THF, benzenesulfinate, thus leading to 3- and 4-alkylated dimethyl heptalene-4,5-dicarboxylates, respectively (*Schemes 8–13*). The configuration of the addition reaction of the nucleophiles to the inherently chiral heptalenes is discussed in detail (*cf. Schemes 14–19*) on the basis of a number of X-ray crystal-structure determinations as well as by studies of the temperature-dependence of the ^{1}H-NMR spectra of the addition products.

1. Introduction. – Substitution reactions at the 12π-electron annulene core of heptalenes under spontaneous re-establishment of the 12π-electron skeleton, as it is well known for aromatic substitution reactions due to the recovery of aromatization energy, are unknown. The situation changes on the level of transition-metal complexes of heptalenes. In this way, *Vogel* and co-workers [2] synthesized, *e.g.*, heptalene-1,6-dicarboxaldehyde by *Vilsmeier* formylation of the *cis*-configured bis(tricarbonyliron) complex of heptalene. This type of electrophilic substitution reaction can also be realized, however, with [Fe(CO)$_3$] complexes of open-chain hexa-1,3,5-trienes (see, *e.g.*, [3]). We have recently realized an electrophilic acetoxylation reaction of a MeO-substituted heptalene-4,5-dicarboxylate, taking advantage of a corresponding heptalenone as a relay compound [1]. The principle is displayed in *Scheme 1*. It demonstrates the procedure that generally has to be followed when we undertake substitution reactions at C=C bonds in aliphatic or alicyclic surroundings, where we mostly have to deal with individual addition and elimination steps or, in rarer cases, the reverse steps, respectively.

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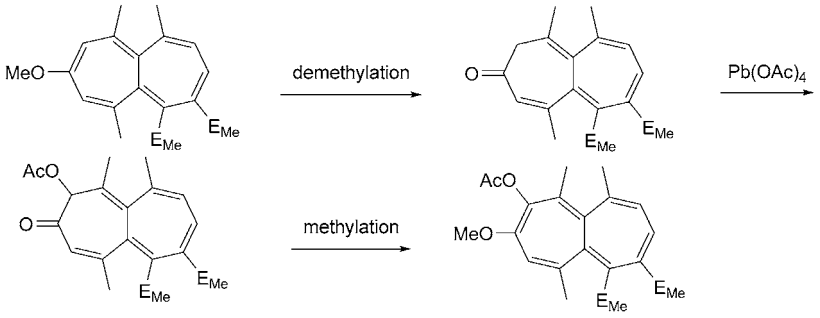
1) Part of the Ph.D. thesis of *Z. A. M.*, University of Zurich, 2002.
2) Part of the M.S. thesis of *P. G.*, University of Zurich, 2000.
3) The locants of heptalene itself are maintained throughout the whole work. See footnote 4 in [1] for reasoning.

Scheme 1

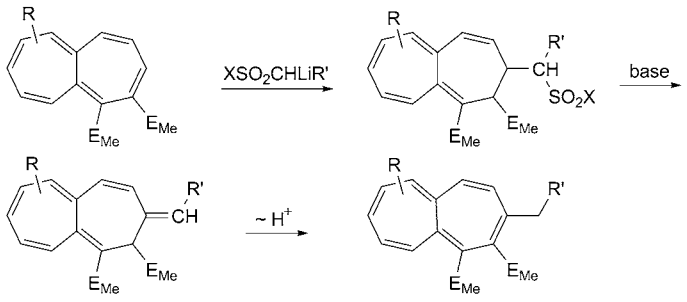


[a]) E_{Me} = COOMe in all *Schemes*.

Here, we report on a new alkylation at C(3) or C(2) of heptalene-4,5-dicarboxylates and one of their pseudoester forms, respectively. It is based on the afore-mentioned two-step principle, involving the *Michael*-addition reaction of α-lithiated alkyl phenyl sulfones in the first step and the base-catalyzed elimination reaction of benzenesulfinate in the second 're-establishment' step.

2. Results and Discussion. – 2.1. *Alkylation of Heptalene-4,5-dicarboxylates at C(3)*. We knew from our earlier alkylation experiments of dimethyl heptalene-4,5-dicarboxylates with lithiomethyl phenyl sulfone (= [(phenylsulfonyl)methyl]lithium) and other lithiomethyl sulfones that these nucleophiles did not react exclusively with the sterically less hindered methoxycarbonyl group at C(4) but also to a varying extent at C(3) of the heptalene skeleton in a *Michael*-type addition reaction [4][5]. We were interested, therefore, to find the optimal conditions for the *Michael*-addition pathway and the optimal base for the planned subsequent elimination reaction of the corresponding sulfinates (*Scheme 2*).

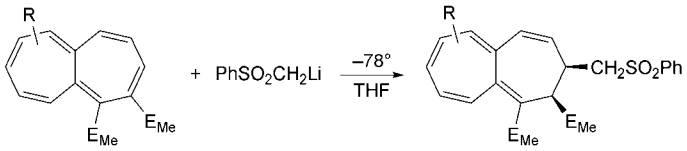
Scheme 2



Dimethyl heptalene-4,5-dicarboxylate (**1**) itself reacted with [(phenylsulfonyl)methyl]lithium in THF at $-78°$ exclusively at C(3) (→**2**), and so did a number of other simply substituted heptalene-4,5-dicarboxylates, *i.e.*, **3**, **5**, **7**, and **9**, leading thus in good yields to the corresponding *cis*-configured 3,4-dihydro-3-[(phenylsulfonyl)methyl]-

heptalene-4,5-dicarboxylates **4**, **6**, **8**, and **10**, respectively, as an almost 1:1 mixture of epimers with respect to the axis (C(5a)–C(10a)) of chirality (*Table 1*).

Table 1. Michael-*Addition Reaction of [(Phenylsulfonyl)methyl]lithium*[a]) *and Dimethyl Heptalene-4,5-dicarboxylates* **1**, **3**, **5**, **7**, *and* **9**



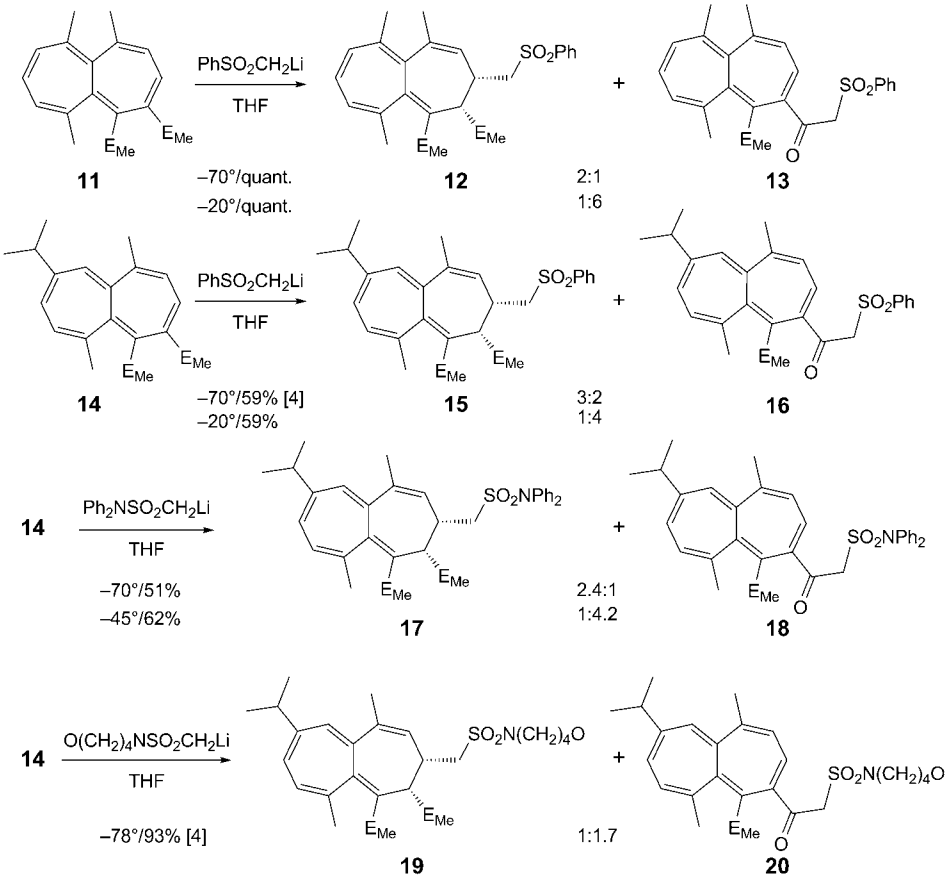
Reactant	R	*Michael* Adduct[b])	Yield [%]
1	H	**2**	69–95
3	1-Me	**4**	67
5	6-Me	**6**	67
7	8-Me	**8**	76
9	1,6-Me_2	**10**	62[c])

[a]) 1.1 mol-equiv. of methyl phenyl sulfone were beforehand lithiated with BuLi at 10°. Larger quantities of the nucleophile led to increasing amounts of tricyclic bis-adducts [4]. [b]) For the structure assignment of the *cis*-configured adducts, see below. [c]) Methyl 1,6-dimethyl-4-[(phenylsulfonyl)acetyl]heptalene-5-carboxylate was formed in minor amount (3%).

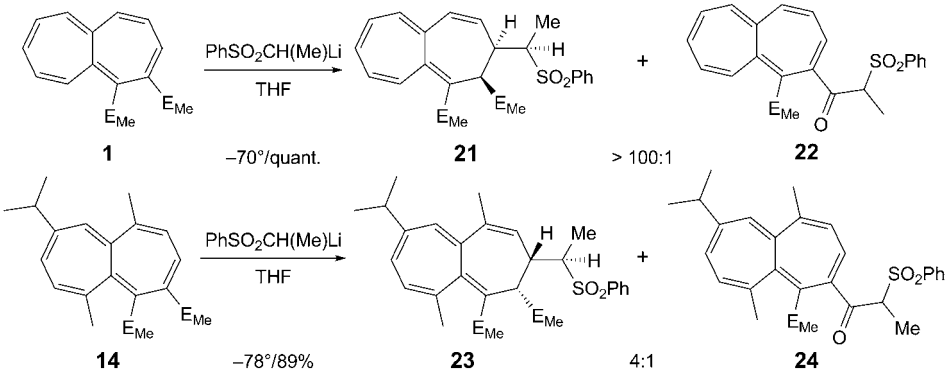
However, the reaction of **9** with [(phenylsulfonyl)methyl]lithium gave as a by-product small amounts of the alkylation product of MeOOC–C(4) as the sterically less hindered ester group, a fact that we had observed already in our former experiments with heptalene-4,5-dicarboxylates with a higher number of *peri*-substituents [4]. A more detailed investigation with the heptalene-4,5-dicarboxylates **11** and **14**, derived from 1,4,8-trimethylazulene and guaiazulene, respectively, showed that the ratio of *Michael* addition at C(3) and the alkylation reaction at MeOOC–C(4) is strongly dependent on the applied reaction temperature (→ **12**/**13** and **15**/**16**, resp.; *Scheme 3*). The observation that the ratio *Michael* adduct/alkylation product changed substantially in favor of the latter at $-20°$ speaks for the fact that the *Michael* addition at C(3) is reversible, whereas the alkylation at MeOOC–C(4) is irreversible due to the rapid elimination of methoxide and deprotonation of the formed (phenylsulfonyl)acetyl group at C(4). The electronic nature of the [(sulfonyl)methyl]lithium nucleophile has no great influence on the said ratio as experiments with *N*,*N*-diphenylmethanesulfonamide and 4-(methylsulfonyl)morpholine demonstrated (→ **17**/**18** and **19**/**20**, resp.).

Much more effective in view of the ratio of *Michael* addition at C(3) *vs.* alkylation at MeOOC–C(4) turned out to be the presence of an α-Me substituent in [(phenylsulfonyl)methyl]lithium as experiments with [1-(phenylsulfonyl)ethyl]lithium showed (→ **21**/**22** and **23**/**24**; see *Scheme 4* and below). The higher nucleophilicity and steric encumbrance of the α-branched ethyllithium reactant favor distinctly its 1,4-addition in comparison with the 1,2-addition.

Scheme 3

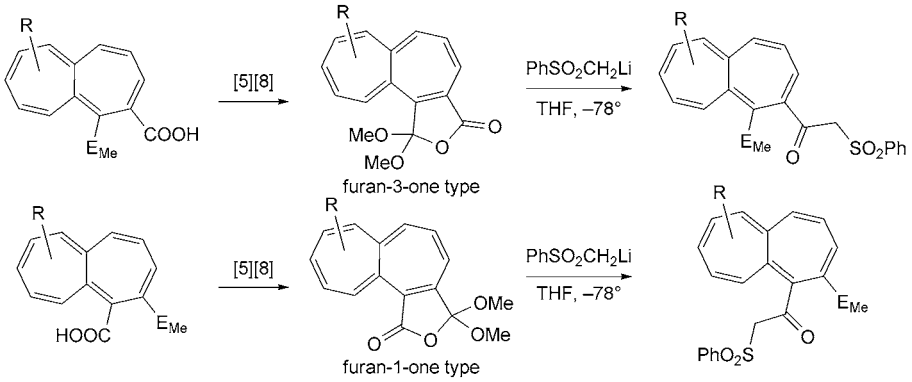


Scheme 4



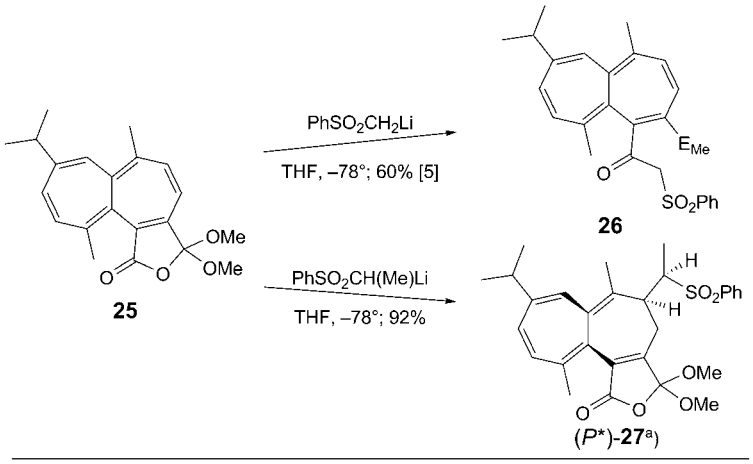
2.2. *Alkylations of Heptalene Pseudoesters at C(5).* As we have reported already in earlier publications, heptalene-4,5-dicarboxylates can be transformed *via* their half-esters into the corresponding regioisomeric pseudoesters [6][7], which allow selective reactions at their C=O groups (*Scheme 5*) [5][8]. In the course of these investigations, we were quite astonished to find that the furanone **25**, derived from heptalenedicarboxylate **14**, reacted with [(phenylsulfonyl)methyl]lithium in the expected manner (→**26**) whereas its reaction with [1-(phenylsulfonyl)ethyl]lithium led to a completely unexpected product, namely, as an X-ray crystal-structure determination (see below) revealed, to the 1,6-addition product (*P**)-**27** (*Scheme 6*). Further experiments disclosed that a Me group at C(11) of the heptaleno[1,2-*c*]furan-1-ones and at the α-position of the [(phenylsulfonyl)alkyl]lithium reactants are decisive for the formation of 1,6-adducts, whereas the presence or absence of a Me group at C(6) has no significant influence on the addition of the alkyllithium nucleophile at C(5) of the heptaleno[1,2-*c*]furanones (see **28** → (*P**)-**30** and **29** → (*P**)-**31**; *Scheme 7*). The crystal structure of the 1,6-adducts (*P**)-**30** and (*P**)-**31** was again determined by an X-ray diffraction analysis (see below). The reaction of heptalenofuranone **32** with [1-(phenylsulfonyl)ethyl]lithium gave mainly alkylation at C(1) resulting in the formation of **33**, and only small amounts of furanone **34** were identified spectroscopically.

Scheme 5



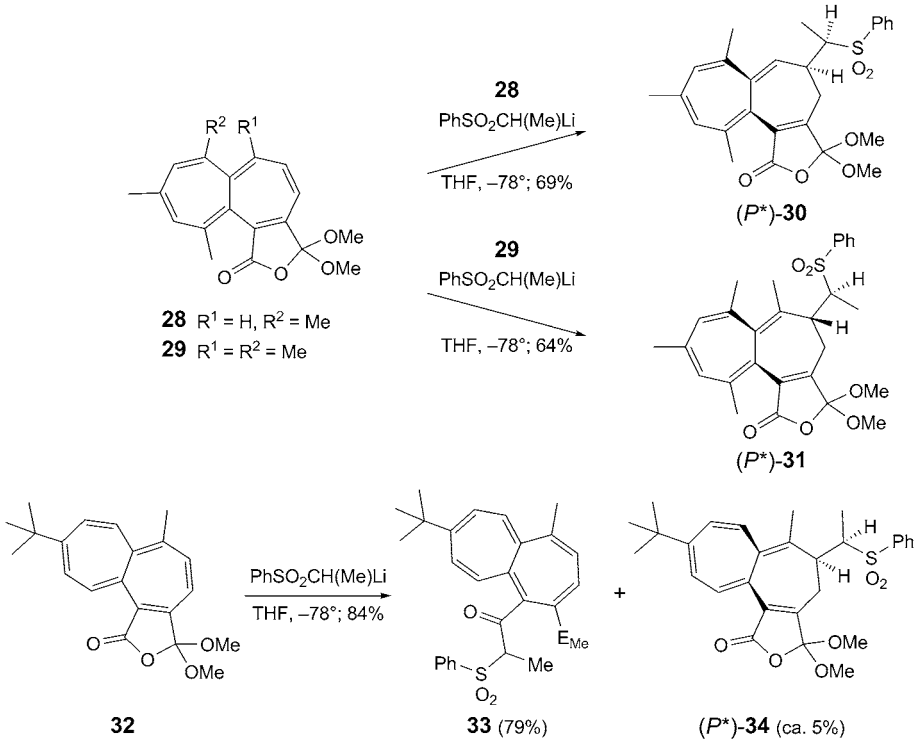
The AM1-calculated structure of heptalenofuranone **25** clearly revealed the reason for its propensity to undergo a 1,6-addition reaction with [1-(phenylsulfonyl)ethyl]-lithium (*Fig. 1*). The perspective view of (*P*)-**25** with the dotted *van der Waals* surface of the O-atom of the C=O group and Me–C(11) plainly demonstrates that the *re*-face of the C=O group is perfectly shielded by Me–C(11) against a nucleophilic attack. On the other hand, the *si*-face of the C=O group cannot take up a nucleophile since the *van der Waals* surfaces of the O-atom of the C=O group and Me–C(11) are touching each other, so that there is no free space for the necessary bending mode of the C=O group when changing from sp^2 to sp^3 hybridization on addition of a nucleophile. Moreover, the torsion angles Θ(O=C(1)–C(11b)–C(3a)) and Θ(C(11b)–C(3a)–C(4)–C(5)) amount to 178° and 25°, respectively, ideal for the uptake of a nucleophile at C(5), which exerts no influence on the packed spatial arrangement at the C=O group since the $sp^2 \rightarrow sp^3$ bending mode takes place at C(5). In the case of heptalenofuranones

Scheme 6



a) The (*P**)-configuration of **27** in the crystals is shown. In solution at room temperature, a 64:36 mixture of (*P**)- and (*M**)-**27** was established in a short time.

Scheme 7



without a Me group at C(11) (*e.g.*, **32**; see also [5]), the spatial interactions at the C=O group are strongly reduced, so that the 1,2-addition of a nucleophile at the C=O group is favored.

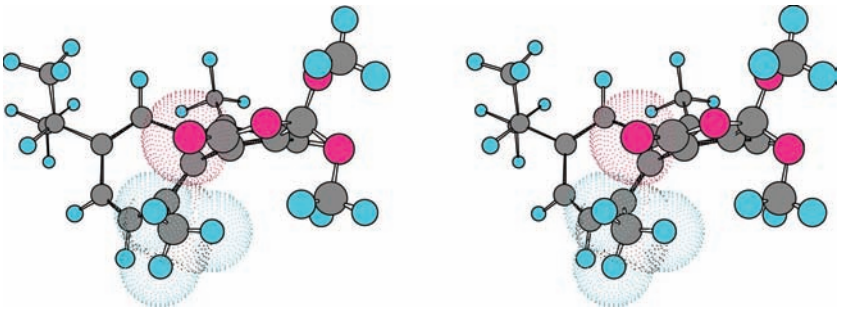
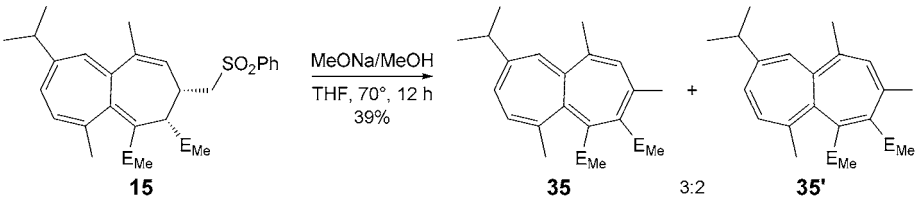


Fig. 1. *Stereoscopic view of the AM1-calculated structure of (*P**,5S*)-4,5-dihydro-8-isopropyl-3,3-dimethoxy-6,11-dimethyl-5-[(1*R**)-1-(phenylsulfonyl)ethyl]heptaleno[1,2-*c*]furan-1-one* ((*P**)-**27**) *with dotted* van der Waals *surfaces of O=C(1) and Me–C(11)*

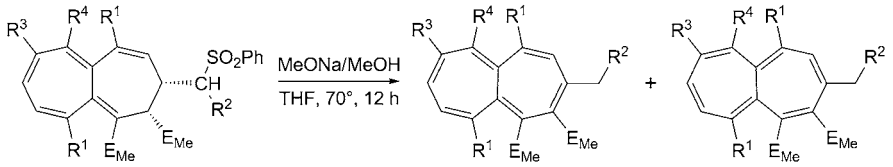
2.3. *Elimination Reactions with the 1,4- and 1,6-Adducts.* After the failure of elimination reactions of the 1,4-adduct **15** with DBU (1,3-diazabicyclo[5.4.0]undecane) or LDA (lithium diisopropylamide) as a base in THF according to *Scheme 2*, we found that MeONa in boiling MeOH/THF was the system of choice for the desired removal of $PhSO_2^-$, followed by base-catalyzed tautomerization (*Scheme 8*). The formed heptalenedicarboxylate was obtained as a thermal equilibrium mixture of **35** and its double-bonds-shifted (DBS) isomer **35′**, which we had obtained already earlier with a number of other products by thermal reaction of 3-methylguaiazulene with dimethyl acetylenedicarboxylate in decalin at 200° (*cf.* [9]). Other leaving groups such as $Ph_2NSO_2^-$ (16% of **35**/**35′**) or $O(CH_2)_4NSO_2^-$ (0% of **35**/**35′**) were less successful. The adduct **17** also reacted with LDA in THF, even though the yield of **35**/**35′** (6%) was low, and **19** gave no product at all under these conditions. Further elimination reactions, which led in moderate to good yields to some new alkylated heptalenedicarboxylates are compiled in *Scheme 9* (see **36**/**36′**, **38**/**38′**, **39**/**39′**, and **40**/**40′**)[4]).

Scheme 8



[4]) The standard elimination procedure applied on **21** did not lead to the formation of 3-ethylheptalenedicarboxylates **37**/**37′** (*cf.* **2** → **36**/**36′** in *Scheme 9*; R^1,R^3,R^4 = H, R^2 = Me). Due to a shortage of starting material, we could not repeat the elimination reaction of **21** with *t*-BuOK in THF (*cf.* **2** → **36**/**36′** in *Scheme 9*).

