Formation of 3-Sulfonyl-Substituted Benzo[*a*]heptalene-2,4-diols from Heptalene-1,2-dicarboxylates and Lithiomethyl Phenyl Sulfones

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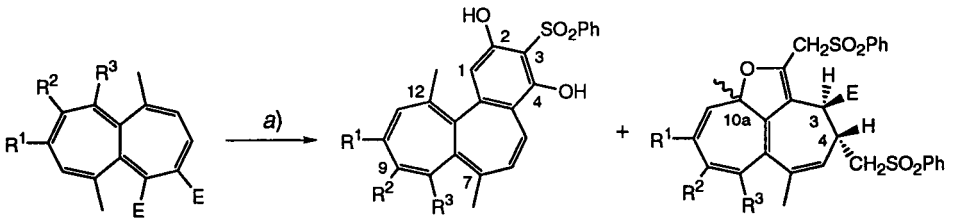
On treatment with 6 mol-equiv. of lithiomethyl phenyl sulfone at −78° in THF, dimethyl 5,6,8,10-tetramethylheptalene-1,2-dicarboxylate (**1′b**) gives, after raising the temperature to −10° and addition of 6 mol-equiv. of BuLi, followed by further warming to ambient temperature, the corresponding 3-(phenylsulfonyl)benzo[*a*]heptalene-2,4-diol **2b** in yields up to 65% (*cf. Scheme 6* and *Table 2*), in contrast to its double-bond-shifted (DBS) isomer **1b** which gave **2b** in a yield of only 6% [1]. The bisanion [**9**]$^{2-}$ of the cyclopenta[*a*]heptalen-1(1*H*)-one **9** (*cf. Fig. 1*), carrying a (phenylsulfonyl)methyl substituent at C(11b), seems to be a key intermediate on the reaction path to **2b**, because **9** is transformed in high yield into **2b** in the presence of 6 mol-equiv. of BuLi in the temperature range of −10° to room temperature (*cf. Scheme 7*). Heptalene-dicarboxylate **1′b** was also transformed into benzo[*a*]heptalene-2,4-diols **2c**–**g** by a number of lithiated methyl X-phenyl sulfones and BuLi (*cf. Scheme 9* and *Table 3*).

1. Introduction. – Recently we reported on a 'one-pot' synthesis of 3-(X-sulfonyl)benzo[*a*]heptalene-2,4-diols **2** (X = Ph or dialkylamino) by reaction of dimethyl heptalene-4,5-dicarboxylates **1** with an excess of lithiated methyl sulfonyl compounds in the presence of BuLi (*Scheme 1*) [1]. A weakness of this otherwise unique, but still not clear transformation was the fact that, beside **2**, appreciable – and in some cases predominating – amounts of methyl 3*H*-heptaleno[1,10-*bc*]furan-3-carbox-

Scheme 1



1a[a]) **1b**

2a (38%)[b]) **2b** (6%)

3a (31%)[c]) **3b** (37%)

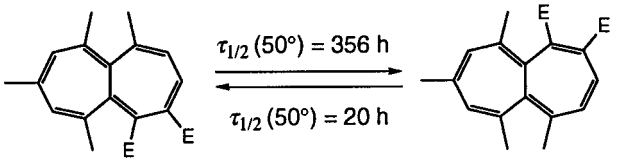
a) 1. 4 Mol-equiv. of $LiCH_2SO_2Ph$/THF, −78 → −10°; 2. 4 mol-equiv. of BuLi/THF, −10° → ambient temp.

[a]) **a**: $R^1 = R^3 = H$, R^2 = i-Pr; **b**: $R^1 = R^3$ = Me, $R^2 = H$. [b]) Similar yields are found when Ph is exchanged by *N*,*N*-dialkylamino (*cf.* [1]). [c]) *Ca.* 1:1 mixture of the Me–C(10a) diastereoisomers.