Scheme 9

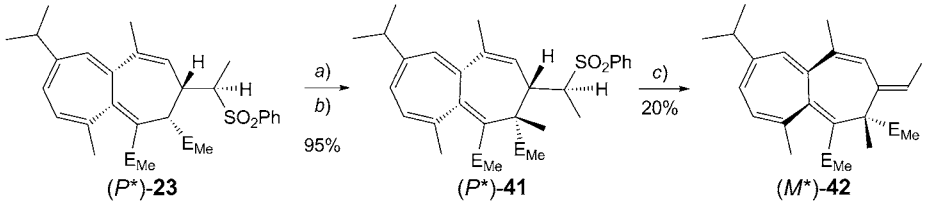


2	R^1 – R4 = H	30%[a])	**36**[b])		**36'**
10	R^1 = Me, R^2 – R4 = H	66%	**38**[c])	2:1	**38'**
12	R^1, R^4 = Me, R^2, R^3 = H	27%	**39** (18%)[d])		**39'** (9%)
23	R^1, R^2 = Me, R^3 = ^{i}Pr, R^4 = H	55%	**40**[b])	3:1	**40'**

[a]) *t*-BuOK/THF was used instead of MeONa/MeOH; for the latter base, see below. [b]) Mainly the 4,5-diester form was recognizable in the NMR spectra. [c]) Slow interconversion of both DBS forms at r.t. [d]) Yield after chromatographic separation and crystallization of both DBS isomers.

The (phenylsulfonyl)methyl or 1-(phenylsulfonyl)ethyl moiety at C(3) of the 3,4-dihydroheptalene-4,5-dicarboxylates should principally allow the nucleophilic introduction of further alkyl groups at C(1) of the sulfonylalkyl substituents. However, the presence of MeOOC–C(4) may favor a nucleophilic alkylation at C(4). This is indeed the case. When (*P**)-**23** was deprotonated with NaH, followed by addition of MeI, the C(4)-methylated 3,4-dihydroheptalene-4,5-dicarboxylate (*P**)-**41** was obtained almost quantitatively (*Scheme 10*)[5]). Its relative configuration was determined by an X-ray crystal-structure analysis (see below). Treatment of (*P**)-**41** under the established elimination conditions led at least in a yield of 20% to the corresponding 3-ethylidene-3,4-dihydroheptalenedicarboxylate (*M**)-**42** (*Scheme 10*). Its (3*E*)-configuration follows from an *anti*-E_2 elimination of $PhSO_2^-$ of (*P**)-**41**[6]), which should deliver (*P**,4*R**)-**42**. However, (*M**,4*R**)-**42** is, according to AM1 calculations, at least by *ca.* 0.7 kcal/mol, energetically favored; therefore, we think that we obtained **42** with (*M**,3*E*,4*R**)-configuration as shown in *Scheme 10*.

Scheme 10



(*P**)-**23** (*P**)-**41** (*M**)-**42**

a) NaH/THF, 4 h, – 10° to r.t. *b*) MeI, 3 d, r.t. *c*) MeONa/MeOH, THF, 70°, 12 h.

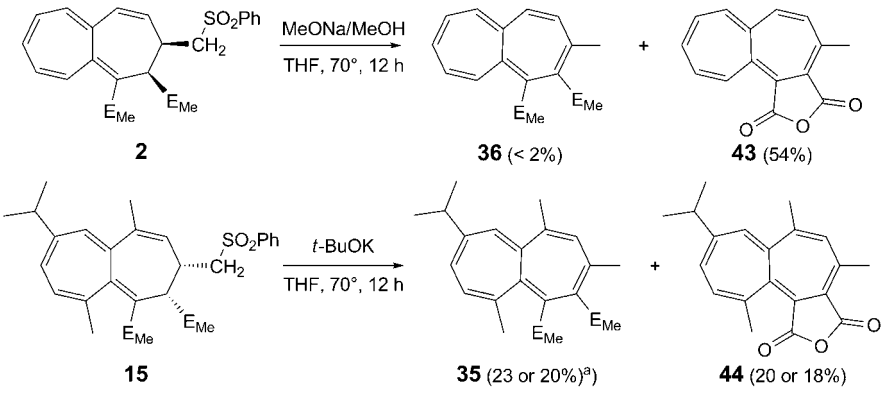
Quite astonishing was the result of the elimination reaction of **2** under our standard conditions with MeONa in MeOH/THF. Instead of the expected heptalenedicarbox-

5) We did not verify the possibility to trap the ester enolate of (*P**)-**23** by silylation, followed by a second deprotonation and then alkylation.

6) The (3*E*)-configuration of **42** is thermodynamically favored by *ca.* 2.5 kcal/mol with respect to the (3*Z*)-form of **42**.

ylate **36**, which was found only in a small amount, we isolated its cyclic anhydride **43** in good yield (*Scheme 11*). Similarly, the (sulfonylmethyl)heptalenedicarboxylate **15** gave with *t*-BuOK or Et_3COK in THF nearly equal amounts of the expected diesters **35**/**35′** and their common cyclic anhydride **44** (*cf.* [6] for DBS in cyclic anhydrides of heptalene-1,2- and heptalene-4,5-dicarboxylic acids). We suppose that, after deprotonation at C(4), the corresponding ester enolate **A** undergoes cyclization to **B**, which then loose methoxide to yield **C**, which represents the enol ether form of the cyclic anhydride of **15**. The final step would then be the base-induced formal elimination of $PhSO_2H$ to give the enol ether **D**. Treatment of the latter in the course of the workup procedure with aqueous 2N HCl yields then the observed cyclic anhydride **44** (*Scheme 12*). Of course, we cannot exclude that the elimination already takes place at the stage of **B** and that the oxido product of this reaction is present in the reaction mixture before working up. In other words, the decisive step in the discussed reaction sequence is the cyclization step, which might be dependent on the intramolecular flexibility of the 3,4-dihydroheptalene-4,5-dicarboxylates. A critical point may also be the elimination of $PhSO_2^-$, which should be dependent on the strength of the used base. Therefore, it is conceivable that the *peri*-substituted 3,4-dihydro-3-(sulfonylmethyl)-heptalene-4,5-dicarboxylates can be transformed to the corresponding heptalene-4,5-dicarboxylates with MeONa in MeOH/THF, whereas it needs the stronger bases *t*-BuOK or Et_3COK in THF to observe, in addition to diester formation, also the formation of the corresponding cyclic anhydride.

Scheme 11

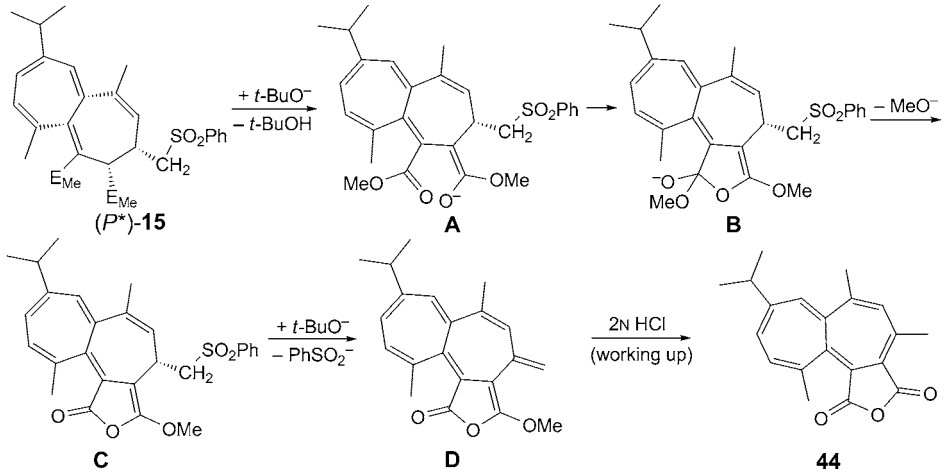


a) 3:1 Mixture of the DBS isomers. The second yield was obtained with Et_3COK as base.

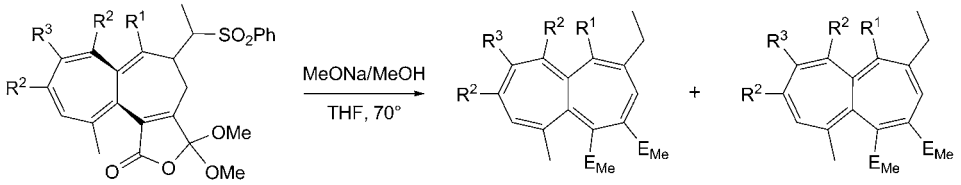
It turned out that heating the 4,5-dihydro-5-[1-(phenylsulfonyl)ethyl]heptaleno-[1,2-*c*]furans with MeONa/MeOH in THF was also successful for the formation of the corresponding 2-ethylated heptalene-4,5-dicarboxylates by elimination of $PhSO_2H$ (*Scheme 13*).

All new heptalenedicarboxylates were fully characterized spectroscopically and the structure of **45** was also determined by an X-ray diffraction analysis (see *Exper. Part*, *Table 7*). It is of interest to note that in the course of the elimination reaction of **31**, epimerization at the axis of chirality of **31** and/or **47** took place only to an extent of

Scheme 12



Scheme 13



(*P**)-**27**	R^1 = Me, R^2 = H, R^3 = ^{i}Pr	3 h; 81%	**45**	> 200 : 1[a])	**45'**
(*P**)-**30**	R^1, R^3 = H, R^2 = Me	3 h; 65%	**46**	3 : 1[a])	**46'**
(*P**)-**31**	R^1, R^2 = Me, R^3 = H	0.75 h; 67%[b])	**47**	1 : 9[c])	**47'**

[a]) Represents the thermal equilibrium mixture. [b]) The anhydride (*P**)-**48** (*ca.* 5%) of (*P**)-**31** was found in addition. [c]) The ratio of the thermal equilibrium mixture for the corresponding 2-/4-methyl analogs at 180° amounted to 3.3:1 (*cf.* [10]).

10%. On standing at room temperature in $CDCl_3$ solution, the 1:9 ratio of **47**/**47′** was slowly reversed. After two months, the ratio approached a value of almost 12:1 in favor of **47**.

2.4. *Structure Characterization of the* Michael *Addition Products.* 2.4.1. *3-Alkylated 3,4-Dihydroheptalene-4,5-dicarboxylates.* In our former reports on the reaction of higher alkylated heptalene-4,5-dicarboxylates with [(X-sulfonyl)methyl]lithium, the relative configuration of the formed 3-alkylated heptalene-4,5-dicarboxylates had been of minor concern [4][8]. We assumed that these compounds possessed relative *cis*- and *trans*-configuration with respect to the spatial arrangements of the substituents (XSO_2CH_2, COOMe) at C(3)–C(4). This view was supported by an X-ray crystal-structure determination of one of the isomers of **19** (*cf. Scheme 3*)[7]), which revealed its

[7]) See compound **6a** in Scheme 3 of [4].

relative *cis*-configuration, whereas the relative (*M**)-configuration at the axis of chirality (C(5a)–C(10a)) had been overlooked, since it was not in the focus of our interest at that time. On this basis, and without any further investigation, we assigned the *trans*-configuration to the second isomer of **19**[8]), found in solution, and which, together with its crystallized form, was only characterized by its ^{1}H-NMR spectrum in C_6D_6[9]).

We were surprised when we found in this work that, with the exception of the mixture of the two isomers of **10**, all the simply substituted 3-alkylated 3,4-dihydroheptalene-4,5-dicarboxylates listed in *Table 1* showed, as mixtures at room temperature, in their ^{1}H-NMR spectra coalescence of almost all of the signals, and it needed temperatures as low as 223 K to get sharp signals of both isomers of the *Michael* adducts. Moreover, a temperature scan in steps of 10 K between 300 to 223 K revealed that at first, most of the signals of both isomers became sharp, followed finally by the signals of H–C(3) and H–C(4) of the isomers. These observations excluded the existence of *cis*/*trans* pairs of isomers, but they were in full agreement with the presence of thermally converting epimers with respect to their axis of chirality. Fortunately, we obtained crystals of one isomer each of the 1-methyl- and 1,6-dimethyl-3,4-dihydroheptalenedicarboxylate **4** and **10**, respectively, which were suitable for an X-ray crystal-structure determination (*Figs. 2* and *3*). Both compounds showed a *cis*-arrangement of the substituents at C(3) and C(4), however, with opposite relative configuration at their axis of chirality (C(5a)–C(10a)). Thus, the crystals of (*P**)-**4** contained the pure (*P**,3*R**,4*R**)-isomer and those of (*P**)-**10** the pure (*P**,3*S**,4*S**)-form[10]).

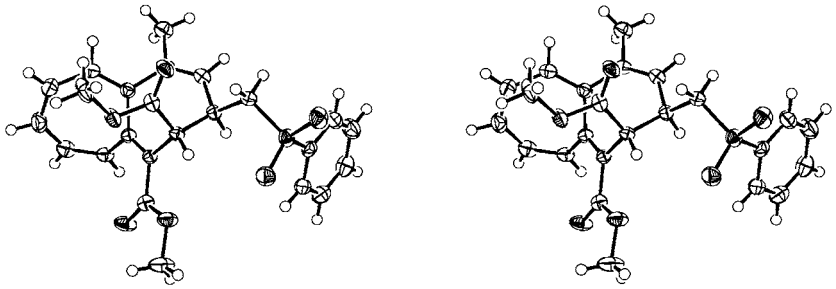


Fig. 2. *Stereoscopic view of the X-ray crystal structure of dimethyl (*P*,*3*R*,*4*R**)-3,4-dihydro-1-methyl-3-[(phenylsulfonyl)methyl]heptalene-4,5-dicarboxylate* ((*P**)-**4**; 50% probability ellipsoids)

Systematic ^{1}H- and ^{13}C-NMR analyses of all prepared dimethyl 3,4-dihydro-3-[1-(X-sulfonyl)alkyl]heptalene-4,5-dicarboxlates (*cf. Table 1*, *Schemes 3*, *4*, and *10*) revealed that all dicarboxylates, which carried no substituent at C(6) (see **2**, **4**, and **8**) appeared with relative (*P**,3*R**,4*R**)-configuration, whereas those with a Me group at C(6) (**6**, **10**, **12**, **15**, **17**, **19**, **23**, and **41**) had the relative (*P**,3*S**,4*S**)-configuration. The observation that all *Michael*-addition products of the heptalene-4,5-dicarboxylates exhibit relative *cis*-configuration of the substituents at C(3)–C(4) is in agreement with

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8) See compound **6b** in Scheme 3 of [4].

9) See Table 10 in [4].

10) The latter, when dissolved at room temperature in C_6D_6, slowly equilibrated to a 2:1 mixture with its (*M**,3*S**,4*S**)-epimer.

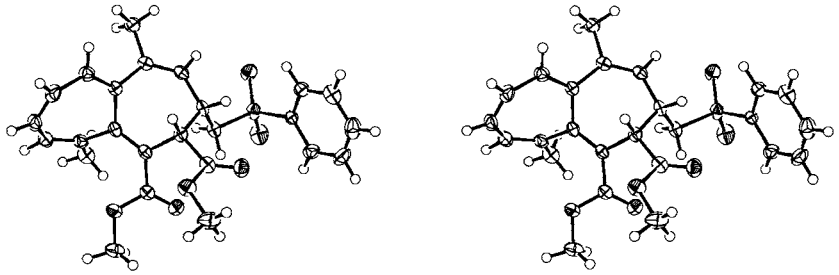

Fig. 3. *Stereoscopic view of the X-ray crystal structure of dimethyl (*P**,3*S**,4*S**)-3,4-dihydro-1,6-dimethyl-3-[(phenylsulfonyl)methyl]heptalene-4,5-dicarboxylate* ((*P**)-**10**; 50% probability ellipsoids)

the fact that the protonation of the primarily formed C(4)-ester enolates takes place in a *trans*-relationship to the bulky [1-(X-sulfonyl)alky] group at C(3)[11]).

Intramolecular H-atom transfer does not seem to play a role in the protonation step. This is evident by the fact that the alkylation experiment of the C(4)-ester enolate of (*P**)-**23** with MeI, which gave exclusively the C(4)-methylated product (*P**)-**41** with retention of configuration at C(4) (*Scheme 10*) as revealed by its X-ray crystal-structure analysis (*Fig. 4*), and which showed the same (*P**,3*S**,4*S**)-configuration at the 3,4-dihydroheptalene core as the starting material (*P**)-**23** (see [5] for the X-ray structure of **23**)[12]). However, the (*R**)-configured 3-[1-(phenylsulfonyl)ethyl] group of (*P**)-**23** underwent, obviously due to the basic conditions of the methylation reaction, complete epimerization to (*S**)-configuration in (*P**)-**41**.

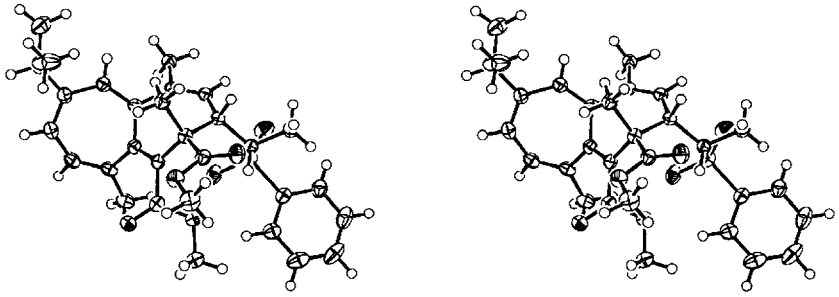

Fig. 4. *Stereoscopic view of the X-ray crystal structure of dimethyl (*P**,3*S**,4*S**)-3,4-dihydro-9-isopropyl-1,4,6-trimethyl-3-[(1*S**)-1-(phenylsulfonyl)ethyl]heptalene-4,5-dicarboxylate* ((*P**)-**41**; 50% probability ellipsoids)

The global events of the formation of the *Michael* products are very simple (*Scheme 14*). Since we found only the *cis*-3,4-dihydroheptalene-4,5-dicarboxylates, the

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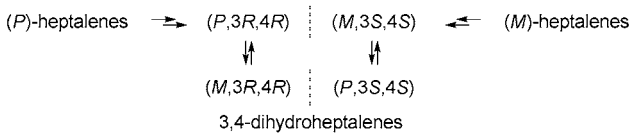
11) AM1 calculations of (*P**)-**4** and (*P**)-**10**, which very well reproduced their crystal structures, showed that the ΔH_f° values of their corresponding *trans*-forms, (*P**,3*R**,4*S**)-**4** and (*P**,3*S**,4*R**)-**10**, respectively, are lying 2.1 and 2.3 kcal/mol, respectively, higher in energy, *i.e.*, the 3,4-*cis*-configured 3,4-dihydroheptalenes are the thermodynamically favored forms.

12) In this case, AM1 calculations showed the *cis*-methylation product to be 3.3 kcal/mol less stable than the *trans*-product, (*P**,1′*S**,3*S**,4*R**)-**41**.

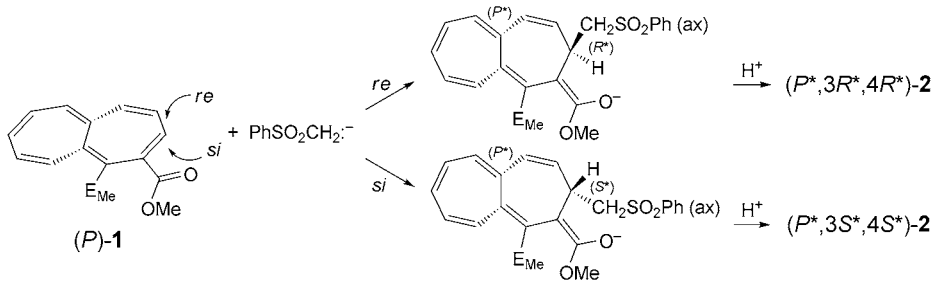
Scheme 14



two epimers of which represent, due to their labile axis of chirality, the thermodynamically controlled products.

However, there are principally two ways by which the uptake of the nucleophile can occur. The simplest mode is shown in *Scheme 15*. It means that the axial attack of the nucleophile would take place only at one of the prochiral sites of C(3). In other words, the decisive step of the alkylation reaction happens with 100% stereoselectivity. The other mode would be that the nucleophile attacks C(3) with a certain stereoselectivity at both of its prochiral sites (*Scheme 15*).

Scheme 15



To get more insight into these two modes, which do not alter the global stereochemical outcome, we performed a number of AM1 calculations. First of all, X-ray crystal-structure determinations as well as calculations show for heptalene-4,5-dicarboxylates an s-*cis*-conformation of the ester C=O group at C(4) in relation to the C(3)=C(4) bond with a Θ of 20° and below, independent of the number of *peri*-substituents (*Table 2*).

AM1 Calculations with methanide as model nucleophile show that the axial *cisoid* ester enolates, formed on the *re* path, are energetically favored by 2.3–5.8 kcal/mol, compared with those resulting from the *si* path (*Table 3*). The reason for this difference can be seen in the almost perfect s-*trans* torsion angle at C(4)–C(5) of the (*P**,*R**)-products, which allows a much better delocalization of the negative charge of the ester-enolates already in the transition state. This torsion angle stays almost constant (around 145°) on the way to the (*P**,*S**)-ester enolates[13]). Therefore, we assume that only the *re* path and the respective *si* path are responsible for the uptake of a nucleophile at C(3) of the discussed (*P*)- and (*M*)-heptalenedicarboxylates.

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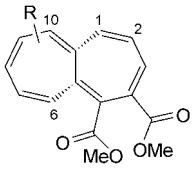
[13]) See the X-ray structures of **5** and **49** with a Θ(C(5a)=C(5)–C(4)–CO_2Me) of 145.3(2)° and 144.6(3)°, respectively (note that in these crystal structures, the atoms have been numbered as C(10a)=C(10)–C(9)–C(12)).

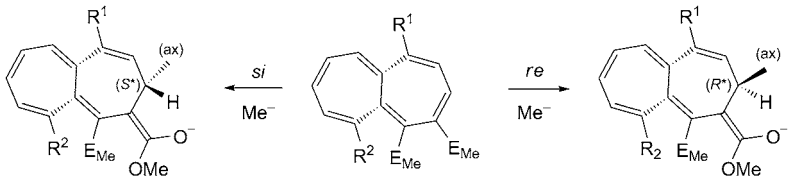
Table 2. *Relevant Torsion Angles Θ* [°][a]) *of Dimethyl Heptalen-4,5-dicarboxylates with Methyl Groups in* peri-*Position*



Torsion angles	**3** (– 73.6)[b])	**5** (– 71.6)[b])	**48** (– 72.6)[b])	**45** (– 107.3)[b])
Θ(C(1)=C(2)–C(3)=C(4))	34.0	32.0 (30.3)	33.5 (33.8)	35.0 (35.4)
Θ(C(5)=C(5a)–C(10a)–C(1))	55.0	57.2 (56.1)	53.9 (56.2)	61.6 (62.6)
Θ(C(6)–C(5a)–C(10a)=C(10))	54.7	56.8 (57.8)	54.0 (59.6)	59.4 (62.0)
Θ(C(3)=C(4)–C=O)	– 20.8	– 9.0 (– 13.0)	– 20.7 (– 19.9)	– 6.3 (– 16.5)
Θ(C(5a)=C(5)–C=O)	– 23.6	– 59.6 (– 47.7)	– 23.8 (– 32.8)	– 61.0 (– 32.8)

[a]) AM1 calculated values; in parentheses, X-ray data (see also *Exper. Part*, *Table 7*); **3**, 1-Me; **5**, 6-Me; **48**, 10-Me; **45**, 1,6-Me_2, 2-Et, and 9-^{i}Pr. [b]) In parentheses, AM1 calculated ΔH_f° values (kcal/mol).

Table 3. *Change of Θ(*C(5a)=C(5)–C(4)=C(OMe)O^-*)* [°] *on Axial* Michael *Addition of Methanide at C(3) of Dimethyl Heptalene-4,5-dicarboxylates* **1**, **3**, **5**, *and* **9**[a])



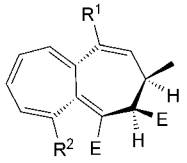
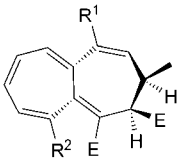
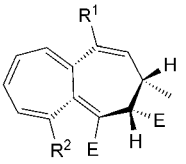
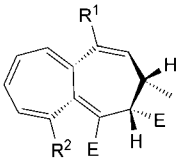
axial (*P**,3*S**) axial (*P**,3*R**)

$R^1 = R^2 = H$	149.5 (– 119.1)	**1**[b])	– 175.2 (– 123.8)
R^1 = Me, R^2 = H	144.6 (– 124.5)	**3**	– 175.6 (– 130.3)
R^1 = H, R^2 = Me	144.9 (– 124.6)	**5**	178.0 (– 126.9)
$R^1 = R^2$ = Me	146.0 (– 130.3)	**9**	178.2 (– 133.7)

[a]) According to AM1 calculations (see also *Table 2*); in parentheses, ΔH_f° value of the shown axial forms. [b]) For X-ray structure analysis of **1**, see [11].

The crystal structures of (*P**,3*R**,4*R**)-**4** and (*P**,3*S**,4*S**)-**10** disclose the presence of principally a third element of chirality, namely that of the helical turn of the 3,4-substituted fragment C(2)–C(3)–C(4)–C(5) with (+)-sc torsion angles of 69.5(3)° and 67.9(2)°, respectively. The fragment is part of a seven-membered ring in a boat-like conformation with C(4) in the bow position. AM1 Calculations of model *Michael* adducts of diesters **1**, **3**, **5**, and **9**, again with methanide as nucleophile, indicate that a second conformation is possible, wherein the fragment possesses (–)-sc conformation, and C(3) takes the bow position (*Table 4*). One recognizes that Me substituents at the heptalene core markedly influence the thermodynamic stability of the two diastereoisomers as well as the preferred conformation of their 3,4-dihydro ring. A Me group at C(6) shifts the relative configuration from (+)-sc-(*P**,3*R**,4*R**) to (+)-sc-

Table 4. ΔH_f° *Values* (kcal/mol) *of the* cis-*Diastereoisomers of Dimethyl 3,4-Dihydro-3-methylheptalene-4,5-dicarboxylates* **1**, **3**, **5**, *and* **9**[a])[b])

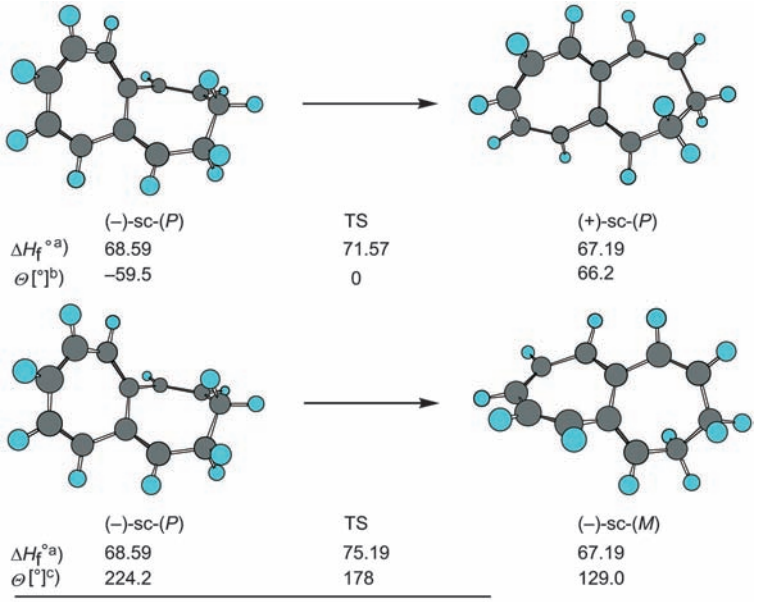
		 (+)-sc-(*P**,3*R**,4*R**)	 (–)-sc-(*P**,3*R**,4*R**)	 (+)-sc-(*P**,3*S**,4*S**)	 (–)-sc-(*P**,3*S**,4*S**)
$R^1 = R^2 = H$	**1**[a])	– 93.75	– 88.98	– 92.25	– 92.61
$R^1 = Me$, $R^2 = H$	**3**[a])	– 99.25	– 95.93	– 99.24	– 99.45
$R^1 = H$, Me	**5**[a])	– 98.23	– 93.81	– 99.09	– 95.70
$R^1 = R^2 = Me$	**9**[a])	– 103.91	– 100.92	– 105.05	– 103.03

[a]) Key no. of the corresponding dimethyl heptalene-4,5-dicarboxylate. [b]) The stereochemical descriptors (+)- and (–)-sc refer to the sign of the ring torsion angle Θ(C(2)–C(3)–C(4)–C(5)).

(*P**,3*S**,4*S**), just as observed in the crystal structures of (*P**)-**4** and (*P**)-**10**. Moreover, one can see that the (+)-sc-(*P**,3*R**,4*R**) forms are without exception by 3–4.8 kcal/mol more stable than their (–)-sc conformers. The situation is more complex for the (*P**,3*S**,4*S**)-configured diastereoisomers. In the cases with no substituent or a Me group at C(1), the (–)-sc forms are energetically slightly favored. However, a Me substituent at C(6) (or C(1) and C(6)) makes the (+)-sc conformations more stable. Taking all together, one can say that the investigated 3,4-dihydroheptalene-4,5-dicarboxylates contain two fixed elements of chirality (centers at C(3) and C(4)) and two principally dynamic elements of chirality (axes at C(5a)–C(10a) and C(3)–C(4)).

To learn more about the molecular dynamics of 3,4-dihydroheptalenes, we calculated the transition state energies of the (*P*),(*M*) and (+)-sc,(–)-sc conversion of 3,4-dihydroheptalene (*Scheme 16*) and of (*P*,3*S*,4*S*)-3,4-dihydro-1,3,6-trimethylheptalene-4,5-dicarboxylic acid (*Scheme 17*), close to the structure of the *Michael* adduct **10** with the highest number of *peri*-substituents. The AM1-calculated data for 3,4-dihydroheptalene itself show its (+)-sc-(*P*) form more stable than its diastereoisomeric (–)-sc form, and the data listed in *Table 4* indicate that substituents in positions 1, 3, 4, 5, and 6 can enlarge this energy gap up to 4.8 kcal/mol. The rotational barrier at the ring bond C(3)–C(4) is with 3.0 and 4.4 kcal/mol expectedly low and clearly below the transition-state energy of 6.6 and 8.0 kcal/mol, respectively, for the change of configuration of the dihydroheptalene skeleton. The rotational barrier of 2.4 and 4.1 kcal/mol at the C(3)–C(4) bond for the above mentioned analog of **10** does not change very much, in contrast to the corresponding inversion barrier of the dihydroheptalene configuration, which amounts to 16.9 and 17.5 kcal/mol, respectively, and are strongly dependent on the number of *peri*-substituents as known from their parent heptalenes (*cf.* [12]). The calculated data are in perfect agreement with the observed rapid, respectively, slow (*P**,3*S**,4*S**) → (*M**,3*S**,4*S**) conversion of **6** and **10** at room temperature in solution. Moreover, the observed mostly broad signals for H–C(3) and H–C(4) in the ^{1}H-NMR spectra of the lower-substituted 3,4-dihydrohep-

Scheme 16



a) kcal/mol. b) Θ(C(2)–C(3)–C(4)–C(5)). c) Θ(C(5)=C(5a)–C(10a)=C(10)).

talene-4,5-dicarboxylates speaks for an active dynamic equilibrium of the (+)-sc and (−)-sc ring conformers at the temperature range used for the NMR measurements of the 3,4-dihydroheptalene-4,5-dicarboxylates.

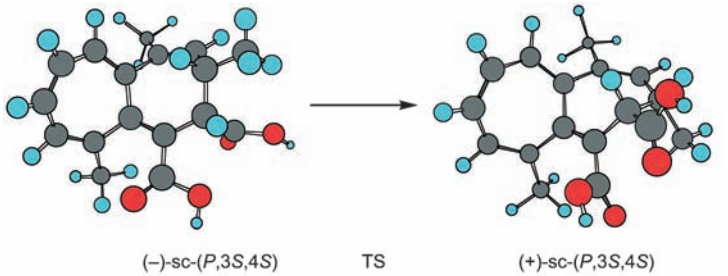
2.4.2. *5-Alkylated 4,5-Dihydro-3,3-Dimethoxyheptaleno[1,2-*c*]furan-1(3*H*)-ones.* The structure and relative configuration of the 4,5-dihydroheptaleno[1,2-*c*]furan-1(3*H*)-ones (*P**)-**27**, (*P**)-**30**, and (*P**)-**31** were determined by X-ray crystal-diffraction analyses (see *Figs. 5* and *6* as well as *Table 7* in the *Exper. Part*). Whereas the two former structures possess the same relative configuration, the latter has (*P**,1′*S**,5*R**)-configuration. (*P**)-**27**, when dissolved in $CDCl_3$ at room temperature, rapidly formed a 2:1 mixture with its (*M**)-epimer (*Scheme 6*). The two other compounds showed no noticeable epimerization during the time of their NMR measurement in $CDCl_3$ solution at normal temperature[14]).

The different relative configuration at C(5) of the 1,6-adducts speaks for the change of the site of the uptake of the nucleophile by the heptalenofuranone as shown in *Scheme 18*. Since all three compounds exhibit the same (+)-sc conformation at the C(4)–C(5) bond with Θ(C(3a)–C(4)–C(5)–C(6)) of 64.8(2)° ((*P**)-**27**[15]), 57.6(2)° ((*P**)-**30**), and 63.0(2)° ((*P**)-**31**), it was of interest for us to look for the reason of this site selectivity. *Table 5* lists the AM1-calculated ΔH_f° values of the dienolate intermediates that are formed with the model nucleophiles methanide and propan-2-

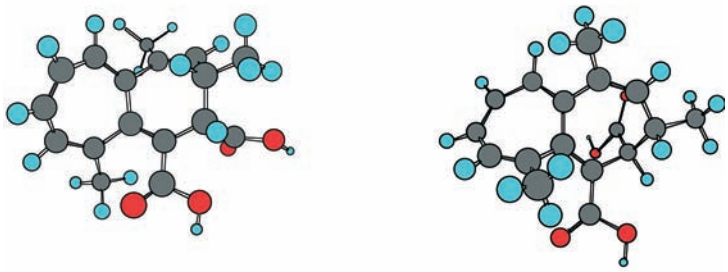
14) See below for the reason.

15) (*P**)-**27** appears in the crystals with two different rotational orientations of the ^{i}Pr group with respect to the heptalene core.

Scheme 17



	(–)-sc-(*P*,3*S*,4*S*)	TS	(+)-sc-(*P*,3*S*,4*S*)
ΔH_f °[a])	–116.74	–114.34	–118.44
Θ [°][b])	–69.5	0	65.0



	(–)-sc-(*P*,3*S*,4*S*)	TS	(–)-sc-(*M*,3*S*,4*S*)
ΔH_f °[a])	–116.74	–99.85	–117.30
Θ [°][c])	234.7	180	119.8

[a]) kcal/mol. [b]) Θ(C(2)–C(3)–C(4)–C(5)). [c]) Θ(C(5)=C(5a)–C(10a)=C(10)).

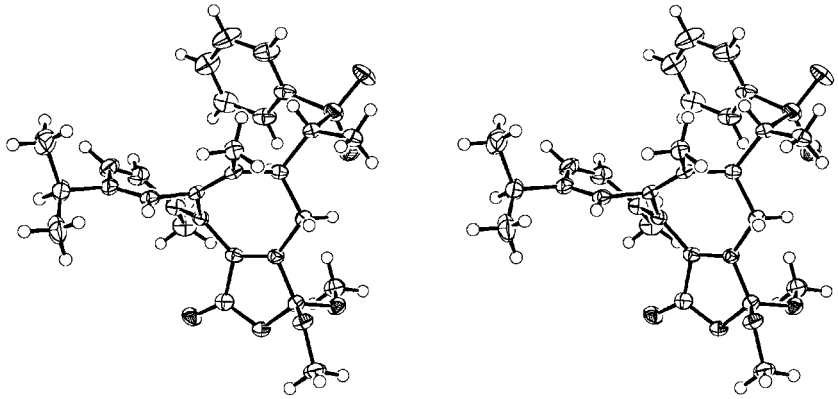


Fig. 5. *Stereoscopic view of the X-ray crystal structure of one of the two symmetry-independent molecules of (*P**,5S*)-4,5-dihydro-8-isopropyl-3,3-dimethoxy-5-[(1R*)-1-(phenylsulfonyl)ethyl]heptaleno[1,2-c]-furan-1(3H)-one* ((*P**)-**27**; 50% probability ellipsoids)

ide by axial attack on the *re* and *si* site of C(5). All relaxed intermediates show (+)-sc conformations with Θ(C(3a)=C(4)–C(5)–C(6)) in the range of 52 – 63° for the

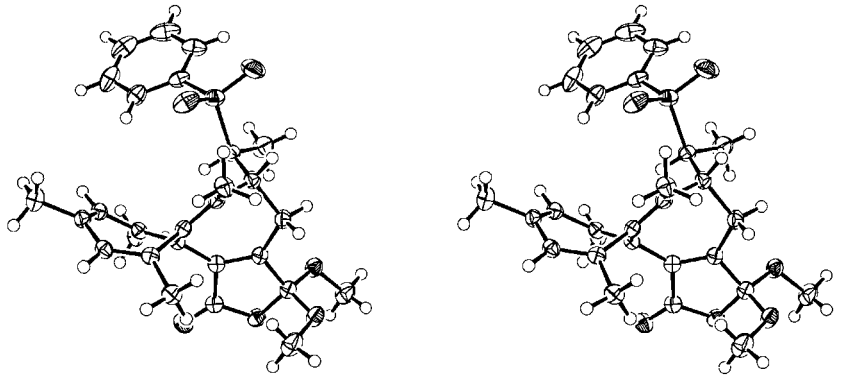
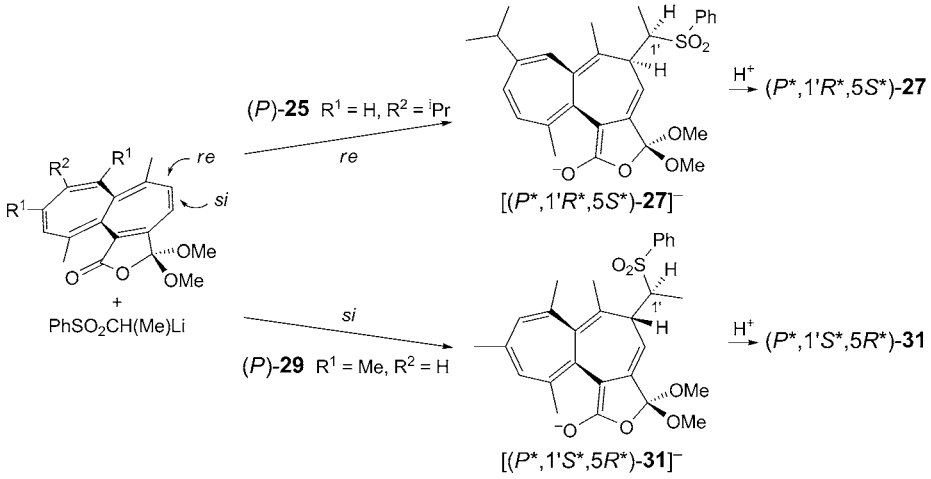


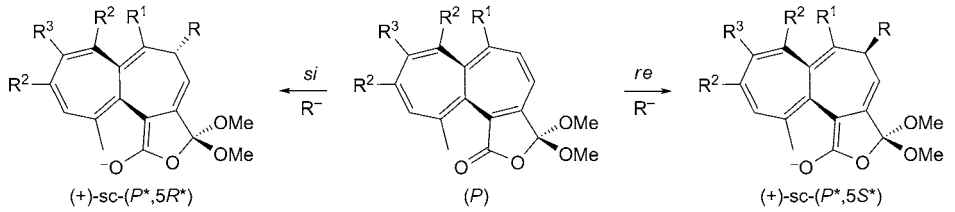
Fig. 6. *Stereoscopic view of the X-ray crystal structure of (*P**,5*R**)*-4,5-dihydro-*3,3-dimethoxy-6,7,9,11-tetramethyl-5-[(1*S**)-1-(phenylsulfonyl)ethyl]heptaleno[1,2-*c*]furan-1(3*H*)-one* ((*P**)-**31**; 50% probability ellipsoids)

Scheme 18



(*P**,5*S**)-forms and 42 – 49° for the (*P**,5*R**)-forms. The two intermediate dienolate structures arising from **28** and methanide are reproduced in *Fig. 7*. From the axial *re* attack results the (+)-sc conformation with the added Me group in a pseudo-equatorial position, whereas the addition on the *si* site delivers the (+)-sc conformation with the Me group in pseudo-axial position. The (+)-sc-(*P**,5*S**)-dienolate intermediates with methanide as nucleophile are by ΔH_f° 0.5 – 1.9 kcal/mol more stable than their (+)-sc-(*P**,5*R**) counterparts, a situation which changes with the α-branched 1-methylethanide (propan-2-ide) as nucleophile, where only the (+)-sc-(*P**,5*S**) form, derived from **30**, is by 1.0 kcal/mol more stable than the corresponding (5*R**) form, whereas it is the (+)-sc-(*P**,5*R**)-form in the other two cases, which is by 1.6 – 1.8 kcal/mol more stable. Therefore, it is reasonable to assume that indeed increasing steric interaction in the

Table 5. *Dienolate Intermediates of the 1,6-Addition of Model Nucleophiles at C(5) of Heptaleno[1,2-c]furan-1-(3*H*)-ones* **25′**, **28**, *and* **29**[a])



	ΔH_f° ((+)-sc-(*P**,5*R**))	No.	ΔH_f° (*P*)	ΔH_f°((+)-sc-(*P**,5*S**))
R = Me; $R^1 = R^3$ = Me, R^2 = H	– 145.7 (42.5)	**25′**	– 79.3	– 146.3 (57.9)
R = Me; $R^1 = R^3$ = H, R^2 = Me	– 146.6 (45.8)	**28**	– 80.5	– 148.5 (52.2)
R = Me; $R^1 = R^2$ = Me, R^3 = H	– 151.7 (49.0)	**29**	– 85.4	– 152.2 (58.6)
R = ^{i}Pr; $R^1 = R^3$ = Me, R^2 = H	– 156.0 (47.7)	**25′**		– 154.3 (62.8)
R = ^{i}Pr$R^1 = R^3$ = H, R^2 = Me	– 157.1 (44.8)	**28**		– 158.1 (56.3)
R = ^{i}Pr; $R^1 = R^2$ = Me, R^3 = H	– 161.9 (48.3)	**29**		– 160.2 (63.0)

[a]) ΔH_f° in kcal/mol; **25′** = **25** with Me–C(8) (R^3) instead of ^{i}Pr–C(8); in parentheses, Θ(C(3a)=C(4)–C(5)–C(6)).

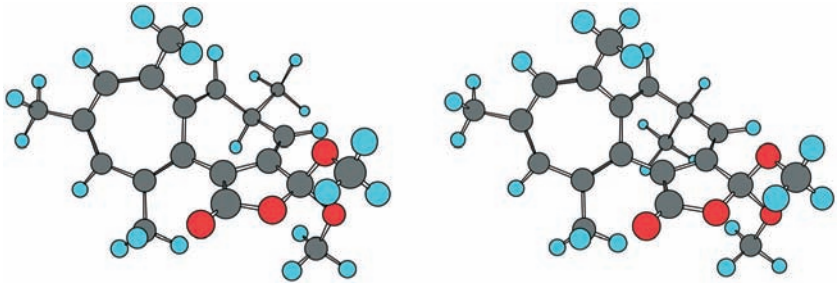


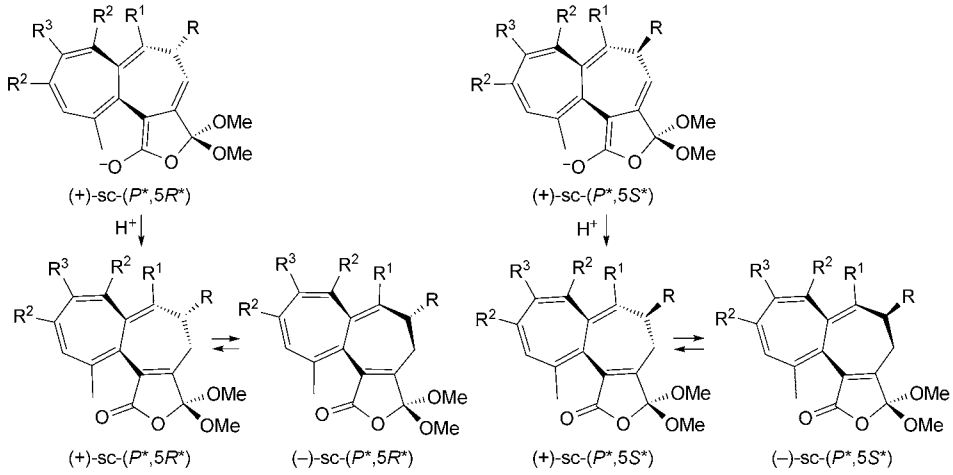
Fig. 7. *AM1-Calculated, hypothetical dienolate structures resulting from* re (left) *and* si (right) *attack, resp., of methanide at C(5) of* (P)*-configured furanone* **28** (see text)

transition state of the 1,6-addition of 1-(phenylsulfonyl)ethanide to the furanones leads to a change of the site of the attack.

Protonation at C(4) of the dienolate intermediates leads to the corresponding 4,5-dihydroheptaleno[1,2-*c*]furan-1(3*H*)-ones, which can also be regarded as furano-fused 3,4-dihydroheptalenes. The calculated ΔH_f° of the (+)- and (−)-sc forms of the model compounds are listed in *Table 6*. One clear answer is that the (+)-sc conformers are principally more stable than the (−)-sc forms in accordance with the X-ray crystal structures of all three heptaleno[1,2-*c*]furanones. Moreover, α-alkyl branching of the substituent at C(5) is sterically mostly slightly better accommodated by the (*P**,5*R**)-configured furanones.

We chose 4,5-dihydro-3,3-dihydroxy-5,6,8,11-tetramethylheptaleno[1,2-*c*]furan-1(3*H*)-one as a model for **27** to get more insight into the molecular dynamics of the furano-fused 3,4-dihydroheptalenes (*Scheme 19*). The ΔH_f° values, listed in *Table 6*,

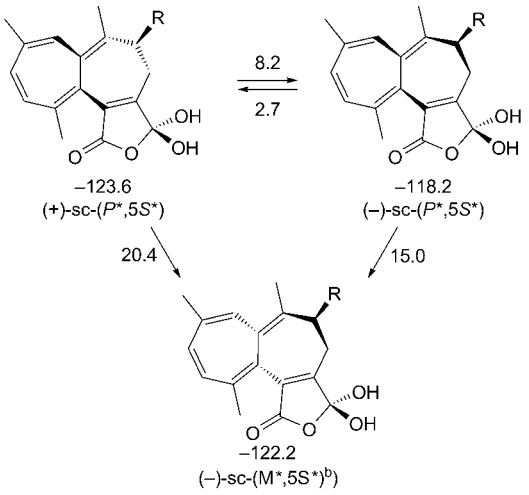
Table 6. ΔH_f° *Data of Model 4,5-Dihydro-3,3-dimethoxy-5-methylheptaleno[1,2-c]furan-1(3H)-ones*[a])



	(+)-sc-(*P**,5*R**)	(–)-sc-(*P**,5*R**)	(+)-sc-(*P**,5*S**)	(–)-sc-(*P**,5*S**)
R = Me; $R^1 = R^3$ = Me, R^2 = H	– 106.40	– 102.45	– 107.77	– 102.29
R = Me; $R^1 = R^3$ = H, R^2 = Me	– 107.19 (– 116.73)	– 105.35 (– 114.16)	– 109.74 (– 119.17)	– 104.76 (– 113.44)
R = Me; $R^1 = R^2$ = Me, R^3 = H	– 112.56 (– 121.91)	– 107.54 (– 115.94)	– 113.74 (– 121.68)	– 107.48 (– 114.65)

[a]) Calculated with AM1; in kcal/mol. [b]) In parentheses, values for R = ^{i}Pr.

Scheme 19



[a]) AM1 Calculated ΔH_f° and $\Delta H_f^\ddagger$ in kcal/mol for R = Me. [b]) (+)-sc-(*M**,5*S**): –118.4.

demonstrated already that the (+)-sc-(*P**,5*S**) forms are much more stable than their (–)-sc relatives. The same is observed in the present case, where this energy difference

amounts to 5.4 kcal/mol. The transition state for the mutual conversion of the two conformers is −115.5 kcal/mol above the ground states. The $\Delta H_f^{\ddagger}$ values for the (*P*,*M*)-epimerization of the two conformers into the most stable (−)-sc-(*M**,5*S**) form amount to 20.4 and 15.0 kcal/mol, in excellent agreement with the observation that (*P**,5*S**)-**27** isomerized reversibly already at room temperature in $CDCl_3$ solution to (*M**,5*S**)-**27**.