[1]) Part of the diploma thesis of *M.L.*, University of Zurich, 1998.

ylates **3** were also formed. We could show that the formation of **3** was the result of an initial *Michael* addition of the lithiomethyl sulfonyl substrates at C(3) of **1**, followed by nucleophilic attack of a second mol-equiv. of lithiated methyl sulfonyl compound at the MeOCO group at C(5) and cyclization to the furan ring. Still open questions were that of the influence of the thermal cyclic double-bond shifts (DBS) at the heptalene skeleton, which had to occur for the formation of **2**, as well as that of the suppression of the formation of the side products **3**. In principle, the DBS isomers of **1** should not undergo *Michael* addition with lithiated methyl sulfonyl compounds and, moreover, they would have their heptalene double bonds just at the right positions for the benzo-anellation reaction. Therefore, we studied the benzo[*a*]heptalene formation in the reaction of the DBS isomer **1′b** of **1b** with lithiomethyl phenyl sulfones in the temperature range of – 78° to 20°, *i.e.*, well below that of the thermal DBS process of **1′b** and **1b**, which starts slowly at 50° (*Scheme 2*) [2][3]. Our findings, which shed some further light on the mechanism of the benzo-anellation reaction, are described below.

Scheme 2[a])



1b **1'b**

[a]) $\tau_{1/2}$ calculated with the activation parameters for perdeuterio-diglyme [2].

2. Results and Discussion. – The thermal reaction of 1,4,6,8-tetramethylazulene and a twofold excess of dimethyl acetylenedicarboxylate was performed in toluene at 130° at a higher concentration than we had used in our earlier experiments [4], with the result that the yield of dimethyl 1,6,8,10-tetramethylheptalene-4,5-dicarboxylate (**1b**) could be improved to 47% (*cf.* [4][5]). Heptalene **1b** was accompanied by 4% of its DBS isomer **1′b** and 27% of dimethyl 4,6,8-trimethylazulene-1,2-dicarboxylate (see *Exper. Part*). The mixture of **1b** and **1′b** was directly subjected to photoisomerization with a high-pressure Hg lamp in MeCN as solvent (*cf.* [4]). After 3 h, a photostationary state was reached, consisting of 52% of **1b** and 48% of **1′b**, in good agreement with our former results in *t*-BuOMe as solvent [4]. Most of **1b** could be removed from the mixture by crystallization from Et_2O/hexane. The residue of the mother liquor, strongly enriched in **1′b**, was chromatographed on silica gel with hexane/Et_2O 4:1 and gave pure **1′b** (47%) and an additional small amount of **1b** (8%).

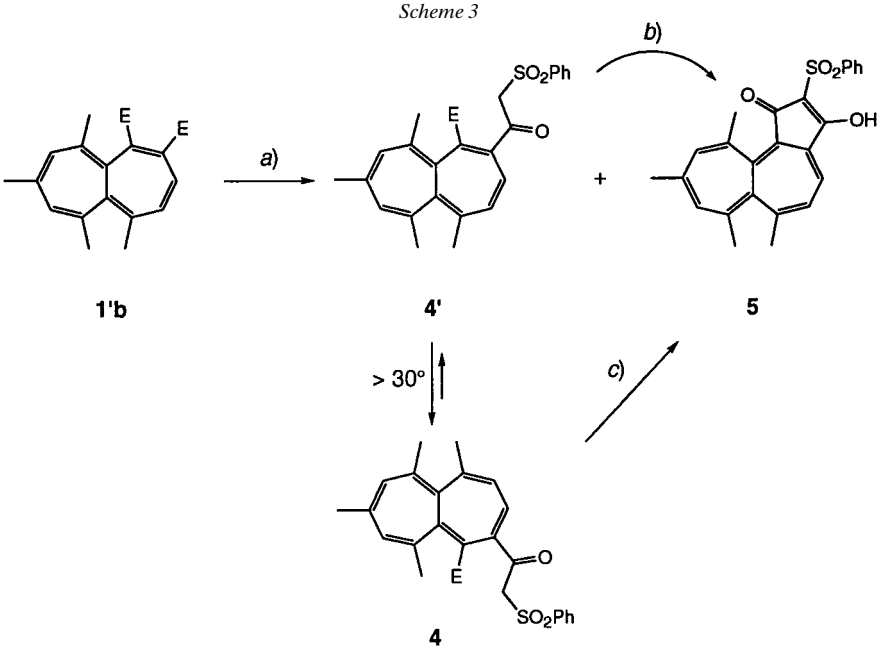
The reaction of **1′b** with up to 2 mol-equiv. of lithiomethyl phenyl sulfone ($LiCH_2SO_2Ph$) in THF at various temperatures and reaction times (*cf. Table 1*) led to the formation of two products, namely the selectively at MeOCO–C(2) (phenylsulfonyl)methylated heptalene **4′**, which, in part, slowly isomerized during the workup procedure to its thermodynamically more stable DBS isomer **4**[2]), and the 3-hydroxy-