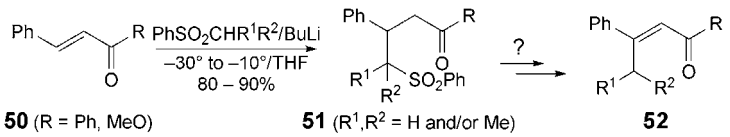
3. Final Remarks. – There are at least two open points left. The first one deals with the directing and decisive steps of the base-catalyzed elimination of $PhSO_2^-$ at the structurally complex dimethyl 3,4-dihydro-3-(phenylsulfonyl)heptalene-4,5-dicarboxylate and 4,5-dihydro-3,3-dimethoxy-5-[1-(phenylsulfonyl)ethyl]heptaleno[1,2-*c*]-furan-1(3*H*)-ones.

Deprotonation and methylation of diester **23** yields the C(4)-methylated diester **41** (*cf. Scheme 10*), which demonstrates that H–C(4) is, as expected, more acidic than H–C(3). Moreover, the base-catalyzed transformation of **41** into **42** indicates that the elimination of $PhSO_2^-$ takes place as a concerted *E*2 process with *anti* stereochemistry. However, what happens when C(4) carries an H-atom as in all the other cases? One possibility would be that deprotonation at C(4) does not hinder the base-catalyzed concerted *E*2 process as discussed above, taking into account that the adjacent negative charge will favor an early transition state on the reaction coordinate of the *E*2 process. However, the fact that we found in some cases, which we have not investigated in detail, beside the alkylated heptalenedicarboxylates also their corresponding anhydrides speaks for an 'anchimeric' assistance of the elimination reaction by the neighbored methoxycarbonyl group as depicted in *Scheme 12*.

The elimination reaction of the dihydroheptalenofuranones (*P**)-**27**, (*P**)-**30**, and (*P**)-**31** seems to follow a concerted *E*2 mechanism since we did not observe an unusual reaction behavior. Nevertheless, it is remarkable that the average yield of the elimination reaction is higher in comparison with that of the dihydroheptalenedicarboxylates, which speaks for an easier *E*2 process of the dihydroheptalenofuranones.

The second point touches the question whether the described alkylation process with [1-(phenylsulfonyl)alkyl]lithium as alkyl-group carrier can also be realized with normal α,β-unsaturated carbonyl system. First experiments show that [1-(phenylsulfonyl)alkyl]lithium reactants are indeed excellent *Michael* addends for α,β-unsaturated compounds such as chalcone (=(2*E*)-1,3-diphenylprop-2-en-1-one) or methyl cinnamate (=methyl (2*E*)-3-phenylprop-2-enoate; *Scheme 20*) [13]. However, the formed products **51** need at least two chemical steps to re-establish unsaturation of the β-alkylated compounds **51** by elimination of benzenesulfinate.

Scheme 20



50 (R = Ph, MeO) **51** (R^1,R^2 = H and/or Me) **52**

We are thankful to our NMR laboratory for specific NMR measurements and to our MS laboratory for mass spectra. Financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. See [4][5][8][16]). All heptalene-4,5-dicarboxylates were prepared according to our published procedures, whereby the corresponding azulenes were heated at 125–130° with 3 mol-equiv. of dimethyl acetylenedicarboxylate in toluene. Under these conditions, 1-methylazulene gave only 1-methylheptalene-4,5-dicarboxylate **3** (m.p. 136.0° (Et_2O)) in a yield of 25% (*cf.* [12]), and 4-methylazulene led to a 3:1 mixture (total yield 35%) of 6-methylheptalene-4,5-dicarboxylate **5** (m.p. 119.1–120.3° (Et_2O); for X-ray data, see *Table 7*) and its 10-methyl analog **49** (m.p. 136.9–137.2° (Et_2O); for X-ray data, see *Table 7*) (*cf.* [12]). Finally, the 1,6,10-trimethylheptalene-4,5-dicarboxylate **11** (golden yellow crystals, m.p. 139.5–141.0° (Et_2O)) was obtained in a yield of 35% from 1,4,8-trimethylazulene, which was prepared by established procedures from 4,8-dimethylazulene [14]. For the synthesis of the 3,3-dimethoxyheptaleno[1,2-*c*]furan-1(3*H*)-ones, see [6].

1. *Dimethyl 3,4-Dihydro-3-[1-(phenylsulfonyl)alkyl]heptalene-4,5-dicarboxylates*. 1.1. *General Procedure*. Under Ar and under stirring, methyl or ethyl phenyl sulfone (4.00 mmol) was dissolved in THF (8 ml) and cooled to −10°. During 10 min, commercial 2.5M BuLi in hexane (1.80 ml, 4.5 mmol) was added drop by drop, whereby the temp. was rising to −2°. After 10 min, a fine colorless precipitate was formed. After a further 30 min at 0°, the soln. was cooled to −78°, and a soln. of the heptalene-4,5-dicarboxylate (1 mmol) in THF (5 ml) was added during 5 min. After consumption of all heptalene-dicarboxylate (TLC (SiO_2, hexane/AcOEt) monitoring), the mixture was poured on ice, acidified with 2N aq. HCl, and extracted with AcOEt. After washing of the extract with H_2O and then with sat. aq. NaCl soln, the extract was dried (Na_2SO_4).

1.2. *Dimethyl (*P**,3*R**,4*R**)- and (*M**,3*R**,4*R**)-3,4-Dihydro-3-[(phenylsulfonyl)methyl]heptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**2**). Yield 0.293 g (69%) of (*P**)/(*M**)-**2** 3:2. Yellow oil. R_f (hexane/AcOEt 2:1) 0.17. IR (KBr): 1733*s* (C=O, ester), 1306*s* and 1148*s* (sulfone). EI-MS: 426 (15, M^+), 366 (2, $[M-MeOCO]^+$), 286 (10), 285 (53, $[M-(MeOCO+PhSO_2)]^+$), 272 (14), 253 (44, $[M-(MeOCO+PhSO_2+MeOH)]^+$), 252 (85, $[M-(MeOCO+PhSO_2H+MeOH)]^+$), 240 (8, $[PhSO_2CH{=}CHCOOMe]^+$), 226 (12), 225 (55), 221 (16), 213 (14), 212 (10), 209 (11), 186 (54, $[C_{10}H_7COOMe]^+$), 135 (100).

*NMR Data of (*P**)-***2**: ^{1}H-NMR (500 MHz, $CDCl_3$): At 300 K, almost all corresponding signals of the two epimeric forms showed coalescence; spectrum at 223 K (C*H*Cl_3 at 7.260; 60% of (*P**)-**2**): 8.00 (*d*, J_o = 7.5, H_o of $PhSO_2$); 7.71 (superimp. signals of H_p of $PhSO_2$ of both forms); 7.63 (superimp. signals of H_m of $PhSO_2$ of both forms); 6.68–6.47 (superimp. signals of H–C(6) to H–C(10) and of H–C(7) to H–C(10) of (*M**)-**2**); 6.35 (*dd*, $^3J(2,1)=11.9$, $^3J(2,3)=6.3$, H–C(2)); 6.24 (*d*, $^3J(1,2)=12.1$, H–C(1)); 3.95 (*dd*, $^2J(H_S,H_R)=13.7$, $^3J(H_S,3)=1.8$, H_S–C(1′)); *ca.* 3.76 (br. *s*, H–C(4)), partly covered by the *s* of MeOOC–C(5) of (*M**)-2); 3.69 (*s*, MeOOC–C(5)); 3.50 (*s*, MeOOC–C(4)); 3.36–3.32 (superimp. signals of H–C(3) of both forms); 3.12 (*t*-like, $\Sigma\ ^2J(H_R,H_S)+{}^3J(H_R,3)=25.7$, H_R–C(1′)). ^{13}C-NMR (125 MHz, $CDCl_3$, 223 K; *C*DCl_3 at 77.00): 171.45 (MeOO*C*–C(4)); 167.08 (MeOO*C*–C(5)); 52.17, 52.14 (*Me*OOC–C(4) and –C(5)).

*NMR Data of (*M**)-***2**: ^{1}H-NMR (500 MHz, $CDCl_3$; 40% of the (*M**)-form): 7.95 (*d*, J_o = 7.5, H_o of $PhSO_2$); 7.71 (superimp. signals of H_p of $PhSO_2$ of both forms); 7.63 (superimp. signals of H_m of $PhSO_2$ of both forms); 6.87 (*d*, $^3J(6,7)=11.4$ H–C(6)); 6.68–6.47 (superimp. signals of H–C(7) to H–C(10) and of H–C(6) to H–C(10) of (*P**)-2); 6.09 (*dd*, $^3J(2,1)=12.1$, $^3J(2,3)=3.0$, H–C(2)); 5.79 (*d*, $^3J(1,2)=12.1$, H–C(1)); 4.56 (br. *s*, H–C(4)); 3.77 (*s*, MeOOC–C(5)); 3.62 (*dd*, $^2J(H_S,H_R)=14.6$, $^3J(H_S,3)=5.6$, H_S–C(1′)); 3.39 (*s*, MeOOC–C(4)); 3.56 (*dd*, $^2J(H_R,H_S)=14.6$, $^3J(H_R,3)=7.1$, H_R–C(1′)); 3.36–3.32 (superimp. signals of H–C(3) of both forms). ^{13}C-NMR (125 MHz, $CDCl_3$, 223 K; *C*DCl_3 at 77.00): 172.08 (MeOO*C*–C(4)); 166.16 (MeOO*C*–C(5)); 52.42, 52.27 (*Me*OOC–C(4) and –C(5)).

1.3. *Dimethyl (*P**,1′*R**,3*S**,4*S**)- and (*M**,1′*R**,3*S**,4*S**)-3,4-Dihydro-3-[(1-phenylsulfonyl)ethyl]-heptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**21**). Heptalenedicarboxylate **1** (1.00 g, 3.70 mmol) was treated with ethyl phenyl sulfone (0.95g, 5.56 mmol) in the usual manner. The product was extracted with

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16) NMR Spectra: δ(H) rel. to Me_4Si (=0 ppm) or $CHCl_3$ (=7.26 ppm), δ(C) rel. to $CDCl_3$ (=77.0 ppm); atoms of the [1-(R-sulfonyl)alkyl] groups have primed locants; $H_S = H_{pro\text{-}S}$, $H_R = H_{pro\text{-}R}$, and f.s. = fine structure.

Table 7. *Crystallographic Data for Compounds* (P*)-**4**, **5**, (P*)-**10**, (P*)-**27**, (P*)-**30**, (P*)-**31**, (P*)-**41**, **45**, *and* **49**

	(*P**)-**4**	**5**	(*P**)-**10**	(*P**)-**27**	(*P**)-**30**	(*P**)-**31**	(*P**)-**41**	**45**	**49**
Crystallized from	AcOEt /hexane	Et_2O/ hexane	Et_2O/ hexane	AcOEt /hexane	AcOEt/ hexane	AcOEt	^{t}BuOMe	$CHCl_3$	Et_2O/ hexane
Empirical formula	$C_{24}H_{24}O_6S$	$C_{17}H_{16}O_4$	$C_{25}H_{26}O_6S$	$C_{29}H_{34}O_6S$	$C_{27}H_{30}O_6S$	$C_{28}H_{32}O_6S$	$C_{30}H_{36}O_6S$	$C_{23}H_{28}O_4$	$C_{17}H_{16}O_4$
M_r	440.51	284.31	454.53	510.64	482.59	496.61	524.67	368.47	284.31
Crystal color, habit	yellow-green, plate	red, rism	colourless, plate	yellow, tablet	yellow, prism	yellow, prism	yellow, plate	yellow, prism	yellow, prism
Crystal dimensions [mm]	0.11 × 0.35 × 0.37	0.30 × 0.42 × 0.50	0.10 × 0.26 × 0.48	0.07 × 0.22 × 0.25	0.08 × 0.15 × 0.22	0.10 × 0.12 × 0.27	0.05 × 0.20 × 0.22	0.17 × 0.20 × 0.32	0.23 × 0.25 × 0.47
Temperature [K]	173 (1)	173 (1)	173 (1)	160 (1)	160 (1)	160 (1)	160 (1)	160 (1)	173 (1)
Crystal system	ortho-rhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	orthor-hombic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$	*Pbca*	$P\bar{1}$	$P2_12_12_1$
Z	4	4	4	8	4	4	8	2	4
Reflections for cell determination	25	25	24	11173	29761	82443	6712	4695	25
2θ Range for cell determination [°]	25 – 35	38 – 40	30 – 40	4 – 52	4 – 55	4 – 55	2 – 55	4 – 56	33 – 39
Unit cell parameters									
a [Å]	12.494 (2)	13.660 (2)	11.698 (2)	22.5162 (3)	16.5768(3)	14.3221(4)	14.4103 (2)	10.2548(4)	8.718 (2)
b [Å]	20.394 (2)	8.538 (2)	8.159 (4)	9.7064 (1)	8.3852(2)	11.6968(3)	17.6883 (2)	10.5119(5)	21.400 (2)
c [Å]	8.542 (2)	13.402 (2)	24.539 (2)	26.0362 (3)	18.5972(4)	14.8916(4)	20.8422 (3)	10.7388(4)	7.816 (2)
α [°]	90	90	90	90	90	90	90	61.856(2)	90
β [°]	90	114.471 (8)	101.910 (8)	109.0997 (6)	101.721(1)	92.471(2)	90	89.446(2)	90
γ [°]	90	90	90	90	90	90	90	86.063(2)	90
V [Å^3]	2176.6 (6)	1422.6 (4)	2292 (1)	5377.0 (1)	2531.10(9)	2492.4(1)	5312.5 (1)	1017.99(8)	1458.3 (5)
F(000)	928	600	960	2176	1024	1056	2240	396	600
D_x [g cm^{-3}]	1.344	1.327	1.317	1.261	1.266	1.323	1.312	1.202	1.295
μ(MoK_α) [mm^{-1}]	0.187	0.0942	0.180	0.161	0.167	0.171	0.165	0.0808	0.0919
Scan type	$\omega/2\theta$	$\omega/2\theta$	ω	ω	ϕ and ω	ϕ and ω	ϕ and ω	ϕ and ω	$\omega/2\theta$
$2\theta_{(max)}$ [°]	55	60	55	52	55	55	55	56	60
Total reflections measured	5742	4566	5917	83621	60677	56776	76106	20553	2907

Table 7 (cont.)

	(*P**)-**4**	**5**	(*P**)-**10**	(*P**)-**27**	(*P**)-**30**	(*P**)-**31**	(*P**)-**41**	**45**	**49**
Symmetry independent reflections	5010	4142	5273	10566	5771	5720	6093	4817	2794
R_{int}	0.024	0.020	0.042	0.066	0.091	0.066	0.084	0.042	0.022
Reflections with $I > 2\sigma(I)$	3943	2979	3502	7327	4020	4332	4154	3582	1996
Reflections used in refinement	5010	4142	5480	10556	5771	5720	6087	4813	2794
Parameters refined	283	194	293	664	314	324	343	263; 13	193
$R(F)$ ($I > 2\sigma(I)$ reflections)	0.0438	0.0591	0.0480	0.0463	0.0462	0.0445	0.0451	0.0537	0.0511
$wR(F^2)$ (all data)	0.1103	0.1770	0.1297	0.1226	0.1175	0.1133	0.1222	0.1451	0.1903
Weighting parameters [a; b][a])	0.041; 0.6247	0.0532; 1.5245	0.048; 0.858	0.0604; 0.6815	0.0523; 0.9278	0.0482; 1.3039	0.0616; 0.9896	0.0648; 0.4016	0.1127; 0.2596
Goodness of fit	1.032	1.115	1.013	1.031	1.021	1.032	1.043	1.026	1.050
Secondary extinction coefficient		0.016(2)	–	0.0022(3)	0.0060(8)	0.0070(9)	0.0013(3)	0.023(5)	–
Final Δ_{max}/σ	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.41; −0.19	0.42; −0.46	0.30; −0.34	0.34; −0.43	0.25; −0.35	0.27; −0.30	0.25; −0.33	0.61; −0.39	0.43; −0.31

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

Et_2O and further purified by CC (SiO_2, hexane/AcOEt 2:1): 1.10 g (67%) of a dark brown oil. NMR: (*P**)/(*M**)-**21** *ca.* 45:55; no signals were identified that could be assigned to **22** (see *Scheme 4*). *(*P**)/(*M**)-**21**: IR (KBr): 1733*s* and 1700*s* (C=O, ester), 1305*s* and 1146*s* (sulfone). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; identified signals): 7.9–7.5 (H of $PhSO_2$ of both forms); 6.85 (*d*, $^3J(6,7) = 11.3$, H–C(6) of (*M**)-**21**); 6.65–6.30 (superimp. signals of both forms); 6.05 (*dd*, $^3J(2,1) = 12.2$, $^3J(2,3) = 2.7$, H–C(2) of (*P**)-**21**); 4.47 (br. *s*, H–C(4) of (*M**)-**21**); 4.06 (*q*, $^3J(1',\text{Me–C}(1')) = 7.1$, H–C(1′) of (*M**)-**21**); 3.70 and 3.37 (2*s*, MeOOC–C(4) and –C(5) of (*M**)-**21**); 3.65, 3.43 (2*s*, MeOOC–C(4) –C(5) of (*P**)-**21**); 1.22 (*d*, $^3J(\text{Me–C}(1'),1') = 7.1$, Me–C(1′) of both forms). ^{13}C-NMR (75 MHz, $CDCl_3$; identified signals): 171.69 (MeOO*C*–C(4) of (*M**)-**21**); 171.00 (MeOO*C*–C(4) of (*P**)-**21**); 167.11 (MeOO*C*–C(5) of (*P**)-**21**); 166.35 (MeOO*C*–C(5) of (*M**)-**21**); 147.16 (C(5a) of (*M**)-**21**); 145.73 (C(5a) of (*P**)-**21**); 63.87 (C(1′) of (*M**)-**21**); 60.11 (C(1′) of (*P**)-**21**); 13.99 (*Me*–C(1′) of (*P**)-**21**); 13.08 (*Me*–C(1′) of (*M**)-**21**). CI-MS: 458.1 (37, $[M+NH_4]^+$), 441.1 (100, $[M+1]^+$), 409.1 (43, $[(M+1)-CH_3OH]^+$), 299.1 (67, $[(M+1)-PhSO_2H)]^+$), 272.1 (15, $[(M+1)-PhSO_2CHMe]^+$), 187.0 (28 $[C_{10}H_8COOMe]^+$).

1.4. *Dimethyl (*P**,3*R**,4*R**)- and (*M**,3*R**,4*R**)-3,4-Dihydro-1-methyl-3-[(phenylsulfonyl)methyl]-heptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**4**). Heptalenedicarboxylate **3** (0.200 g, 0.70 mmol) gave, after crystallization (hexane/AcOEt), 0.206 g (67%) of colorless crystals of (*P**)-**4** (m.p. 157°), as shown by an X-ray crystal-structure determination (*Fig. 2* and *Table 7*). In $CDCl_3$ soln. at r.t., a (*P**)/(*M**)-**4** *ca.* 45:55 was formed within minutes, and the corresponding signals of the epimers showed coalescence. R_f (hexane/AcOEt 2:1) 0.16.

*Data of (*P**)-**4***: IR (KBr): 1712*s* (C=O, ester), 1334*s* and 1155*s* (sulfone). ^{1}H-NMR (700 MHz, $CDCl_3$, 270 K; 45% of (*P**)-**4**; C*H*Cl_3 at 7.276): 8.02 (*d*, $J_o = 7.6$, H_o of $PhSO_2$); 7.702 (*t*, H_p of $PhSO_2$); 7.63 (*t*, $J_o = 7.6$, H_m of $PhSO_2$); 6.53 (*dd*, $^3J(9,10) \approx 7$, $^3J(9,8) \approx 11$, H–C(9)); 6.52 (*d*, $^3J(10,9) \approx 6$, H–C(10)); 6.46 (*dd*, $^3J(7,8) = 6.3$, $^3J(7,6) = 11.1$, H–C(8)); 6.29 (*d*, $^3J(2,3) = 5.3$, H–C(2)); 3.96 (*d*, $^2J(H_S,H_R) = 13.4$, H_S–C(1′)); 3.80 (br. *s*, partly covered by the *s* of MeOOC–C(5) of (*M**)-**4**, H–C(4)); 3.50 (*s*, MeOOC–C(5)); 3.43 (br. *s* with spike amid, H–C(3)); 3.37 (*s*, MeOOC–C(4)); 3.07 (*t*-like, $\Sigma\,{}^2J(H_R,H_S) + {}^3J(H_R,3) = 26.5$, H_R–C(1′)); 1.94 (*s*, Me–C(1)). ^{13}C-NMR (176 MHz, $CDCl_3$, 270 K; *C*DCl_3 at 77.02): 171.45 (MeOO*C*–C(4)); 166.57 (MeOO*C*–C(5)); 148.71 (C(5a)); 139.27 (C_{ipso} of $PhSO_2$); 133.71 (C_p of $PhSO_2$); 132.50 (C(1)); 131.29 (C(10a)); 131.06 (C(6)); 130.15 (C(2)); 129.34 (C_m of $PhSO_2$); 129.10 (C(7)); 128.48 (C(7)); 128.03 (C_o of $PhSO_2$)); 125.81 (C(8)); 125.61 (C(9)); 120.20 (C(5)); 57.99 (C(1′)); 51.93 (*Me*OOC–C(5)); 51.88 (*Me*OOC–C(4)); 44.56 (C(4)); 34.10 (C(3)); 27.37 (*Me*–C(1)). EI-MS: 440 (6, M^+), 299 (32, $[M-(MeOCO+PhSO_2)]^+$), 267 (6), 239 (10), 201 (11), 200 (100, $[MeC_{10}H_6COOMe]^+$). Anal. calc. for $C_{24}H_{24}O_6S$ (440.48): C 65.44, H 5.49, S 7.28; found: C 65.36, H 5.43, S 7.41.

*Data of (*M**)-**4***: ^{1}H-NMR (700 MHz, $CDCl_3$, 270 K; 55% of (*M**)-**4**): 7.97 (*d*, $J_o = 7.6$, H_o of $PhSO_2$); 7.698 (*t*, H_p of $PhSO_2$); 7.61 (*t*, $J_o = 7.7$, H_m of $PhSO_2$); 6.76 (*d*, $^3J(6,7) = 11.1$, H–C(6)); 6.69 (*dd*, $^3J(9,10) = 7.1$, $^3J(9,8) = 10.5$, H–C(8)); 6.66 (*d*, $^3J(10,9) = 6.8$, H–C(10)); 6.63 (*dd*, $^3J(8,9) = 10.6$, $^3J(8,7) = 6.5$, H–C(8)); 6.43 (*dd*, $^3J(7,8) = 6.5$, $^3J(7,6) = 10.8$, H–C(7)); 5.64 (*s*, H–C(2)); 4.34 (br. *s*, H–C(4)); 3.79 (*s*, MeOOC–C(5)); 3.65 (*dd*, $^2J(H_S,H_R) = 14.6$, $^3J(H_S,3) = 5.5$, H_S–C(1′)); 3.55 (*dd*, $^2J(H_R,H_S) = 14.6$, $^3J(H_R,3) = 6.8$, H_R –C(1′)); 3.37 (*s*, MeOOC–C(4)); 3.29 (br. *s*, H–C(3)); 1.86 (*s*, Me–C(1)). ^{13}C-NMR (176 MHz, $CDCl_3$, 270 K; *C*DCl_3 at 77.02): 171.98 (MeOO*C*–C(4)); 165.83 (MeOO*C*–C(5)); 149.03 (C(5a)); 139.13 (C_{ipso} of $PhSO_2$); 133.83 (C_p of $PhSO_2$); 132.55 (C(1)); 132.32 (C(10a)); 130.56 (C(8)); 130.17 (C(9)); 129.34 (C_m of $PhSO_2$); 129.14 (C(2), C(10)); 128.00 (C_o of $PhSO_2$)); 125.86 (C(6)); 125.36 (C(7)); 122.67 (C(5)); 60.44 (C(1′)); 52.17 (*Me*OOC–C(5)); 52.02 (*Me*OOC–C(4)); 45.80 (C(4)); 34.19 (C(3)); 26.83 (*Me*–C(1)).

1.5. *Dimethyl (*P**,3*S**,4*S**)- and (*M**,3*S**,4*S**)-3,4-Dihydro-6-methyl-3-[(phenylsulfonyl)methyl]-heptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**6**). Crystallization (hexane/AcOEt) gave colorless crystals of (*P**)-**6** (0.295 g, 67%; m.p. 157°). In $CDCl_3$ soln. at r.t., a 3:1 ratio of (*P**)/(*M**)-**6** was established within minutes. Over a longer period, the ratio approached a final value of 3:2. R_f (hexane/AcOEt 2:1) 0.14.

*Data of (*P**)-**6***: IR (KBr): 1743*s* (C=O, ester), 1309*s* and 1132*s* (sulfone). ^{1}H-NMR (500 MHz, $CDCl_3$, 250 K; 75% of the (*P**)-**6**): 8.01 (*dd*-like, $J_o \approx 7.3$, $J_m \approx 1.4$, H_o of $PhSO_2$); 7.71 (*tt*-like, H_p of $PhSO_2$); 7.63 (*t*-like, H_m of $PhSO_2$); 6.53–6.48 (5 line *m*, H–C(8) and H–C(9) of (*P**)-**6**, H–C(9) of (*M**)-**6**); 6.40 (*d*, $^3J(10,9) = 6.9$, H–C(10)); 6.33 (*dd*, $^3J(2,1) = 11.7$, $^3J(2,3) = 6.4$, H–C(2)); 6.29–6.27 (br.,

slightly structured signal, H–C(7) of both forms); 6.23 (*d*, $^3J(1,2) = 11.7$, H–C(1)); 4.03 (*dd*, $^2J(H_S,H_R) = 14.1$, $^3J(H_S,3) = 1.9$, H_S–C(1′)); 3.91 (*d*, $^3J(4,3) = 2.1$, H–C(4)); 3.71 (*s*, MeOOC–C(5)); 3.47 (*s*, MeOOC–C(4)); 3.36 – 3.32 (br., slightly structured signal, H–C(3)); 3.08 (*dd*, $^2J(H_R,H_S) = 14.0$, $^3J(H_R,3) = 11.7$, H_R–C(1′)); 2.03 (*d*, ^4J(Me–C(6),7) ≈ 0.8, Me–C(6)). ^{13}C-NMR (125 MHz, $CDCl_3$, 250 K; 75% of (*P**)-**6**; *C*DCl_3 at 77.00;): 171.00 MeOO*C*–C(4)); 168.16 (MeO*OC*–C(5)); 149.32 (C(5a)); 138.62 (C_{ipso} of $PhSO_2$); 133.83 (C_p of $PhSO_2$); 133.55 (C(2)); 131.14 (C(6)); 129.95 (C(8)); 129.88 (C(10)); 129.23 (C_m of $PhSO_2$); 128.70 (C(10a)); 128.11 (C(1)); 128.07 (C_o of $PhSO_2$); 127.69 (C(9)); 124.26 (C(7)); 122.48 (C(5)); 58.57 (C(1′)); 52.40 (*Me*OOC–C(5)); 52.06 (*Me*OOC–C(4)); 46.09 (C(4)); 31.80 (C(3)); 24.88 (*Me*–C(6)). EI-MS: 440 (51, M^+), 300 (8), 299 (44, $[M - (MeOCO + PhSO_2)]^+$), 283 (8), 240 (6, $[PhSO_2CH{=}CHCOOMe]^+$), 239 (26), 209 (10), 208 (10), 207 (31), 201 (13), 200 (100, $[MeC_{10}H_6COOMe]^+$). Anal. calc. for $C_{24}H_{24}O_6S$ (440.48): C 65.44, H 5.49, S 7.28; found: 65.38, H 5.42, S 7.35.

*Data of (*M**)-**6***: ^{1}H-NMR (500 MHz, $CDCl_3$, 250 K; 25% of (*M**)-**6**): 7.98 (*dd*-like, $J_o \approx 7.3$, $J_m \approx 1.4$, H_o of $PhSO_2$); 7.69 (*tt*-like, H_p of $PhSO_2$); 7.61 (*t*-like, H_m of $PhSO_2$); 6.50 (signals of H–C(8) of (*M**)-**6**, mostly covered by those of H–C(8) and H–C(9) of (*P**)-**6**); 6.39 (*dd*, $^3J(9,8) = 11.3$, $^3J(9,10) = 6.9$, H–C(9)); 6.31 (*d*, H–C(10), partly covered by the signals of H–C(2) of (*P**)-**6**); 6.29 – 6.27 (br., slightly structured signal, H–C(7) of both forms); 6.10 (*dd*, $^3J(2,1) = 11.9$, $^3J(2,3) = 3.1$, H–C(2)); 5.83 (*dt*-like, $^3J(1,2) = 11.9$, H–C(1)); 4.35 (*d*-like, $^3J(4,3) \approx 1.2$, H–C(4)); 3.80 (*s*, MeOOC–C(5)); 3.475 (br. signal, mostly covered by the signal of MeOOC–C(4) of (*P**)-**6**, H–C(3)); 3.58, 3.57 (*ABX*, $^2J_{AB} = 14.4$, $^3J_{AX} = 4.3$, $^3J_{BX} = 8.5$, CH_2(1′)); 3.40 (*s*, MeOOC–C(4)); 2.09 (br. *s*, Me–C(6)). ^{13}C-NMR (125 MHz, $CDCl_3$, 250 K; 25% of (*M**)-**6**; *C*DCl_3 at 77.00;): 171.87 MeOO*C*–C(4)); 166.42 (MeO*OC*–C(5)); 151.21 (C(5a)); 139.06 (C_{ipso} of $PhSO_2$); 133.96 (C_p of $PhSO_2$); 133.52 (C(1)); 132.13 (C(6)); 130.54 (C(8)); 129.38 (C_m of $PhSO_2$); 129.54 (C(10)); 128.59 (C(10a)); 127.89 (C_o of $PhSO_2$); 126.47 (C(9)); 125.87 (C(2)); 123.82 (C(5)); 123.00 (C(7)); 58.57 (C(1′)); 52.40 (*Me*OOC–C(5)); 52.06 (*Me*OOC–C(4)); 46.09 (C(4)); 31.80 (C(3)); 24.88 (*Me*–C(6)).

1.6. *Dimethyl (*P**,3*R**,4**R**)- and (*M**,3*R**,4*R**)-3,4-Dihydro-8-methyl-3-[(phenylsulfonyl)methyl]-heptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**8**). Heptalenedicarboxylate **7** (0.200 g, 0.70 mmol) was treated with methyl phenyl sulfone (0.440 g, 2.81 mmol) according to *Exper. 1.1* to give (*P**)/(*M**)-**8** *ca.* 3 : 2 as a yellow oil. R_f (AcOEt/hexane 1 : 2) 0.18. IR (KBr): 1730*s* (C=O, ester), 1308*s* and 1150*s* (sulfone).

*NMR Data of (*P**)-**8***: ^{1}H-NMR (500 MHz, $CDCl_3$): At 300 K, coalescence of the corresponding signals of (*P**)- and (*M**)-**8** was observed; spectrum at 223 K (C*H*Cl_3 at 7.260), 60% of (*P**)-**8**): 7.98 (d, $J_o = 7.5$, H_o of $PhSO_2$); 7.69 (superimp. signals of H_p of $PhSO_2$ of both forms); 7.60 (superimp. signals of H_m of $PhSO_2$ of both forms); 6.52 (*d*, $^3J(6,7) = 11.7$, H–C(6)); 6.49 (*d*, $^3J(9,10) = 7.7$, H–C(9)); 6.40 (*d*, $^3J(10,9) = 7.6$, H–C(10)); 6.29 (*d*, $^3J(7,6) = 11.4$, H–C(7)); 6.25 (*dd*, $^3J(2,1) = 12.0$, H–C(2)); 6.19 (*d*, $^3J(1,2) = 12.1$, H–C(1)); 3.93 (*dd*, $^2J(H_S,H_R) = 13.7$, $^3J(H_S,3) = 1.9$, H_S–C(1′)); 3.75 (br. *s*, H–C(4)); 3.67 (*s*, MeOOC–C(5)); 3.49 (*s*, MeOOC–C(4)); 3.34 – 3.28 (superimp. signals of H–C(3) of both forms); 3.11 (*t*-like, $\Sigma\ ^2J(H_R,H_S) + {}^3J(H_R,3) = 25.9$, H_R–C(1′)); 2.08 (Me–C(8)). ^{13}C-NMR (125 MHz, $CDCl_3$, 223 K; *C*DCl_3 at 77.00; assigned signals): 171.52 (MeOO*C*–C(4)); 167.06 (MeO*OC*–C(5)); 147.91 (C(5a)); 141.55 (C(8)); 138.16 (C_{ipso} of $PhSO_2$); 119.15 (C(5)); 58.39 (C(1′)); 52.09 (*Me*OOC–C(5)); 52.02 (*Me*OOC–C(4)); 46.32 (C(4)); 31.71 (C(3)); 24.75 (*Me*–C(8)).

*NMR Data of (*M**)-**8***: ^{1}H-NMR (500 MHz, $CDCl_3$, 223 K; 40% of (*M**)-**8**): 7.93 (*d*, $J_o = 7.5$, H_o of $PhSO_2$); 7.69 (superimp. signals of H_p of $PhSO_2$ of both forms); 7.60 (superimp. signals of H_m of $PhSO_2$ of both forms); 6.83 (*d*, $^3J(6,7) = 11.9$, H–C(6)); 6.40 (*d*, $^3J(9,10) = 7.7$, H–C(6)); 6.34 (*d*, $^3J(10,9) \approx 7.6$, H–C(10)); 6.25 (*d*, $^3J(7,6) = 11.4$, H–C(6)); 6.09 (*dd*, $^3J(2,1) = 12.2$, $^3J(2,3) = 2.8$, H–C(2)); 5.70 (*d*, $^3J(1,2) = 12.1$, H–C(1)); 4.56 (br. *s*, H–C(4)); 3.75 (*s*, MeOOC–C(5)); 3.62 (*dd*, $^2J(H_S,H_R) = 14.7$, $^3J(H_S,3) = 5.7$, H_S–C(1′)); 3.53 (*dd*, $^2J(H_R,H_S) = 14.7$, $^3J(H_R,3) = 7.2$, H_R–C(1′)); 3.40 (*s*, MeOOC–C(4)); 3.34 – 3.28 (superimp. signals of H–C(3) of both forms); 2.07 (Me–C((8)). ^{13}C-NMR (125 MHz, $CDCl_3$, 223 K; assigned signals): 172.06 (MeOO*C*–C(4)); 166.22 (MeO*OC*–C(5)); 147.65 (C(5a)); 141.80 (C(8)); 138.20 (C_{ipso} of $PhSO_2$); 121.70 (C(5)); 60.50 (C(1′)); 52.27 (*Me*OOC–C(5)); 52.20 (*Me*OOC–C(4)); 47.54 (C(4)); 32.38 (C(3)); 24.69 (*Me*–C(8)).

1.7. *Dimethyl (*P**,3*S**,4*S**)- and (*M**,3*S**,4*S**)-3,4-Dihydro-1,6-dimethyl-3-[(phenylsulfonyl)methyl]heptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**10**). Chromatography gave orange crystals of methyl

1,6-dimethyl-4-[(phenylsulfonyl)acetyl]heptalene-5-carboxylate (0.011 g, 2.6%) and colorless crystals of (*P**)-**10** (0.280 g, 62%).

*Data of (*P**)*-**10**: M.p. 163–164° (AcOEt/hexane). R_f (AcOEt/hexane 1:2) 0.13. On standing at r.t. in C_6D_6 soln., (*P**)-**10** gave (*P**)/(*M**)-**10** 2:1. ^{1}H-NMR (600 MHz, C_6D_6, 300 K; 67% of (*P**)-**10**; C_6D_5H at 7.160): 8.04 (*d* with f.s., $J_o \approx 7.3$, H_o of $PhSO_2$); 6.97–6.93 (superimp. signals of H_m of $PhSO_2$ with those of H_m and H_p of (*M**)-**10**); 6.91 (*t* with f.s., $J_o \approx 7.6$, H_p of $PhSO_2$); 6.61 (*d* with f.s., $^3J(7,8) = 5.9$, H–C(7)); 6.25–6.23 (superimp. signals of H–C(8) and H–C(9) with one of (*M**)-**10**); 6.15–6.12 (superimp. signal of H–C(10) with two of (*M**)-**10**); 5.99 (*dd*-like, $^3J(2,3) = 3.4$, $^4J(2,\text{Me–C(1)}) = 1.4$, H–C(2)); 4.78 (*dd*, $^2J(H_S,H_R) = 14.0$, $^3J(H_S,3) = 1.9$, H_S–C(1′)); 3.72 (*d*, $^3J(4,3) = 2.4$, H–C(4)); 3.68–3.61 (superimp. signals of H–C(3) of both forms); 3.36 (*dd*, $^2J(H_R,H_S) = 14.0$, $^3J(H_R,3) = 11.4$, H_R–C(1′)); 3.22 (*s*, MeOOC–C(5)); 3.09 (*s*, MeOOC–C(4)); 1.76 (*d*-like, $^4J(\text{Me–C(1)},2) \approx 1$, Me–C(1)); 1.71 (*s*, Me–C(6)). EI-MS: 454 (22, M^+), 315 (5), 281 (7), 253 (5), 249 (4), 221 (8), 215 (14), 214 (100, $[Me_2C_{10}H_5COOMe]^+$). Anal. calc. for $C_{25}H_{26}O_6S$ (454.51): C 66.06, H 5.76, S 7.05; found: C 65.90, H 5.73, S 7.19.

The structure of (*P**)-**10** was finally established by an X-ray crystal-structure determination (see *Table 7* and *Fig. 3*).

*Data of (*M*)*-**10**: ^{1}H-NMR (600 MHz, C_6D_6, 300 K; 33% of (*M**)-**10**): 7.83 (*d* with f.s., $J_o \approx 8$, H_o of $PhSO_2$); 6.97–6.93 (superimp. signals of H_m and H_p of $PhSO_2$ with those of H_m of (*M**)-**10**); 6.91 (*t* with f.s., $J_o \approx 7.6$, H_p of $PhSO_2$); 6.61 (*d* with f.s., $^3J(7,8) = 5.9$, H–C(7)); 6.25–6.23 (superimp. signals of H–C(10) with those of two H of (*P**)-**10**); 6.15–6.12 (superimp. signals of H–C(8) and H–C(9) with one H of (*P**)-**10**); 6.04 (*d*, $^3J(7,8) = 6.2$, H–C(7)); 5.64 (*s* with f.s., H–C(2)); 4.63 (*d* with f.s., $^3J(4,3) = 3.1$, H–C(4)); 3.75 (*dd*, $^2J(H_S,H_R) = 14.3$, $^3J(H_S,3) = 6.2$, H_S–C(1′)); 3.68–3.61 (superimp. signals of H–C(3) of both forms); 3.51 (*dd*, $^2J(H_R,H_S) = 14.3$, $^3J(H_R,3) = 6.5$, H_R–C(1′)); 3.35 (*s*, MeOOC–C(5)); 3.13 (*s*, MeOOC–C(4)); 2.00 (*s*, Me–C(6)); 1.67 (*dd*, $^4J(\text{Me–C(1)},2) = 1.4$, $^5J(\text{Me–C(1)},10) = 2.2$, Me–C(1)).

Methyl 1,6-Dimethyl-4-[(phenylsulfonyl)acetyl]heptalene-5-carboxylate. M.p. 216.7–217.1° (CH_2Cl_2/hexane). R_f (AcOEt/hexane 1:2) 0.07. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.89–7.86 (H_o of $PhSO_2$); 7.66–7.50 (H_p and H_m of $PhSO_2$); 7.33 (*d*, $^3J(3,2) = 5.6$, H–C(3)); 6.48 (H–C(8), H–C(9); 6.24 (*dd*-like, $^3J(2,3) = 6.3$, $^4J(2,\text{Me–C(1)}) = 1.4$, H–C(2)); 6.19 (signals of H–C(7)); 5.94 (signals of H–C(10)); 4.48, 4.44 (*AB*, $J_{AB} = 14.1$, $PhSO_2CH_2$); 3.59 (*s*, MeOOC–C(5)); 2.09, 2.05 (2*s*, Me–C(1), Me–C(6)). EI-MS: 422 (22, M^+), 313 (9), 281 (51, $[M - PhSO_2]^+$), 249 (39, $[M - (PhSO_2 + MeOH)]^+$), 239 (11), 221 (19, $[M - (PhSO_2 + MeOH + CO)]^+$), 214 (34), 179 (48), 156 (100, $[Me_2C_{10}H_6]^+$), 152 (20), 77 (20, Ph).

1.8. *Dimethyl (*P*,3S*,4S*)- *and (*M*,3S*,4S*)-3,4-Dihydro-9-isopropyl-1,6-dimethyl-3-[(phenylsulfonyl)methyl]heptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**15**) *and Methyl 9-Isopropyl-1,6-dimethyl-4-[(phenylsulfonyl)acetyl]heptalene-5-carboxylate* (**16**) [5]. Methyl phenyl sulfone (1.02 g, 6.50 mmol) and heptalenedicarboxylate **14** (1.00 g, 2.94 mmol) gave, according to *Exper. 1.1* and after workup, CC (SiO_2, hexane/AcOEt 3:1), and crystallization from AcOEt/hexane 2:1, colorless crystals of (*P**)-**15** (0.470 g, 35%) and orange crystals of **16** (0.306 g, 24%). At r.t., in $CDCl_3$ soln., (*P**)-**15** epimerized rapidly to (*P**)/(*M**)-**15** 3:1.

*Data of (*P*)*-**15**: See [5]. ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; in the presence of 25% of (*M**)-**15**; $CHCl_3$ at 7.260): 8.02–7.97 (H_o of $PhSO_2$ of both forms); 7.69–7.65 (H_p of $PhSO_2$ of both forms); 7.64–7.55 (H_m of $PhSO_2$ of both forms); 6.38 (*s*, H–C(10)); 6.28 (*d*, $^3J(8,7) = 6.6$, H–C(8)); 6.20 (*dd*, $^3J(2,3) = 5.8$, $^4J(2,\text{Me–C(1)}) = 1.0$, H–C(2)); 6.15 (*dd*, $^3J(7,8) = 6.5$, $^4J(7,\text{Me–C(6)}) = 1.2$, H–C(7)); 4.01 (*dd*, $^2J(H_S,H_R) = 14.1$, $^3J(H_S,3) = 1.9$, H_S–C(1′)); 3.88 (*d*, $^3J(4,3) = 2.5$, H–C(4)); 3.68 (*s*, MeOOC–C(5)); 3.46 (*s*, MeOOC–C(4)); *ca.* 3.43 (br. *s*, mostly covered by ester signals of both forms, H–C(3)); 3.04 (*dd*, $^2J(H_R,H_S) = 14.1$, $^3J(H_R,3) = 11.4$, H_R–C(1′)); 2.55 (*sept.*, Me_2CH–C(9)); 1.98 (*s*, Me–C(6)); 1.90 (s, Me–C(1)); 1.13, 1.11 (2*d*, superimp. to *t*, $J_{vic} = 6.8$, Me_2CH–C(9)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; assigned signals): 170.98 (MeO*O*C–C(4)); 167.43 (MeO*O*C–C(5)); 151.52 (C(5a)); 146.88 (C(9)); 139.83 (C_{ipso} of $PhSO_2$); 58.41 (C(1′)); 51.84 (*Me*OOC–C(5)); 51.64 (*Me*OOC–C(4)); 44.77 (C(4)); 35.83 (Me_2*C*H–C(9)); 34.13 (C(3)); 26.10 (*Me*–C(1)); 23.45, 22.41 (Me_2CH–C(9)); 23.28 (*Me*–C(6)). Full analysis of the ^{1}H-NMR showed that the crystals contained the (*P**,3*S**,4*S**)-**15**.

*Data of (*M*)*-**15**: ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; in the presence of 75% of (*P**)-**15**; recognizable signals): 6.31 (*s*, H–C(10)); 6.30–6.15 (H–C(8), H–C(7); signals covered by those of (*P**)-

15); 5.62 (br. *s*, H–C(2)); 4.24 (*dd*, *J* = 3.2, 1.1, H–C(4)); 2.48 (*sept.*, Me_2CH–C(9)); 2.00 (*s*, Me–C(6)); 1.86 (*dd*, *J* = 2.2, 1.4, Me–C(1)); 1.10, 1.09 (2*d*, superimp. to *t*, J_{vic} = 6.8, Me_2CH–C(9)).

Data of **16**: Identical with those reported in [5].

1.9. *Dimethyl (*P**,3*S**,4*S**)- and (*M**,3*S**,4*S**)-3,4-Dihydro-1,6,10-trimethyl-3-[(phenylsulfonyl)methyl]heptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**12**)) *and Methyl 1,6,10-Trimethyl-4-[(phenylsulfonyl)acetyl]heptalene-5-carboxylate* (**13**). From heptalenedicarboxylate **11** (1.00 g, 3.21 mmol) according to *Exper. 1.1.* CC (SiO_2, hexane/AcOEt 3 : 1) gave crude (*P**)/(*M**)-**12** (0.80 g, 63%) as a colorless oil and **13**, after crystallization from AcOEt/hexane 2 : 1, in golden yellow needles (0.445 g, 37%).

*Data of (*P**)/(*M**)-***12*** *55 : 45:* IR (film): 1731*s* and 1700*s* (C=O, ester), 1307*s* and 1152*s* (sulfone). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; identified signals, first value for (*P**)-**12**, second for (*M**)-**12**): 171.80, 171.57 (MeOO*C*–C(4)); 166.84, 165.57 (MeOO*C*–C(5)); 156.94, 155.31 (C(5a)); 139.78, 139.31 (C_{ipso} of $PhSO_2$); 59.74, 58.58 (C(1′)); 52.03, 51.88 (*Me*OOC–C(5)); 51.30, 51.22 (*Me*OOC–C(4)); 44.73, 44.37 (C(4)); 34.50, 33.29 (C(3)).

Data of **13**: M.p. 171 – 172°. ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; C*H*Cl_3 at 7.260): 7.87 (*d* with f.s., H_o of $PhSO_2$); 7.62 (*tt*-like, H_p of $PhSO_2$); 7.51 (*t*, H_m of $PhSO_2$); 7.35 (*dd*-like, ^3J(3,2) = 5.9, ^5J(3, Me–C(1)) = 0.9, H–C(2)); 6.42 (*dd*, ^3J(8,9) = 11.1, ^3J(8,7) = 5.6, H–C(8)); 6.33 (*d*, ^3J(9,8) = 11.1, H–C(9)); 6.32 (*dd*-like, ^3J(2,3) = 5.9, H–C(2)); 6.13 (*d*, ^3J(7,8) = 5.8, H–C(7)); 4.44 (*s*, CH_2(1′)); 3.57 (*s*, MeOOC–C(5)); 2.03 (*t*-like, Me–C(6)); 1.97 (*t*-like, Me–C(1)); 1.78 (Me–C(1)). EI-MS: 496 (98, M^+), 295 (40, [*M* – $PhSO_2$]$^+$), 263 (36, [*M* – ($PhSO_2$ + MeOH)]$^+$), 228 (14, [*M* – $PhSO_2CH_2C(O)C{\equiv}CH$]$^+$), 170 (100, [$Me_3C_{10}H_5$]$^+$).

1.10. *Dimethyl (*P**,3*S**,4*S**)- and (*M**,3*S**,4*S**)-3,4-Dihydro-9-isopropyl-1,6-dimethyl-3-[(morpholinosulfonyl)methyl]heptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**19**) [4]. We used the material prepared in 1996. According to our present analysis, **6a** in [4] represents the (*P**)-epimer as shown by its ^{1}H-NMR (Table 10 in [4]) and its X-ray crystal-structure determination [4]. In turn, **6b** in [4] is the corresponding (*M**)-form.