[2]) The thermal equilibrium mixture at 100° (toluene) consists of 84% **4** and 16% **4′**.

cyclopenta[*d*]heptalen-1(1*H*)-one **5** with shifted double bonds at the heptalene core as compared to the starting heptalene **1′b** (*Scheme 3*). Upon treatment with KOH in MeOH at room temperature, **4** was transformed quantitatively into **5**. Similarly, **4′** reacted to **5** in the presence of $LiCH_2SO_2Ph$. On the other side, very short treatment of **1′b** with 3 mol-equiv. of $LiCH_2SO_2Ph$ at $-78°$ resulted in an almost quantitative transformation into **4′** (*cf. Table 1*). We assume that traces of **5**, which were isolated after workup of the reaction mixture, were formed during the workup procedure.

The product scene changed when **1′b** was introduced into a solution of 4 mol-equiv. of $LiCH_2SO_2Ph$ in THF at $-78°$ (*Scheme 4*). As long as the temperature was kept below $-40°$, only **4′** and small amounts of **5** could be found in the reaction mixture by

Scheme 3



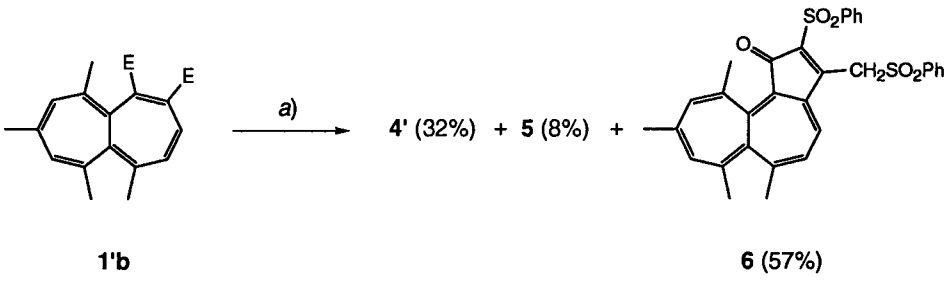
a) See *Table 1*. *b*) 1.4 Mol-equiv. of $LiCH_2SO_2Ph$/THF, $-30°$/3 d; 93% of **5**. *c*) 0.35M KOH/MeOH, ambient temp./0.5 h; 92%.

Table 1. *Formation of Methyl 5,6,8,10-Tetramethyl-2-[(phenylsulfonyl)acetyl]heptalene-1-carboxylate* (**4′**) *by (Phenylsulfonyl)methylation of Dimethyl 5,6,8,10-Tetramethylheptalene-1,2-dicarboxylate* (**1′b**)

$MeSO_2Ph$ [mol-equiv.]	BuLi [mol-equiv.]	Reaction conditions		Yield [%]		
		Time [h]	Temp. [°]	**4′**[a])	**5**	**6**
2	2.2	2	$-78 \rightarrow -40$	56	0	33
3	1.2	3	$-78 \rightarrow 0$	51	37	10
1.2	1.3	4	$-78 \rightarrow 0$	65	15	–[b])
1.3	1.4	4	$-78 \rightarrow 0$	66	3	–[b])
3	3	0.17	-78	98	0	1

[a]) Partial isomerization to the thermodynamically favored DBS isomer **4** occurred during workup (*cf. Footnote 2*). [b]) Compound **6** was not looked for.