1.11. *Dimethyl (*P**,3*S**,4*S**)- and (*M**,3*S**,4*S**)-3-{[(Diphenylamino)sulfonyl]methyl}-3,4-dihydro-9-isopropyl-1,6-dimethylheptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**17**)) *and Methyl 4-{[(Diphenylamino)sulfonyl]acetyl-9-isopropyl-1,6-dimethyl)heptalene-5-carboxylate* (**18**). According to *Exper. 1.1* with *N*,*N*-diphenylmethanesulfonamide (0.740 g, 3.00 mmol) [14] and heptalenedicarboxylate **14** (0.465 g, 1.36 mmol). Workup and CC (SiO_2, hexane/AcOEt 3 : 1) gave (*P**)/(*M**)-**17** 3 : 1 (0.585 g, 36%) as a yellow-brown oil and **18** (0.186 g, 12%) as a dark brown oil. Both oils were not purified further.

*Data of (*P**)-***17***: Thermal equilibrium mixture of 75% of (*P**)-**17** and 25% of (*M**)-**17**. IR (film): 1732*s* and 1712*s* (C=O, ester), 1347*s* and 1157*s* (sulfonamide). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; in the presence of 25% of (*M**)-**17**): 7.55 – 7.20 (arom. H of both forms); 6.38 (*s*, H–C(10)); 6.28 (*d*, ^3J(8,7) = 5.9, H–C(8)); 6.14 (*dd*-like, ^3J(7,8) = 6.6, ^4J(7,Me–C(6)) = 1.4, H–C(7)); 6.11 (*dd*-like, ^3J(2,3) = 5.9, ^4J(2,Me–C(1)) = 1.0, H–C(2)); 4.31 (*dd*, ^2J(H_S,H_R) = 14.0, ^3J(H_S,3) = 2.0, H_S–C(1′)); 3.98 (*d*, ^3J(4,3) = 2.4, H–C(4)); 3.72 (*dd*, partly covered by ester signals, ^2J(H_R,H_S) = 14.0, ^3J(H_R,3) ≈ 8, H_R–C(3)); 3.67 (*s*, MeOOC–C(5)); 3.58 (*s*, MeOOC–C(4)); 3.42 (br. *s*, H–C(3)); 2.54 (*sept.*, Me_2CH–C(9)); 1.90 (*s*, Me–C(1)); 1.85 (*t*-like, Σ ^4J(Me–C(6),7 + ^5J(Me–C(6),8)) = 2.4, Me–C(6)); 1.13 and 1.11 (2*d*, J_{vic} = 6.9, Me_2CH–C(9)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; in the presence of 25% of the (*M**)-**17**; assigned signals): 171.15 (MeOO*C*–C(4)); 167.12 (MeOO*C*–C(5)); 151.83 (C(5a)); 146.72 (C(9)); 141.10 (C_{ipso} of Ph); 123.96 (C(8)); 123.10 (C(7)); 120.79 (C(5)); 55.99 (C(1′)); 51.71 (*Me*OOC–C(4) and –C(5)); 44.80 C(4)); 35.70 (Me_2*C*H–C(9)); 34.62 (C(3)); 25.95 (*Me*–C(1)); 23.14 (Me_2CH–C(9)); 22.33 (*Me*–C(6)). CI-MS: 605.4 (22, [*M* + NH_4]$^+$), 588.4 (100, [*M* + 1]$^+$), 556.4 (39, [*M* + 1 – MeOH]$^+$), 419.2 (24, [*M* + 1 – Ph_2N]$^+$), 355.3 (54, [*M* + 1 – Ph_2NSO_2]$^+$), 256.2 (11, [^{i}Pr$Me_2C_{10}H_4$COOMe]$^+$).

*Data of (*M**)-***17***: ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; in the presence of *ca.* 75% of the (*P**)-**17**; identified signals): 6.32 (H–C(10)); 6.30 – 6.09 (H–C(8), H–C(7); covered by the signals of (*P**)-**17**); 5.76 (br. *s*, H–C(2)); 3.76 (s, MeOOC–C(5)); 3.42 (*s*, MeOOC–C(4)); 2.48 (*sept.*, Me_2CH–C(9)); 2.02 (Me–C(6)); 1.87 (*t*-like, Σ ^4J(Me–C(1),2) + ^5J(Me–C(1),10) = 2.2, Me–C(1)); 1.11, 1.09 (2*d*, J_{vic} = 6.9, Me_2CH–C(9)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; in the presence of *ca.* 75% of (*P**)-**17**; assigned signals): 171.33 (MeOO*C*–C(4)); 166.29 (MeOO*C*–C(5)); 151.94 (C(5a)); 145.91 (C(9)); 141.52 (C_{ipso} of $PhSO_2$); 124.43 (C(8)); 122.50 (C(7)); 120.00 (C(5)); 57.36 (C(1′)); 51.89 (*Me*OOC–C(4) and –C(5)); 46.25 (C(4)); 35.94 (Me_2*C*H–C(9)); 35.40 (C(3)); 25.69 (*Me*–C(1)); Me_2CH–C(9)); 22.62 (*Me*–C(6)).

Data of **18**: ^{1}H-NMR (300 MHz, $CDCl_3$; significant signals only): 6.3–6.1 (H–C(2), H–C(3), H–C(7), H–C(8)); 5.85 (*s*, H–C(10)); 4.50, 4.44 (*AB*, J_{AB} = 13.9, CH_2(2′)); 2.45 (*sept.*, Me_2CH–C(9)); 2.07 (*d*-like, ^4J(Me–C(1),2) = 1.1, Me–C(1)); 1.06, 1.01 (2*d*, J_{vic} = 6.9, Me_2CH–C(9)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K): 188.45 (O=C–C(4)); 167.64 (MeOO*C*–C(5)).

1.12. *Dimethyl (*P**,3S*,4S*)-3,4-Dihydro-isopropyl-1,6-dimethyl-3-[(1*R**)-1-(phenylsulfonyl)ethyl]-heptalene-4,5-dicarboxylate* ((*P**)-**23**) *and Methyl (*P**)-9-Isopropyl-1,6-dimethyl-4-[(2*S**)-1-oxo-2-(phenylsulfonyl)propyl]heptalene-5-carboxylate* (**24**). See [5] for the X-ray crystal structure of (*P**)-**23**. The ^{1}H- and ^{13}C-NMR spectra of (*P**)-**23** were again measured and all atom positions fully assigned; some had to be corrected with respect to those reported in [5]. ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K; *C*HCl_3 at 7.260): 8.00 (*dd*-like, J_o = 7.3, $J_m \approx$ 1.4, H_o of $PhSO_2$); 7.65 (*tt*, J_o = 7.4, $J_m \approx$ 1.1, H_p of $PhSO_2$); 7.58 (*t*, J_o = 7.7, H_m of $PhSO_2$); 6.32 (*s*, H–C(10)); 6.28 (*d*, ^3J(8,7) = 6.5, H–C(8)); 6.14 (*dd*-like, ^3J(7,8) = 6.5, ^4J(7, Me–C(6)) ≈ 1, H–C(7)); 6.02 (*dd*-like, ^3J(2,3) = 5.2, ^4J(2,Me–C(1)) ≈ 0.7, H–C(2)); 3.98 (br. *q*, ^3J(1′,Me–C(1′)) = 6.8, ^3J(1′,3) ≤ 0.6, H–C(1′)); 3.97 (*d*, ^3J(4,3) = 3.3, H–C(4)); 3.85 (very br., slightly structured *s*, H–C(3)); 3.69 (*s*, MeOOC–C(5)); 3.48 (*s*, MeOOC–C(4)); 2.55 (*sept.*, Me_2CH–*C*(9)); 1.96 (*s*, Me–C(6)); 1.95 (*t*-like, ^4J(Me–C(1′)) ≈ 2, · ^5J(Me–C(1),10) ≈ 1.3, Me–C(1)); 1.31 (*d*, ^3J(Me–C(1′),1′) = 7.0, Me–C(1′)); 1.13, 1.09 (2*d*, J_{vic} = 6.9, Me_2CH–C(9)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K; *C*Cl_3 at 77.00): 171.14 (MeOO*C*–C(4)); 167.52 (MeOO*C*–C(5)); 150.31 (C(5a)); 147.10 (C(9)); 138.29 (C_{ipso} of $PhSO_2$); 133.98 (C(1)); 133.35 (C_p of $PhSO_2$); 131.81 (C(10a)); 129.14 (C_o of $PhSO_2$); 129.09 (C(6)); 128.95 (C_m of $PhSO_2$); 127.80 (C(2)); 127.08 (C(10)); 123.96 (C(8)); 123.48 (C(7)); 121.32 (C(5)); 59.93 (C(1′)); 51.91 (*Me*OOC–C(5)); 51.75 (*Me*OOC–C(4)); 44.71 (C(4)); 36.68 (C(3)); 35.95 (Me_2*C*H–C(9)); 26.54 (*Me*–C(1)); 24.41, 22.46 (Me_2CH–C(9)); 11.25 (*Me*–C(1′)).

1.13. *Dimethyl (*P**,3S*,4S*)-3,4-Dihydro-9-isopropyl-1,4,6-trimethyl-3-[(1*S**)-1-phenylsulfonyl)-ethyl]heptalene-4,5-dicarboxylate* ((*P**)-**41**). NaH (0.025 g, 1.05 mmol; obtained from an NaH suspension in mineral oil by washing with hexane) in THF (0.5 ml) was cooled to −10°, followed by the addition of (*P**)-**23** (0.425 g, 0.83 mmol) dissolved in THF (3 ml). The mixture was stirred for 4 h without further cooling, and then MeI (0.185 g, 0.08 ml, 1.30 mmol) was added. After 3 d stirring at r.t., H_2O was added. The product was extracted with Et_2O and crystallized from Et_2O; (*P**)-**41** (0.420 g, 95%). Pale yellow crystals.

M.p. 127–128°. IR (KBr): 1740*s* and 1701*s* (C=O, ester), 1325*s* and 1148*s* (sulfone). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): 7.93 (*d* with f.s., $J_o \approx$ 8, H_o of $PhSO_2$); 7.56–7.47 (superimp. signals of H_p and H_m of $PhSO_2$); 6.35 (*s*, H–C(10)); 6.28 (*d*, ^3J(8,7) = 6.4, H–C(8)); 6.17(*dd*-like, ^3J(2,3) = 6.0, ^4J(2, Me–C(1)) = 1.1, H–C(2)); 6.11 (*dd*-like, ^3J(7,8) = 6.5, ^4J(7,Me–C(6)) = 1.3, H–C(7)); 4.30 (br. *q*, ^3J(1′,Me–C(1′)) ≈ 6.5, H–C(1′)); 3.81 (*s*, MeOOC–C(5)); 3.57 (*s*, MeOOC–C(4)); 3.08 (br. *d*, ^3J(3,2) = 5.5, H–C(3)); 2.58 (*sept.*, Me_2CH–*C*(9)); 2.11 (*s*, Me–C(6)); 2.06 (*s*, Me–C(1)); 1.66 (br. *s*, Me–C(4)); 1.51 (*d*, ^3J(Me–C(1′),1′) = 7.0, Me–C(1′)); 1.15 (*d*, J_{vic} = 6.9, *pro-R*-Me of Me_2CH–C(9)); 1.10 (*d*, J_{vic} = 6.8, *pro-S*-Me of Me_2CH–C(9)). Relevant ^{1}H-NOE: *pro-R*-Me of Me_2CH–C(9)/Me–C(4) and H–C(8); *pro-S*-Me of Me_2CH–C(9)/H–C(10); these ^{1}H-NOE established also the (*P**)-configuration of the 3,4-dihydroheptalene skeleton and the (*S*)-configuration at C(4). ^{13}C-NMR (75 MHz,$CDCl_3$, 300 K): 176.36 MeOO*C*–C(4)); 170.88 (MeOO*C*–C5)); 145.79 (C(9)); 144.94 (C(5a)); 140.92 (C_{ipso} of $PhSO_2$); 135.23 (C(1)); 132.64 (C_p of $PhSO_2$); 131.04 (C(6)); 130.74 (C(10a)); 128.77 (C_o of $PhSO_2$); 128.53 (C_m of $PhSO_2$); 127.47 (C(10)); 125.10 C(5)); 124.25 (C(2)); 124.11 (C(8)); 123.22 (C(7)); 61.89 (C(1′)); 52.45 (*Me*OOC–C(5)); 52.05 (*Me*OOC–C(4)); 51.62 (C(4)); 50.09 (C(3)); 36.23 (Me_2*C*H–C(9)); 25.59 (*Me*–C(1)); 23.76 and 22.50 (Me_2CH–C(9)); 23.18 (*Me*–C(6)); 19.36 (*Me*–C(1′)). CI-MS: 525.2 (100, $[M+1]^+$), 493.2 (10, $[M+1-MeOH]^+$), 404.2 (10), 386.2 (16), 286.1 (57), 257.2 (74, $[(^iPrMe_2C_{10}H_5COOMe]^+$).

The structure and rel. configuration of (*P**)-**41** was finally established by an X-ray crystal-structure analysis (*cf. Table 7* and *Fig. 4*).

2. *4,5-Dihydro-3,3-dimethoxy-5-[1-(phenylsulfonyl)ethyl]heptaleno[1,2-*c*]furan-1(3*H*)-ones.* 2.1. *General Procedure.* At 0° and under Ar and stirring, a soln. of [1-(phenylsulfonyl)ethyl]lithium in THF (25 ml) was prepared from the sulfone (1.76 mmol) and 2.5M BuLi in hexane (2.20 mmol). The soln. was then cooled to −78°, and the 3,3-dimethoxyheptaleno[4,5-*c*]furan-1(3*H*)-one (1.50 mmol) in THF (5 ml) was added drop by drop. After 3 h stirring at −78°, the mixture was quenched with ice-cooled

17% aq. HCl (soln.). After extraction with AcOEt, the AcOEt phase was washed, dried (Na_2SO_4) and concentrated, and the residue re-crystallized.

2.2. *(*P**,5S*)- and (*M**,5S*)-4,5-Dihydro-8-isopropyl-3,3-dimethoxy-6,11-dimethyl-5-[(1*R**)-1-(phenylsulfonyl)ethyl]heptaleno[1,2-*c*]furan-1(3*H*)-one* ((*P**)- *and* (*M**)-**27**). Furanone (*P**)-**25** (0.50 g, 1.47 mmol) [7] was treated with $EtSO_2Ph$ (0.306 g, 1.76 mmol) according to *Exper. 2.* Recrystallization from Et_2O gave (*P**)-**27** as pale yellow crystals (0.625 g, 92%). Dissolution of the crystals in $CDCl_3$ at 243 K showed only the presence of (*P**)-**27** (^{1}H-NMR); at ambient r.t., a 64:36 mixture of (*P**)- and (*M**)-**27** was established in a short time.

*Data of (*P**)-**27***. M.p. 158.0–160.1°. R_f (AcOEt/hexane 1:2) 0.59. IR (KBr): 1768*s* (C=O, five-ring lactone). ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K, in the presence of 36% of (*M**)-**27**; C*H*Cl_3 at 7.264): 7.765 (*dd*-like, $J_o = 8.3$, $J_m = 1.1$, H_o of $PhSO_2$); 7.627 (*tt*-like, $J = 7.5$, 1.1, H_p of $PhSO_2$); 7.504 (*t* with f.s., $J = 7.9$, H_m of $PhSO_2$); 6.318 (*dd*, $^3J(9,10) = 11.8$, $^4J(9,7) = 1.1$, H–C(9)); 6.225 (*d*, $^3J(10,9) = 11.9$, H–C(10)); 5.838 (br. *s*, H–C(7)); 3.472 (s, $(MeO)_2C(3)$)[17]); 3.409 (br. *dt*-like, $^3J(5,H_R–C(4)) = 12.6$, $\Sigma\ ^3J(5,H_S–C(4)) + {}^3J(5,1') = 4.4$, H–C(5)); 3.339 (*qd*, $^3J(1',Me–C(1')) = 7.1$, $^3J(1',5) = 2.4$, H–C(1′)); 2.842 (*dd*, $^2J(H_S,H_R) = 20.0$, $^3J(H_S,5) = 2.0$, H_S–C(4)); 2.458 (*sept.*, $Me_2CH–C(8)$); 2.255 (*dd*, $^2J(H_R,H_S) = 20.0$, $^3J(H_R,5) = 12.5$, H_R–C(4); 1.967 (*s*, Me–C(11)); 1.590 (*d*-like, ^5J(Me–C(6),7) ≈ 0.8, Me–C(6)); 1.526 (*d*, ^3J(Me–C(1′),1′) = 7.1, Me–C(1′)); 1.073/1.062 (2*d*, *t*-like superimp., $^3J = 6.7$, 6.6, Me_2CH–C(8)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K, in the presence of 36% of (*M**)-**27**; *C*DCl_3 at 77.00): 166.27 (C(1)); 158.71 (C(3a)); 144.13 (C(8)); 137.75 (C(11)); 137.47 (C_{ipso} of $PhSO_2$); 134.77 (C(6a)); 133.82 (C(10)); 133.52 (C_p of $PhSO_2$); 131.74 (C(9)); 129.35 (C(11b)); 129.11 (C_m of $PhSO_2$); 128.82 (C(6)); 128.67 (C_o of $PhSO_2$); 121.42 (C(7)); 119.47 (C(11a)); 118.46 (C(3)); 59.89 (C(1′)); 51.59 (*Me*O–C(3), *pro-R*); 51.48 (*Me*O–C(3), *pro-S*); 35.39 (C(5)); 34.37 ($Me_2CH–C(8)$); 24.19 (C(4)); 22.76, 22.41 (Me_2CH–C(8)); 22.41 (*Me*–C(11)); 12.08 (*Me*–C(6)); 9.99 (*Me*–C(1′)). CI-MS: 533.1 (100, $[M + Na]^+$), 391.1 (15, $[M + Na - PhSO_2H]^+$).

The rel. configuration of (*P**)-**27** was established by an X-ray crystal-structure analysis (see *Fig. 5* and *Table 7*).

*Data of (*M**)-**27***: ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K; in the presence of 64% of (*P**)-**27**; C*H*Cl_3 at 7.264): 7.726 (*dd*-like, $J_o = 8.3$, $J_m = 1.1$, H_o of $PhSO_2$); 7.583 (*tt*-like, J = 7.5, 1.1, H_p of $PhSO_2$); 7.463 (*t* with f.s., $J = 7.9$, H_m of $PhSO_2$); 6.456 (*dd*, $^3J(9,10) = 11.8$, $^4J(9,7) = 1.1$, H–C(9)); 6.365 (*d*, $^3J(10,9) = 11.8$, H–C(10)); 5.744 (br. *s*, H–C(7)); 3.783 (*qd*, $^3J(1',Me–C(1')) = 7.2$, $^3J(1',5) = 9.5$, H–C(1′)); 3.460 (*s*, MeO–C(3), *pro-R*); 3.290 (*s*, MeO–C(3), *pro-S*); 3.783 (*ddd*, $\Sigma\ ^3J(5,H_R–C(4)) + {}^3J(5,H_S–C(4)) + {}^3J(5,1') = 17.9$, H–C(5)); 2.656 (*dd*, $^2J(H_R,H_S) = 21.0$, $^3J(H_R,5) = 3.4$, H_R–C(4)); 2.523 (*dd*, $^2J(H_S,H_R) = 21.0$, $^3J(H_S,5) = 4.6$, H_S–C(4)); 2.469 (*sept.*, $Me_2CH–C(8)$); 1.930 (*s*, Me–C(11)); 1.599 (*d*, ^5J(Me–C(6),7) = 1.0, Me–C(6)); 1.231 (*d*, ^3J(Me–C(1′),1′) = 7.2, Me–C(1′)); 1.108, 1.090 (2*d*, $^3J = 6.9$, 6.8, Me_2CH–C(8)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K, in the presence of 36% of (*P**)-**27**; *C*DCl_3 at 77.00): 166.12 (C(1)); 157.67 (C(3a)); 143.55 (C(8)); 138.53 (C_{ipso} of $PhSO_2$); 137.72 (C(11)); 133.63 (C(9)); 133.34 (C_p of $PhSO_2$); 133.20 (C(10)); 133.10 (C(6)); 131.79 (C(6a)); 129.35 (C_m of $PhSO_2$); 128.88 (C(11b)); 128.67 (C_o of $PhSO_2$); 122.76 (C(7)); 120.33 (C(11a)); 118.08 (C(3)); 60.91 (C(1′)); 51.68 (*Me*O–C(3), *pro-R*); 51.51 (*Me*O–C(3), *pro-S*); 39.81 (C(5)); 34.31 ($Me_2CH–C(8)$); 25.58 (C(4)); 22.77, 22.69 (Me_2CH–C(8)); 22.54 (*Me*–C(11)); 18.81 (*Me*–C(6)); 12.76 (*Me*–C(1′)).

2.3. *(*P**,5S*)-4,5-Dihydro-3,3-dimethoxy-7,9,11-trimethyl-5-[(1*R**)-1-(phenylsulfonyl)ethyl]heptaleno[1,2-*c*]furan-1(3*H*)-one* ((*P**)-**30**). Furanone **28** (0.50 g, 1.60 mmol)[18]) in THF (5 ml) was treated with $EtSO_2Ph$ (0.327 g, 1.92 mmol) in THF (20 ml) according to *Exper. 2.1.* CC (SiO_2, hexane/AcOEt 3:1) and crystallization from AcOEt/hexane gave pure (*P**)-**30** (0.530 g, 69%). Pale yellow crystals. M.p. 196.3–197.3°. R_f (hexane/AcOEt 3:2) 0.49. IR (KBr): 1766*s* (C=O, five-ring lactone). ^{1}H-NMR (500 MHz, $CDCl_3$, 300 K; C*H*Cl_3 at 7.264): 7.803 (*d* with f.s., $J_o = 7.3$, H_o of $PhSO_2$); 7.640 (*t*, $J_o = 7.5$, H_p of $PhSO_2$); 7.520 (*t*, $J_o = 7.8$, H_m of $PhSO_2$); 6.124 (br. *s*, H–C(10)); 5.880 (br. *s*, H–C(8)); 5.342 (*d*, $^3J(6,5) =$

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17) At 243 K, two *s* appeared at δ(H) 3.458 and 3.425, corresponding presumably to the *pro-R*- and *pro-S*-MeO group, resp.

18) The semi-orthoanhydride **28** (m.p. 118.0–119.0° (Et_2O/hexane)) was prepared from the corresponding heptalene half-ester in the described manner [7] (for spectral details, see [15]).

6.8, H–C(6)); 3.442 (*s*, MeO–C(3), *pro-R*); 3.338 (*s*, MeO–C(3), *pro-S*); 3.26–3.19 (superimp. signals of H–C(1′) and H–C(5)); 2.923 (*dd*, $^2J(H_S,H_R) = 20.2$, $^3J(H_S,5) = 2.8$, H_S–C(4)); 2.318 (*dd*, $^2J(H_R,H_S) = 20.2$, $^3J(H_R,5) = 12.4$, H_R–C(4)); 2.004 (*s*, Me–C(9)); 1.984 (*s*, Me–C(7)); 1.960 (*s*, Me–C(11)); 1.372 (*d*, ^3J(Me–C(1′),1′) = 6.9, Me–C(1′)). ^{1}H-NMR (600 MHz, [$^2H_6$]acetone, 300 K): 7.74 H_o of $PhSO_2$); 7.64 (H_p of $PhSO_2$); 7.53 (H_m of $PhSO_2$); 6.04 (br. *s*, H–C(10)); 5.80 (*t*-like, $J \approx 1.2$, H–C(8)); 5.43 (*d*, $^3J(6,5) = 7.2$, H–C(6)); 3.34 (*qd*, ^3J(1′, Me–C(1′)) = 7.2, $^3J(1',5) \approx 3.6$, H–C(1′)); 3.31 (*s*, MeO–C(3), *pro-R*); 3.18 (*s*, MeO–C(3), *pro-S*); 3.06 (*dquint.*, $^3J(5,H_R$–C(4)) = 12.6, $^3J(5,6) = 7.2$, $^3J(5,H_S$–C(4)) ≈ $^3J(5,1') \approx 3.3$–3.6, H–C(5)); 2.81 (*dd*, $^2J(H_S,H_R) = 20.4$, $^3J(H_S,5) = 3.6$, H_S–C(4)); 2.28 (*dd*, $^2J(H_R,H_S) = 20.4$, $^3J(H_R,5) = 12.6$, H_R–C(4)); 1.86 (*d*-like, $^4J \approx 1$, Me–C(9)); 1.85 (*d*-like, $^4J \approx 1$, Me–C(7)); 1.78 (*s*, Me–C(11)); 1.24 (*d*, ^3J(Me–C(1′),1′) = 7.2, Me–C(1′)). ^{13}C-NMR (125 MHz, $CDCl_3$, 300 K; $CDCl_3$ at 77.00): 166.43 (C(1)); 157.48 (C(3a)); 144.66 (C(6a)); 139.55 (C(9)); 139.29 (C(11)); 137.78 (C_{ipso} of $PhSO_2$); 136.35 (C(7)); 133.68 (C_p of $PhSO_2$); 129.95 (C(10)); 129.09 (C_m of $PhSO_2$); 128.92 (C(11b)); 128.78 (C_o of $PhSO_2$); 126.66 (C(8)); 123.52 (C(6)); 118.49 (C(3)); 113.61 (C(11a)); 62.49 (C(1′)); 51.59 (*Me*O–C(3), *pro-R*); 51.27 (MeO–C(3), *pro-S*); 33.25 (C(5)); 25.91 (C(4)); 25.60 (*Me*–C(9)); 24.72 (*Me*–C(7)); 23.28 (*Me*–C(11)); 10.41 (*Me*–C(1′)). CI-MS: 505.1 (100, $[M + Na]^+$), 363.1 (6, $[M + Na - PhSO_2H]^+$).

The rel. configuration of (*P**)-**30** was established by an X-ray crystal-structure analysis (see *Table 7*).

Heating of pure (*P**)-**30** in $CDCl_3$ at 45° gave, after 2 h, *ca.* 10% of the diastereoisomer (*P**,5*S**)-4,5-dihydro-3,3-dimethoxy-7,9,11-trimethyl-5-[(1*S**)-1-(phenylsulfonyl)ethyl]heptaleno[1,2-*c*]furan-1(3*H*)-one, and, after further heating for 6 h at 45°, a 2:1 ratio of (*P**)-**30** and its C(1′)-epimer. Epimerization at the heptalene axis of chirality was not observed. Moreover, heating of pure (*P**)-**30** in [$^2H_6$]acetone at 45° (4 h) left the compound unchanged.

*(*P*,5S**)-4,5-Dihydro-3,3-dimethoxy-7,9,11-trimethyl-5-[(1S*)-1-(phenylsulfonyl)ethyl]heptaleno-[1,2-c]furan-1(3*H*)-one:* ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K; in the presence of 66% of (*P**)-**30**; $CHCl_3$ at 7.264): 7.83 (*d*, H_o of $PhSO_2$); 7.65 (*t*, H_p of $PhSO_2$); (*t*, H_m of $PhSO_2$); 6.18 (*s*, H–C(10)); 5.92 (*s*, H–C(8)); 5.41 (*d*, $^3J(6,5) = 7.2$, H–C(6)); 3.44 (*s*, MeO–C(3), *pro-R*); 3.34 (*s*, MeO–C(3), *pro-S*); 3.25–3.18 (*m*, H–C(1′) and H–C(5) of (*P**)- and (*M**)-form); 2.52 (*dd*, $^2J(H_R,H_S) = 20.3$, $^3J(H_R,5) = 12.5$, H_R–C(4)); 2.36–2.29 (H_S–C(4), covered by H_R–C(4) of (*P**)-form); 2.03 (*s*, Me–C(9)); 2.02 (*s*, Me–C(7)); 2.01 (*s*, Me–C(11)); 1.37 (*d*, ^3J(Me–C(1′),1′) = 7.1, Me–C(1′)).

2.4. *(*P*,5R**)-4,5-Dihydro-3,3-dimethoxy-6,7,9,11-tetramethyl-5-[(1S*)-1-(phenylsulfonyl)ethyl]heptaleno[1,2-c]furan-1(3*H*)one* ((*P**)-**31**). Furanone **29** (0.180 g, 0.55 mmol) [7] in THF (5 ml) was treated with $EtSO_2Ph$ (0.204 g, 1.20 mmol) in THF (10 ml) according to *Exper. 2.1.* CC (SiO_2, hexane/AcOEt 5:2) and crystallization from AcOEt/hexane gave pure (*P**)-**31** (0.378 g, 64%). Pale yellow crystals. M.p. 211.9–212.4°. R_f (hexane/AcOEt 3:1) 0.34. IR (KBr): 1775*s* (C=O, five-ring lactone). ^{1}H-NMR (500 MHz, $CDCl_3$, 300 K; C*H*Cl_3 at 7.263): 7.734 (*d* with f.s., $J_o = 8.2$, H_o of $PhSO_2$); 7.610 (*tt*, $J_o = 7.5$, $J_m = 1.2$, H_p of $PhSO_2$); 7.495 (*t* with f.s., $J_o = 7.5$, H_m of $PhSO_2$); 6.165 (br. *s*, H–C(10)); 5.948 (br. *s*, H–C(8)); 3.749 (*qd*, $^3J(1',5) = 9.3$, ^3J(1′,Me–C(1′)) = 7.2, H–C(1′)); 3.489 (*s*, MeO–C(3), *pro-R*); 3.236 (*s*, MeO–C(3), *pro-S*); 2.922 (*ddd*, $\Sigma\,^3J(5,H_R$–C(4)) + $^3J(5,H_S$–C(4)) + $^3J(5,1') = 17.4$, H–C(5)); 2.677 (*dd*, $^2J(H_S,H_R) = 21.0$, $^3J(H_S,5) = 3.5$, H_S–C(4)); 2.517 (*dd*, $^2J(H_R,H_S) = 21.0$, $^3J(H_R,5) = 4.6$, H_R–C(4)); 2.083 (*d*, ^4J(Me–C(9),10) = 0.9, Me–C(9)); 1.893 (*d*, ^4J(Me–C(7),8) = 1.2, Me–C(7)); 1.885 (*s*, Me–C(11)); 1.694 (*s*, Me–C(6)); 1.200 (*d*, ^3J(Me–C(1′),1′) = 7.2, Me–C(1′)). ^{13}C-NMR (125 MHz, $CDCl_3$, 300 K; *C*DCl_3 at 77.00): 166.17 (C(1)); 157.49 (C(3a)); 141.23 (C(9)); 138.44 (C_{ipso} of $PhSO_2$); 136.78 (C(11)); 135.84 (C(7)); 133.42 (C_p of $PhSO_2$); 132.63 (C(6a)); 132.57 (C(6)); 129.55 (C(10)); 128.83 (C_m of $PhSO_2$); 128.64 (C(11b)); 128.60 (C_o of $PhSO_2$); 126.78 (C(8)); 118.24 (C(3)); 115.91 (C(11a)); 61.31 (C(1′)); 51.58 (*Me*O–C(3), *pro-R*); 51.23 (*Me*O–C(3), *pro-S*); 39.29 (C(5)); 26.27 (C(4)); 25.11 (*Me*–C(9)); 22.70 (*Me*–C(7)); 21.93 (*Me*–C(11)); 19.90 (*Me*–C(6)); 13.21 (*Me*–C(1′)). CI-MS: 519.1 (100, $[M + Na]^+$), 377.2 (7, $[M + Na - PhSO_2H]^+$).

The rel. configuration of (*P**)-**31** was established by an X-ray crystal-structure determination (see *Fig. 6* and *Table 7*).

2.5. *Methyl* 8-(tert-*Butyl*)-*1-methyl-5-[1-oxo-2-(phenylsulfonyl)propyl]heptalene-4-carboxylate* (**33**) *and (*P*,5S**)-9-(*tert-*Butyl*)-*4,5-dihydro-3,3-dimethoxy-6-methyl-5-[(1*R*)-1-(phenylsulfonyl)ethyl]hep-

taleno[1,2-c]furan-1(3H)-one ((*P**)-**34**). Furanone **32** (0.340 g, 1.00 mmol)[19]) in THF (5 ml) was treated with $EtSO_2Ph$ (0.204 g, 1.20 mmol) in THF (10 ml) according to *Exper. 2.1.* CC (SiO_2, hexane/AcOEt 5:2) gave, after crystallization from Et_2O/hexane, **33** (0.378 g, 79%) as an orange crystal powder. (*P**)-**34** could be enriched (in total $< 5\%$) in the mother liquor.

Data of **33**: M.p. 136.5 – 140.5°. R_f (hexane/AcOEt 5:2) 0.28. The compound formed in $CDCl_3$ soln. a 3:1 mixture, presumably of the (*P**)- and (*M**)-epimers, with unknown rel. configuration of the 1-oxo-2-(phenylsulfonyl)propyl substituent at C(5). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; major epimer): 7.84 (*d*, $J_o = 7.4$, H_o of $PhSO_2$); 7.66 (*t*-like, H_p of $PhSO_2$); 7.55 (*t*-like, H_m of $PhSO_2$); 7.47 (*d*, $^3J(3,2) = 6.2$, H–C(3)); 6.39 (*d*, $^3J(9,10) = 7.0$, H–C(9)); 6.38 (*d*, $^3J(7,6) = 11.5$, H–C(7)); 6.02 (*d*, $^3J(6,7) = 11.5$, H–C(6)); 5.91 (superimp. *d*, $^3J = 7.0$, H–C(2), H–C(10)); 4.11 (*q*, $^3J = 6.9$, H–C(2′)); 3.71 (*s*, *Me*OOC–C(4)); 2.00 (*s*, Me–C(1)); 1.46 (*d*, $^3J = 6.9$, Me–C(2′)); 1.16 (*s*, Me_3C–C(8)). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; minor epimer): 7.99 (*d*, $J_o = 7.6$, H_o of $PhSO_2$); 7.64 (*t*-like, H_p of $PhSO_2$); 7.54 (*t*-like, H_m of $PhSO_2$); 7.38 (*d*, $^3J(3,2) = 6.3$, H–C(3)); 6.73 (*d*, $^3J(7,6) = 11.2$, H–C(7)); 6.56 (*d*, $^3J(9,10) = 6.6$, H–C(9)); 6.29 (*d*, $^3J(6,7) = 11.2$, H–C(6)); 6.09 (*d* with f.s., $^3J(2,3) = 6.3$, H–C(2)); 6.00 (*d*, $^3J(10,9) = 7$, H–C(10)); 4.87 (*q*, $^3J = 6.8$, H–C(2′)); 3.55 (*s*, *Me*OOC–C(4)); 2.03 (*s*, Me–C(1)); 1.46 (*d*, $^3J = 6.9$, Me–C(2′)); 1.20 (*s*, Me_3C–C(8)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; major epimer): 191.41 (C(1′)); 167.49 (MeOO*C*–C(4)); 154.70 (C(8)); 146.46 (C(1)); 143.85 (C(3)); 143.76 (C(5a)); 137.92 (C_{ipso} of $PhSO_2$); 133.69 (C_p of $PhSO_2$); 133.50 (C(10a)); 132.61 (C(4)); 131.07 (C(7)); 129.00 (C_o of $PhSO_2$); 128.86 (C(10)); 128.62 (C_m of $PhSO_2$); 124.31 (C(9)); 125.88 (C(2)); 123.90 (C(6)); 122.10 (C(5)); 68.86 (C(2′)); 52.28 (*Me*OOC–C(4)); 36.23 Me_3C–C(8)); 29.90 (Me_3C–C(8)); 26.37 (*Me*–C(1)); 11.91 (*Me*–C(2′)).

*Data of (*P*)-**34**: Enrichment *ca.* 80%. Rel. configuration in analogy to (*P**)-**27** and (*P**)-**31**, presumably (*P**,1′*S**,5*R**). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): 7.81 (*d*-like, $J_o \approx 7.1$, H_o of $PhSO_2$); 7.66 (*t*-like, $J_o \approx 7.3$, H_p of $PhSO_2$); 7.56 (*t*-like, H_m of $PhSO_2$); 6.91 (*d*, $^3J(10,11) = 7.1$, H–C(10)); 6.29 (*d*, $^3J(11,10) = 7.1$, H–C(11)); 6.24 (*dd*-like, $^3J(7,8) = 11.3$, $^5J(7,\text{Me–C(6)}) \approx 1.6$, H–C(7)); 5.90 (*d*, $^3J(8,7) = 11.3$, H–C(8)); 3.53 (*s*, MeO–C(3), *pro-R*); 3.45 (s, MeO–C(3), *pro-S*); 3.60 – 3.40 (superimp. signals of H–C(1′) and H_S–C(4)); 2.90 (*dt*-like, $^3J(5,H_S\text{–C(4)}) \approx 10.8$, H–C(5)); 2.74 (*dd*, $^2J(H_R,H_S) = 20.7$, $^3J(H_R,5) = 3.6$, H_R–C(4)); 1.75 (*d*, $^5J(\text{Me–C(6)},7) \approx 1.1$, Me–C(6)); 1.10 (*s*, Me_3C–C(9)); 0.93 (*d*, $^3J = 7.0$, Me–C(1′)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; some assignments are tentative): 167.46 (C(1)); 154.59 (C(9)); 154.33 (C(3a)); 137.49 (C_{ipso} of $PhSO_2$); 133.60 (C_p of $PhSO_2$); 129.05 (C_m of $PhSO_2$); 128.80 (C_o of $PhSO_2$); 127.95 (C(8)); 126.49 (C(11)); 126.40 (C(10)); 122.04 (C(7)); 118.51 (C(3)); residual signals in the range of δ(C) 150 – 120 not assignable; 59.46 (C(1′)); 51.92 (*Me*O–C(3), *pro-R*); 51.48 (*Me*O–C(3), *pro-S*); 42.03 (C(5)); 35.48 (Me_3C–C(9)); 29.83 (Me_3C–C(9)); 21.24 (*Me*–C(6)); 13.86 (*Me*–C(1′)).

3. *Alkylated Dimethyl Heptalene-4,5- and -1,2-dicarboxylates by Base-Catalyzed Elimination of Benzenesulfinic Acid from the Corresponding Sulfonyl Derivatives.* 3.1. *General Procedure.* Sodium methoxide (2.2 mmol) was freshly prepared from Na in MeOH (3 ml). The sulfonyl derivative (2.2 mmol) was added in THF (3 ml) and the mixture heated under reflux for 3 to 12 h. Then, after cooling, aq. 1N HCl was added and the mixture extracted with Et_2O. The thus obtained dimethyl heptalenedicarboxylate, in some cases accompanied by the corresponding cyclic anhydride, was purified by CC (SiO_2).

3.2. *Dimethyl 3-Methylheptalene-4,5-dicarboxylate* (**36**) *and Dimethyl 3-Methylheptalene-4,5-dicarboxylic Anhydride (= 4-Methylheptaleno[4,5-c]furan-1,3-dione*; **43**). 3.2.1. With MeONa/MeOH: Sulfonyl derivative (*P**)/(*M**)-**2** (0.150 g, 0.352 mmol) was heated for 12 h according to *Exper. 3.1:* mainly **43** (0.045 g, 54%) as a dark red oil and only trace amounts ($< 2\%$) of **36**. **43**: IR (film): 1790.5*s* and 1740*s* (C=O, 5-ring anhydride). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; C*H*Cl_3 at 7.260): 6.60 (*d*, $^3J(6,7) = 11.4$, H–C(6)); 6.45 (*dd*, $^3J(9,8) = 10.8$, $^3J(9,10) = 7.6$, H–C(9)); 6.37 (*ddd*, $^3J(7,6) = 11.4$, $^3J(7,8) = 7.1$, $^4J(7,9) = 1.1$, H–C(7)); 6.21 (*ddd*, $^3J(8,9) = 10.8$, $^3J(8,7) = 7.1$, $^4J(8,6) = 0.7$, H–C(8)); 5.76 (*d*, $^3J(1,2) = 11.4$, H–C(1)); 5.48 (*d*, $^3J(10,9) = 7.6$, H–C(10)); 5.33 (d, $^3J(2,1) = 11.3$, H–C(2)); 2.36 (*s*, Me–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; $CDCl_3$ at 77.00): 163.75 and 160.22 (C=O, 5-ring anhydride); 151.05; 148.58;

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[19]) The semi-orthoanhydride **32** (m.p. 162.0 – 163.0° (Et_2O/hexane)) was prepared from the corresponding heptalene half-ester in the described manner [7] (for spectral details, see [15]).

139.09; 137.92; 136.52; 135.92; 135.73; 135.25; 133.58; 128.80; 126.47; 118.94; 20.85 (*Me*–C(3)). EI-MS: 238 (55, M^+), 181 (20), 165 (25), 153 (30); 134 (25); 109 (65), 95 (100).

3.2.2. *With* t-*BuOK*. Sulfonyl derivative (*P**)/(*M**)-**2** (0.150 g, 0.352 mmol) was dissolved in THF (3 ml), and *t*-BuOK (0.080 g, 0.69 mmol) in THF (1 ml) was added. After 2 h stirring at r.t., workup was performed under the standard condition to yield **36** (0.031 g, 31%). Orange oil. ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): 6.50 – 5.70 (*m*, 7 H); 2.26 (*s*, Me–C(3)). EI-MS: 284 (52, M^+), 186 (100, [M – MeC≡CCOOMe]$^+$).

3.3. *Dimethyl 1,3,6-Trimethylheptalene-4,5-dicarboxylate* (**38**) *and Dimethyl 3,5,10-Trimethylheptalene-1,2-dicarboxylate* (**38′**). Sulfonyl derivative (*P**)-**10** (0.060 g, 0.132 mmol) was treated for 12 h according to *Exper. 3.1:* thermally equilibrated 2 : 1 mixture **38**/**38′** (0.027 g, 66%). Dark yellow oil. IR (film): 1726*s* and 1709*s* (C=O, ester). EI-MS: 312 (90, M^+), 297 (77, [M – Me]$^+$), 214 (100, [M – MeC≡CCOOMe]$^+$).

Data of **38**: ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; 67% in the mixture of DBS isomers): *ca.* 6.49 (^3J = 6.5, H–C(7), and H–C(10)); *ca.* 6.21 (signals superimp. with those of H–C(7) of **38′**, H–C(8) or H–C(9)); 6.01 (*d*-like, ^4J(2,Me–C(1)) = 1.4, H–C(2)); *ca.* 5.95 (signals superimp. with those of H–C(6) of **38′**, H–C(9) or H–C(8)); 3.68 (*s*, MeOOC–C(5)); 3.62 (*s*, MeOOC–C(4)); 2.26 (*s*, Me–C(3)); 2.03 (*d*, ^4J(Me–C(1),2) = 1.3, Me–C(1)); 2.00 (*d*, ^4J(Me–C(6),7) = 1.4, Me–C(6)).

Data of **38′**: ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; 33% in the mixture of DBS isomers): 6.43 (*s*, H–C(4)); 6.42 (*d*, ^3J(9,8) = 11.4, H–C(9)); 6.38 (*dd*, ^3J(8,9) = 11.3, ^3J(8,7) = 5.6, H–C(8)); 6.22 (*dd*, partly covered by signals of **38**, ^3J(7,8) = 5.6, H–C(7)); *ca.* 5.95 (*d*, mostly covered by signals of **38**, ^3J(6,7) ≈ 11, H–C(6)); 3.90 (*s*, MeOOC–C(5)); 3.66 (*s*, MeOOC–C(4)); 2.01 (*d*, ^4J(Me–C(3),4) = 1.2, Me–C(3)); 1.75 (*s*, Me–C(10)); 1.67 (*s*, Me–C(5)).

3.4. *Dimethyl 1,3,6,10-Tetramethylheptalene-4,5-dicarboxylate* (**39**) *and Dimethyl 3,5,6,10-Tetramethylheptalene-1,2-dicarboxylate* (**39′**). Sulfonyl derivative (*P**)/(*M**)-**12** (0.100 g, 0.229 mmol) was treated for 12 h according to *Exper. 3.1.* The thermally equilibrated 2 : 1 mixture **39**/**39′** was separated by TLC (SiO_2, hexane/Et_2O 4 : 1) to give , after crystallization from Et_2O/hexane 1 : 4, pure **39** (0.013 g, 18%) and pure **39′** (0.007 g, 9%).

Data of **39**: M.p. 145 – 146°. IR (KBr): 1724*s* and 1704*s* (C=O, ester). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; $CHCl_3$ at 7.260): 6.44 (*dd*, ^3J(8,9) = 11.3, ^3J(8,7) = 6.0, H–C(8)); 6.37 (*d*, ^3J(9,8) = 11.3, H–C(9)); 6.13 (*dd*-like, ^3J(7,8) = 5.8, H–C(7)); 6.09 (*d*-like, ^4J(2,Me–C(1)) = 1.4, H–C(2)); 3.66 (*s*, MeOOC–C(5)); 3.60 (*s*, MeOOC–C(4)); 2.27 (*s*, Me–C(3)); 1.98 (*t*-like, ^4J(Me–C(6),7) ≈ 2 × ^5J(Me–C(6),8) = 1.3, Me–C(6)); 1.94 (*d*, ^4J(Me–C(1),2) = 1.4, Me–C(1)); 1.79 (*s*, Me–C(10)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; $CDCl_3$ at 77.00): 168.10 (MeO*O*C–C(4)); 167.45 (MeO*O*C–C(5)); 148.03 (C(3)); 147.00 (C(5a)); 140.07 (C(6)); 132.72 (C(8)); 132.11 (C(9)); 131.69 (C(1)); 130.20 (C(7)); 129.20 (C(10)); 127.48 (C(4)); 126.94 (C(10a)); 124.49 (C(2)); 122.78 (C(5)); 51.78 (*Me*OOC–C(5)); 51.46 (*Me*OOC–C(4)); 22.70 (*Me*–C(1)); 22.25, 22.13 (*Me*–C(6), *Me*–C(10)); 18.07 (*Me*–C(3)). EI-MS: 326 (79, M^+), 311 (60, [M – Me]$^+$), 267 (31, [M – COOMe]$^+$), 252 (24, [M – (COOMe + Me)]$^+$), 228 (100, [M – MeC≡CCOOMe]$^+$).

Data of **39′**: M.p. 131 – 132°. ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; $CHCl_3$ at 7.260): 6.45 (*d*-like, ^4J(4,Me–C(3)) = 1.2, H–C(4)); 6.32 (*dd*, ^3J(8,9) = 11.1, ^3J(8,7) = 6.3, H–C(8)); 6.30 (*d*, ^3J(9,8) = 11.1, H–C(9)); 6.15 (*dd*-like, ^3J(7,8) = 6.3, ^4J(7,Me–C(6)) ≈ 1.5, H–C(7)); 3.69 (*s*, MeOOC–C(5)); 3.67 (*s*, MeOOC–C(4)); 2.03 (*d*, ^4J(Me–C(3),4) = 1.2, Me–C(3)); 1.99 (*d*, ^4J(Me–C(6),7) = 1.5, Me–C(6)); 1.76 (*s*, Me–C(10)); 1.67 (s, Me–C(5)). EI-MS: 326 (100, M^+), 311 (94, [M – Me]$^+$), 295 (22, [M – MeO]$^+$), 267 (18, [M – COOMe]$^+$), 252 (35, [M – (COOMe + Me]$^+$), 228 (73, [M – MeC≡CCOOMe]$^+$).

3.5. *Dimethyl 9-Isopropyl-1,3,6-trimethylheptalene-4,5-dicarboxylate* (**35**)*, Dimethyl 7-Isopropyl-3,5,10-trimethylheptalene-1,2-dicarboxylate* (**35′**)*, and 9-Isopropyl-1,3,6-trimethyl-4,5-dicarboxylic Anhydride* (*= 8-Isopropyl-4,6,11-trimethylheptaleno[4,5-c]furan-1,3-dione*; **44**). 3.5.1. *With MeONa/MeOH*. According to *Exper. 3.1*, sulfonyl derivative (*P**)-**15** (0.080 g, 0.161 mmol) yielded, after 12 h, a 3 : 2 mixture **35**/**35′** (0.022 g, 39%) (*cf.* [9]).