Scheme 4

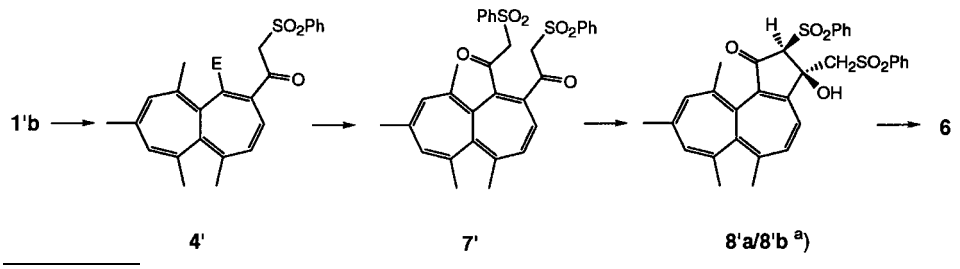


a) 4 Mol-equiv. of $LiCH_2SO_2Ph$/THF, $-78 \rightarrow -40°$ (1 h) $\rightarrow 0°$ (3 h).

TLC analysis. All starting material had been consumed. At temperatures above $-40°$, two new products with slightly different R_f values were formed as indicated by TLC analysis (*cf. Exper. Part*). However, during the acidic workup procedure both new products were converted into a single further compound with a distinctly larger R_f value as compared to those of the two intermediate products. Spectroscopic analysis showed the new product to be the 3-(phenylsulfonyl)methylated cyclopenta[*d*]heptalen-1(1*H*)-one **6**. As we have already demonstrated in other cases [1], cyclopenta[*d*]heptalen-1(1*H*)-ones of type **5** are not the precursors of the corresponding benzo[*a*]heptalene-2,4-diols. On the other hand, the mono-alkylated heptalene **4′** yielded **6** on treatment with an excess of $LiCH_2SO_2Ph$ in THF above $-40°$. Therefore, the most conceivable reaction sequence for the formation of **6** would be that shown in *Scheme 5*. Compound **4′**, already formed at $-78°$, is further (phenylsulfonyl)methylated at MeOCO–C(1) in the presence of a larger excess of $LiCH_2SO_2Ph$ and at temperatures $> -78°$ (**4′** $\rightarrow$ **7′**), before ring closure of deprotonated **4′** to **5′** – which by DBS yields **5** – takes place to a larger extent. At temperatures $\geq -40°$, deprotonated **7′** cyclizes to **8′a**/**8′b**. We assume that the relative configuration at C(2) and C(3) of **8′a**/**8′b** is that depicted in *Scheme 5*, *i.e.*, *trans* with respect to the relative orientations of the two SO_2-bearing substituents, as we have demonstrated in the case of other pairs of diastereoisomers of this type (*cf.* Scheme 7 in [1]). The diastereoisomerism arises from the inherent chirality of the heptalene core. Under the acidic workup procedure **8′a**/**8′b** or their DBS isomers (**8a**/**8b**) lose water to give – from **8′a**/**8′b** after DBS – the final product **6**. An analogue (*i.e.*, $Ph=N(CH_2CH_2)_2O$) had already been isolated by us from the reaction mixture of **1b** and excess of $LiCH_2SO_2N(CH_2CH_2)_2O$ in THF [1]. Compound **6** is stable in the presence of an excess of $LiCH_2SO_2Ph$ and BuLi.

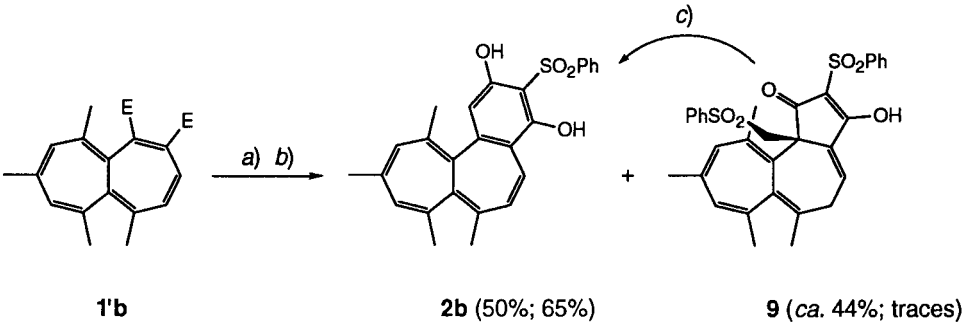
Formation of **8′a**/**8′b** requires in total 4 mol-equiv. of $LiCH_2SO_2Ph$, since 2 mol-equiv. are necessary for the formation of **7′** and the other 2 mol-equiv. will be consumed by deprotonation reactions of **7′** (at $PhSO_2CH_2$–C(1)) as well as of **8′a**/**8′b** (at C(2)). Therefore, no benzo[*a*]heptalene-2,4-diol is formed in recoverable amounts under such conditions. However, when the reaction of **1′b** was started at $-78°$ with 4 mol-equiv. of $LiCH_2SO_2Ph$, and the temperature was then raised within 90 min to $-10°$, followed by the addition of 4 mol-equiv. of BuLi and further warming up of the reaction mixture to ambient temperature, the expected benzo[*a*]heptalene-2,4-diol **2b** [1] could be isolated by chromatography on SiO_2 in a yield of 50% (see *Scheme 6* and *Table 2*). Moreover, benzo[*a*]heptalene **2b** was accompanied by a highly polar and, therefore, slow-moving