Data of **35**: M.p., UV, and IR, see [9]. We report here again the ^{1}H-NMR since the locants of the heptalene skeleton had been reversed in the meantime according to the IUPAC recommendations (C(5) old → C(1) new, *etc.*), and some atomic positions of **35** and of **35′** had to be reassigned according to our new full ^{1}H,^{13}C analysis. ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K, C*H*Cl_3 at 7.270; 60% of **35**): 6.291

(*d*, $^3J(8,7) = 6.6$, H–C(8)); 6.134 (*dd*-like, $^3J(7,8) = 6.5$, $^4J(7,\text{Me–C(6)}) = 1.0$, H–C(7)); 6.006 (*d*-like, $^4J(2,\text{Me–C(1)}) = 1.2$, H–C(2)); 5.862 (*s*, H–C(10)); 3.685 (*s*, MeOOC–C(5)); 3.625 (*s*, MeOOC–C(4)); 2.500 (*sept.*, Me_2CH–C(9)); 2.269 (*s*, Me–C(3)); 2.019 (*d*, $^4J(\text{Me–C(1)},2) = 1.3$, Me–C(1)); 2.003 (*s*, Me–C(6)); 1.102, 1.069 (2*d*, $J_{vic} = 6.9$, 6.8, Me_2CH–C(9)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K; $CDCl_3$ at 77.00; 60% of **35**): 168.12 (MeOO*C*–C(4)); 167.74 (MeOO*C*–C(5)); 148.27 (C(3)); 148.10 (C(9)); 145.71 (C(5a)); 141.31 (C(1)); 131.70 (C(2)); 131.39 (C(10a)); 128.81 (C(6)); 127.91 (C(4)); 126.10 (C(7)); 125.07 (C(8)); 124.39 (C(10)); 123.16 (C(5)); 51.89 (*Me*OOC–C(5)); 51.45 (*Me*OOC–C(4)); 35.58 (Me_2CH–C(9)); 25.11 (*Me*–C(1)); 22.98 and 22.59 (Me_2CHC(9)); 22.71 (*Me*–C(3)); 22.57 (*Me*–C(6)). GC-MS: 354 (60, M^+), 339 (50, $[M - \text{Me}]^+$), 295 (10, $[M - \text{COOMe}]^+$), 256 (100, $[M - \text{MeC}{\equiv}\text{CCOOMe}]^+$).

Data of **35′**: ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K, $CHCl_3$ at 7.270; 40% of **35′**; see also [9]): 6.438 (br. *s*, H–C(4)); 6.378 (*d*, $^3J(9,8) = 11.9$, H–C(9)); 6.345 (*dd*-like, $^3J(8,9) = 11.9$, $^4J(8,6) \approx 1.0$, H–C(8)); 5.730 (*s*, H–C(6)); 3.878 (*s*, MeOOC–C(5)); 3.658 (*s*, MeOOC–C(4)); 2.543 (*sept.*, Me_2CH–C(7)); 2.008 (*d*, $^4J(\text{Me–C(5)},4) = 1.1$, Me–C(5)); 1.746 (*s*, Me–C(3)); 1.652 (*s*, Me–C(10)); 1.134, 1.127 (2*d*, $J_{vic} = 6.9$, 6.8, Me_2CH–C(7)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K, $CDCl_3$ at 77.00; 40% of **35′**): 168.90 (MeOO*C*–C(5)); 165.43 (MeOO*C*–C(4)); 148.40 (C(7)); 146.06 (C(5a)); 138.89 (C(4)); 135.51 (C(9)); 135.48 (C(2)); 132.96 (C(10)); 132.90 (C(5)); 131.98 (C(8)); 129.67 (C(3)); 127.50 (C(10a)); 121.83 (C(6)); 120.52 (C(1)); 52.41 (*Me*OOC–C(5)); 52.29 (*Me*OOC–C(4)); 34.84 (Me_2CH–C(7)); 22.88 and 22.63 (Me_2CH–C(7)); 22.48 (Me–C(5)); 17.37 (*Me*–C(10)); 17.15 (*Me*–C(3)).

3.5.2. *With* t-*BuOK*. Treatment of sulfonyl derivative (*P**)-**12** (0.130 g, 0.262 mmol) according to *Exper.* 3.2.2 gave, after CC (SiO_2, hexane/AcOEt 2:1), a 3:2 mixture **35**/**35′** (0.021 g, 23%) and, after crystallization from AcOEt/hexane 1:2, **44** (0.016 g, 20%). Orange crystals. M.p. 141–142°. IR (KBr): 1806*s* and 1754*s* (5-ring anhydride). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): 6.40 (*dd*-like, $^3J(7,8) = 7.0$, $^4J(7,\text{Me–C(6)}) = 1.3$, H–C(7)); 6.26 (*d*, $^3J(8,7) = 7.0$, H–C(8)); 6.17 (br. *s*, H–C(2)); 5.93 (*s*, H–C(10)); 2.49 (*sept.*, partly covered by signal of Me–C(3), Me_2CH–C(9)); 2.45 (*s*, Me–C(3)); 2.29 (s, Me–C(1)); 2.17 (*s*, Me–C(6)); 1.10, 1.08 (2*d*, $J_{vic} = 6.7$, 6.6, Me_2CH–C(9)). CI-MS: 326.2 (100, $[M + \text{NH}_4]^+$), 309.2 (80, $[M + 1]^+$).

3.6. *Dimethyl 3-Ethyl-9-isopropyl-1,6-dimethylheptalene-4,5-dicarboxylate* (**40**) *and Dimethyl 3-Ethyl-7-isopropyl-5,10-dimethylheptalene-1,2-dicarboxylate* (**40′**). Sulfonyl derivative (*P**)/(*M**)-**23** (0.200 g, 0.392 mmol) was treated according to *Exper. 3.1*. CC gave a 3:1 mixture **40**/**40′** (0.080 g, 55%). Orange oil.

Data of **40**/**40′** *3:2:* IR (film): 1732*s* (C=O, ester). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): 6.48 (br. *s*, H–C(4) of **40′**); 6.40–6.32 (superimp. signals of H–C(8) and H–C(9) of **40′** and H–C(8) of **40**); 6.15 (*d*-like, H–C(7) of **40**); 6.02 (*d*-like, $^4J(2,\text{Me–C(1)}) = 1.4$, H–C(2) of **40**); 5.84 (*s*, H–C(10) of **40**); 5.75 (br. *s*, H–C(6) of **40′**); 3.86, 3.64 (2*s*, MeOOC–C(5) and MeOOC–C(4) of **40′**); 3.67, 3.61 (2*s*, MeOOC–C(5) and MeOOC–C(4) of **40**); 2.70–2.40 (superimp. signals of MeCH_2–C(3), Me_2CH–C(9), Me_2CH–C(7) of **40** and **40′**); 2.02–1.99 (superimp. signals of Me–C(1) and Me–C(6) of **40** and Me–C(5) of **40′**); 1.66 (*s*, Me–C(10) of **40′**); 1.15–1.05 (superimp. signals of *Me*CH_2–C(3), Me_2CH–C(9), and Me_2CH–C(7) of **40** and **40′**). EI-MS: 368 (51, M^+), 353 (47, $[M - \text{Me}]^+$), 309 (15, $[M - \text{COOMe}]^+$), 256 (100, $[M - \text{EtC}{\equiv}\text{CCOOMe}]^+$).

3.7. *Dimethyl (*M**,3*E*,4*S**)-3-Ethylidene-9-isopropyl-1,4,6-trimethylheptalene-4,5-dicarboxylate* ((*M**)-**42**). Sulfonyl derivative (*P**)-**41** (0.100 g, 0.191 mmol) was treated according to *Exper. 3.1* with MeONa/MeOH. TLC (SiO_2, hexane/Et_2O 4:1) gave (*M**)-**42** (0.015 g, 21%). Orange oil. IR (film): 1732s (C=O, ester). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): 6.55 (br. *s*, H–C(2)); 6.33 (*s*, H–C(10)); 6.26 (*d*, $^3J(8,7) = 6.9$, H–C(8)); 6.11 (*dd*-like, $^3J(7,8) = 6.8$, $^4J(7,\text{Me–C(6)}) = 1.4$, H–C(7)); 5.69 (*q*, $^3J(1',\text{Me–C(1')}) = 7.0$, H–C(1′)); 3.74 (*s*, MeOOC–C(5)); 3.49 (*s*, MeOOC–C(4)); 2.51 (*sept.*, Me_2CH–C(9)); 2.01 (*s*, Me–C(1)); 1.887 (*d*, $^3J(\text{Me–C(1')},1') = 6.8$, Me–C(1′)); 1.875 (*s*, Me–C(6)); 1.49 (*s*, Me–C(4)); 1.17, 1.16 (2*d*, $J_{vic} = 6.9$, 6.8, Me_2CH–C(9)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K): 176.19 (MeOO*C*–C(4)); 168.79 (MeOO*C*–C(5)); 146.79 (C(9)); 141.74 (C(5a)); 135.82 (C(3)); 133.31 (C(10a)); 129.97 (C(1)); 129.31 (C(5)); 128.89 (C(6)); 128.31 (C(10)); 127.00 (C(2)); 124.96 (C(1′)); 124.61 (C(8)); 124.59 (C(7)); 52.57 (*Me*OOC–C(5)); 51.86 (C(4)); 51.67 (*Me*OOC–C(4)); 26.12 (*Me*–C(1)); 23.68, 22.80 (Me_2CH–C(9)); 22.92 (*Me*–C(6)); 21.56 (*Me*–C(4)); 14.02 (*Me*–C(1′)). CI-MS:

400.5 (73, $[M+NH_4]^+$), 385.5 (100, $[M+1]^+$), 351.4 (25, $[M+1-MeOH]^+$), 279.3 (8, $[M+1-(2\,MeOH+C_3H_4)]^+$).

3.8. *Dimethyl 2-Ethyl-9-isopropyl-1,6-dimethylheptalene-4,5-dicarboxylate* (**45**). Furanone (*P**)-**27** (0.050 g, 0.098 mmol) was treated for 3 h according to *Exper. 3.1.* CC (SiO_2, hexane/Et_2O 2:1) and crystallization from $CHCl_3$ gave **45** (0.027 g, 81%). No traces of **45′** were found. **45**: Orange crystals. M.p. 142.2–143.1°. R_f (hexane/AcOEt 1:1) 0.60. UV/VIS (cyclohexane): max. 323 (sh, 3.13; long tailing up to 400), 283 (3.80), 253 (3.91), 212 (4.06); min. 274 (3.80), 241.5 (3.89). IR (ATR): 1714 (C=O, ester). ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K; C*H*Cl_3 at 7.264): 7.527 (*s*, H–C(2)); 6.254 (*d*, $^3J(8,7)=6.5$, H–C(8)); 6.152 (*d*, $^3J(7,8)=6.5$, H–C(7)); 5.787 (*s*, H–C(10)); 3.705 (*s*, MeOOC–C(5)); 3.697 (*s*, MeOOC–C(4)); 2.476 (*sept.*, Me_2CH–C(9)); 2.324 (symm. 8 line signal, $J_{gem}=14.8$, $J_{vic}\approx 7.4$, $MeCH_2$–C(2)); 1.993 (*s*, Me–C(6)); 1.985 (*s*, Me–C(1)); 1.107 (*t*, $J_{vic}=7.6$, *Me*CH_2–C(2)); 1.081, 1.041 (2*d*, $J_{vic}=6.9$, 6.8, Me_2CH–C(9)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K; *C*DCl_3 at 77.23): 167.99 (MeOO*C*–C(5)); 167.91 (MeOO*C*–C(4)); 148.78 (C(9)); 144.25 (C(3)); 138.19 (C(2)); 137.10 (C(1)); 133.61 (C(10a)); 130.90 (C(5)); 128.50 (C(6)); 126.88 (C(7)); 125.35 (C(10)); 124.70 (C(8)); 121.99 (C(4)); 52.23 (*Me*OOC–C(4)); 52.13 (*Me*OOC–C(5)); 35.92 (Me_2*C*H–C(9)); 26.71 (Me*C*H_2–C(2)); 23.32, 22.72 (Me_2CH–C(9); corr. with 1.107 and 1.080, resp.); 22.41 (*Me*–C(6)); 21.78 (*Me*–C(1)); 13.69 (*Me*CH_2–C(2)).

The structural parameters of **45** were determined by an X-ray crystal-structure analysis (*cf. Table 7*).

3.9. *Dimethyl 2-Ethyl-6,8,10-trimethylheptalene-4,5-dicarboxylate* (**46**) *and Dimethyl 4-Ethyl-6,8,10-trimethylheptalene-1,2-dicarboxylate* (**46′**). Furanone (*P**)-**30** (0.100 g, 0.207 mmol) was treated and worked up in analogy to *Exper. 3.2*. A thermally equilibrated 3:1 mixture **46**/**46′** (0.046 g, 65%) was obtained as brownish oil. R_f (hexane/AcOEt 2:1) 0.70.

Data of **46**: ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K; 74% of **46**; C*H*Cl_3 at 7.260): 7.50 (*s*, H–C(3)); 6.13 (br. *s*, H–C(9)); 5.94 (br. *s*, H–C(7)); 5.79 (br. *s*, H–C(1)); 3.72 (s, MeOOC–C(4)); 3.69 (s, MeOOC–C(5)); 2.33 (symm. *m*, $J_{gem}=15.0$, $J_{vic}=7.5$, ^4J(Me*C*H_2–C(2),1) = 1.3, Me*C*H_2–C(2)); 2.01 (br. *s*, Me–C(8)); 1.97 (*d*, ^4J(Me–C(6),7) = 1.1, Me–C(6)); 1.73 (*s*, Me–C(10)); 1.16 (*t*, $J_{vic}=7.5$, *Me*CH_2–C(2)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K; 74% of **46**; *C*DCl_3 at 77.00): 167.96 (MeOO*C*–C(4)); 167.53 (MeOO*C*–C(5)); 148.43 (C(5a)); 143.70 (C(2)); 142.55 (C(3)); 139.46 (C(8)); 132.98 (C(4)); 132.05 (C(10)); 130.24 (C(9)); 129.90 (C(6)); 129.80 (C(1)); 129.20 (C(7)); 122.87 (C(5)); 122.54 (C(10a)); 52.12 (*Me*OOC–C(4)); 51.87 (*Me*OOC–C(5)); 29.06 (Me*C*H_2–C(2)); 24.91 (*Me*–C(8)); 23.31 (*Me*–C(6)); 17.84 (*Me*–C(10)); 14.01 (*Me*CH_2–C(2)).

Data of **46′**: ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K, 24% of **46′**; C*H*Cl_3 at 7.260): 6.26 (*q*-like, ^4J(3,Me*C*H_2–C(4)) ≈ ^4J(3,5) = 1.1, H–C(3)); 6.09 (br. *s*, H–C(9)); 5.91 (*quint.*-like, H–C(7)); 5.72 (*d*, ^4J(5,3) = 1.1, H–C(5)); 3.83 (*s*, MeOOC–C(2)); 3.70 (*s*, MeOOC–C(1)); 2.30 (symm. *m*, $J_{gem}=14.0$, $J_{vic}=$ 7.4, ^4J(Me*C*H_2–C(4),3) ≈ 0.7, Me*C*H_2–C(4)); 2.11 (*d*, ^4J(Me–C(6),7) = 1.1, Me–C(6)); 1.96 (*d*, ^4J(Me–C(8),9) = 1.1, Me–C(8)); 1.63 (*s*, Me–C(10)); 1.08 (*t*, $J_{vic}=7.5$, *Me*CH_2–C4)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K; 24% of **46′**; *C*DCl_3 at 77.00; assigned signals): 168.82 (MeOO*C*–C(4)); 166.97 (MeOO*C*–C(5)); 151.53 (C(4)); 144.18 (C(5a)); 141.46 (C(10)); 139.19 (C(8)); 134.79 (C(6)); 134.11 (C(1)); 131.29 (C(9)); 130.03 (C(7)); 125.30 (C(5)); 124.58 (C(2)); 122.53 (C(10a)); 122.25 (C(3)).

3.10. *Dimethyl 2-Ethyl-1,6,8,10-tetramethylheptalene-4,5-dicarboxylate* (**47**) *and Dimethyl 4-Ethyl-5,6,8,10-tetramethylheptalene-1,2-dicarboxylate* (**47′**). Furanone (*P**)-**31** (0.091 g, 0.203 mmol) was treated in analogy to *Exper. 3.8*. All starting material had been consumed after 0.75 h. CC (SiO_2, hexane/AcOEt 3:1) gave first a 1:9 mixture **47**/**47′** as brownish oil (0.048 g, 67%), followed by small amounts (*ca.* 5 mg, 5%) of the corresponding anhydride of (*P**)-**31**, *(*P*,5R*)-*4,5-dihydro-6,7,9,11-tetramethyl-5-[(1*S**)-1-(phenylsulfonyl)ethyl]heptaleno[1,2-*c*]furan-1,3-dione* ((*P**)-**48**). On standing in $CDCl_3$ soln. over two month at r.t. in the laboratory, the 1:9 mixture **47**/**47′** was nearly completely converted into **47** (residual amount of **47′** max. 8%).

Data of **47** *After Isomerization.* ^{1}H-NMR (600 MHz, $CDCl_3$; *C*DCl_3 at 7.260): 7.56 (*d*-like, ^5J(3,Me–C(1)) ≈ 0.7, H–C(3)); 6.14 (br. *s*, H–C(9)); 6.01 (br. *s*, H–C(7)); 3.70 (*s*, MeOOC–C(4)); 3.69 (*s*, MeOOC–C(5)); 2.34 (symm. 10 line *m*, $J_{gem}=12.0$, $J_{vic}=7.6$, Me*C*H_2–C(2)); 2.04 (*d*, ^4J(Me–C(8),9) = 1.2, Me–C(8)); 1.96 (*d*, ^4J(Me–C(6),7) = 1.2, Me–C(6)); 1.90 (*d*-like, ^5J(Me–C(1),Me*C*H_2–C(2)) ≈ ^5J(Me–C(1),3) ≈ 0.7, Me–C(1)); 1.70 (*s*, Me–C(10)); 1.11 (*t*, $J_{vic}=7.6$, *Me*CH_2–C(2)). ^{13}C-NMR

(150 MHz, $CDCl_3$; *C*DCl_3 at 77.00): 167.85 (MeOO*C*–C(4)); 167.75 (MeOO*C*–C(5)); 146.89 (C(5a)); 143.36 (C(3)); 138.49 (C(2)); 138.47 (C(8)); 136.07 (C(1)); 130.31 (C(9)); 130.23 (C(6)); 130.15 (C(4)); 129.45 (C(10)); 128.59 (C(7)); 127.49 (C(10a)); 121.36 (C(5)); 52.01 (*Me*OOC–C(4)); 51.79 (*Me*OOC–C(5)); 25.86 (Me*C*H_2–C(2)); 25.04 (*Me*–C(6)); 19.81 (*Me*–C(1)); 18.20 (*Me*–C(10)); 13.68 (*Me*CH_2–C(2)).

Data of **47′**: ^{1}H-NMR (300 MHz, $CDCl_3$; in the presence of *ca.* 10% of **47**; C*H*Cl_3 at 7.260): 6.44 (*s*, H–C(3)); 6.05 (br. *s*, H–C(9)); 5.96 (br. *s*, H–C(7)); 3.82 (*s*, MeOOC–C(2)); 3.70 (s, MeOOC–C(1)); 2.42 (*ddd*, J_{gem} = 15.0, J_{vic} = 7.5, $^4J(H_A,3)$ = 1.3, H_A of MeCH_2–C(4)); 2.28 (*ddd*, J_{gem} = 15.0, J_{vic} = 7.4, $^4J(H_B,3)$ = 0.8, H_B of MeCH_2–C(4)); 2.04 (*d*, ^4J(Me–C(6),7) = 1.2, Me–C(6)); 1.99 (*d*, ^4J(Me–C(8),9) = 1.1, Me–C(8)); 1.75 (*s*, Me–C(10)); 1.00 (*t*, J_{vic} = 7.4, *Me*CH_2–C(4)). ^{13}C-NMR (75 MHz, $CDCl_3$; *C*DCl_3 at 77.00; assigned signals): 129.96 (C(9)); 128.85 (C(7)); 122.76 (C(3)); 52.40 (*Me*OOC–C(2)); 52.21 (*Me*OOC–C(1)); 30.15 (Me*C*H_2–C(4)); 24.97 (*Me*–C(8)); 22.54 (*Me*–C(5)); 17.60 (*Me*–C(10)); 14.55 (Me–C(6)); 13.82 (*Me*CH_2–C(4)).

*Data of (*P**)-***48**: ^{1}H-NMR (300 MHz, $CDCl_3$; $CHCl_3$ at 7.260): 7.73 (H_o of $PhSO_2$); 7.64 (H_p of $PhSO_2$); 7.52 (H_m of $PhSO_2$); 6.20 (*s*, H–C(10)); 6.00 (*s*, H–C(8)); 3.65 (*sext.*-like, ^3J(1′,Me–C(1′)) = 7.2, ^3J(1′,5) = 9.5, H–C(1′)); 3.01 (*dt*, ^3J(5,1′) = 9.5, ^4J(1′,H_S–(4)) = 3.4, ^4J(1′,H_R–(4)) = 4.4, H–C(5)); 2.86 (*dd*, $^2J(H_S,H_R)$ = 14.7, ^3J(H_S,5) = 3.4, H_S–C(4)); 2.79 (*dd*, ^2J(H_R,H_S) = 14.7, ^3J(H_R,5) = 4.4, H_R–C(4)); 2.11 (*s*, Me–C(9)); 1.94 (*s*, Me–C(7)), 1.92 (*s*, Me–C(11)); 1.75 (*s*, Me–C(6)); 1.15 (*d*, ^3J(Me–C(1′),1′) = 7.2, Me–C(1′)).

4. *Crystal-Structure Determination of (*P**)-***4**, **5**, *(*P**)-***10**, *(*P**)-***27**, *(*P**)-***30**, *(*P**)-***31**, *(*P**)-***41**, **45**, *and* **49** (*Table 7* and *Figs. 2–6*)[20]). All measurements were conducted with graphite-monochromated MoK_α radiation (λ 0.71073 Å). For (*P**)-**27**, -**30**, -**31**, and -**41** and **45**, a *Nonius-KappaCCD* area detector diffractometer [16][17] and an *Oxford-Cryosystems-Cryostream-700* cooler were employed, while data for the remaining compounds were collected on a *Rigaku-AFC5R* diffractometer [18] mounted on a 12 kW rotating anode generator. The data collection and refinement parameters are given in *Table 7*, views of the molecules are shown in *Figs. 2–6*. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method [19] was applied for (*P**)-**30** and (*P**)-**31**. Each structure was solved by direct methods with either SIR92 [20] or SHELXS97 [21], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined, with a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent atom (1.5 U_{eq} for the Me groups). The refinement of each structure was carried out on F^2 by full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied in the cases of **5**, (*P**)-**27**, -**30**, -**31**, and -**41** and **45**. For (*P**)-**41** and **45**, six and four reflections, resp., whose intensities were considered to be extreme outliers, were omitted from the final refinement.

Compound (*P**)-**4** crystallized in a non-centrosymmetric polar space group, and refinement of the absolute structure parameter yielded a value of 0.47(9), which indicated that the crystals are inversion twins and that the compound is racemic. Compound **49** also crystallized in a non-centrosymmetric polar space group, but the absolute structure was not determined and was assigned arbitrarily. The structure of (*P**)-**27** has two symmetry-independent molecules in the asymmetric unit. In the structure of **45**, one terminal Me group of the ^{i}Pr group was disordered. Two positions were defined for this group, and refinement of constrained site occupation factors yielded a value of 0.850(6) for the major conformation. Similarity restraints were applied to the bond lengths involving the disordered C-atoms, and they were restrained to have similar atomic displacement parameters.

Neutral-atom scattering factors for non-H-atoms were taken from [22a], and the scattering factors for H-atoms were taken from [23]. Anomalous dispersion effects were included in F_c [24]; the values for f' and f'' were those of [22b]. The values of the mass attenuation coefficients were those of [22c]. All

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[20]) CCDC-761780–761788 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data request/cif.

calculations were performed with the SHELXL97 program [21]. The crystallographic diagrams were drawn with ORTEPII [25].

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