Scheme 5



a) See text

Scheme 6



a) 1. 4 Mol-equiv. of $LiCH_2SO_2Ph$/THF, $-78 \rightarrow -10°$ (1.5 h), 2. 4 mol-equiv. of BuLi/THF, $-10° \rightarrow$ ambient temp. (1.5 h). *b*) As under *a*), however, with 6 mol-equiv. of both reactants. *c*) 6 Mol-equiv. of BuLi/THF, $-10° \rightarrow$ ambient temp.; 61% of **2b**.

compound **9** which was eluted from the column by acetone in a yield of *ca.* 44%[3]). Recrystallization from CH_2Cl_2/hexane gave yellow prisms suitable for an X-ray crystal-structure analysis (*Fig. 1*)[4]), which revealed the presence of the fused ring system of a 5,11b-dihydrocyclopenta[*a*]heptalen-1(1*H*)-one with a $PhSO_2$ group at C(2) and a $PhSO_2CH_2$ substituent, linked, surprisingly, to C(11b). The OH group at C(3) forms, according to an O–H···O distance of 189 pm, a strong intramolecular H-bond with one of the O-atoms of the adjacent $PhSO_2$ substituent at C(2). Both seven-membered rings have a boat conformation and form together a twisted-bowl shape. The alternative combination, in which one ring puckers upward while the other puckers downward to build an S-shaped global conformation seems less likely, because the bowl shape serves to reduce steric interactions between the pairs of substituents adjacent to each end of the C–C bond common to the two seven-membered rings. Conversely, the fused five-membered ring is planar. The crystal lattice of **9** contains disordered solvent molecules, comprising one site half-filled by a disordered CH_2Cl_2 molecule and four different sites also partially occupied by H_2O molecules[5]).

3) It might be that we have overlooked compounds of this type in our earlier investigations [1] due to their highly polar character.

4) The spectral data did not allow a clear-cut structural assignment of **9**.

5) In the air, at room temperature, the crystals of **9** rapidly lose solvent molecules and disintegrate.

Table 2. *Formation of 6,7,9,11-Tetramethyl-3-(phenylsulfonyl)benzo[*a*]heptalene-2,4-diol* (**2b**) *by Reaction of Dimethyl 5,6,8,10-Tetramethylheptalene-1,2-dicarboxylate* (**1′b**) *with an Excess of* $LiCH_2SO_2Ph$

$MeSO_2Ph$ [mol-equiv.]	Addition of BuLi [mol-equiv]		Reaction time[c]) [h]	Yield of **2b** [%]
	first[a])	second[b])		
4	4.5	4	4	50[d])
4	4	5[e])	3.5	24
4	4.5	5	3	28
4	4.5	5	4	38
6	6	6	6	65[f])
8	8	6	5	57

[a]) First addition of BuLi at $-78°$. [b]) Second addition of BuLi at $-10°$. [c]) Total reaction time from $-78°$ to ambient temperature. [d]) Cyclopenta[*a*]heptalen-1(1*H*)-one **9** was isolated in *ca.* 44% yield (*cf. Scheme 6*). If not otherwise stated, the presence of **9** in the reaction mixture was not proved. [e]) LDA was used instead of BuLi. [f]) See also *Scheme 6*.

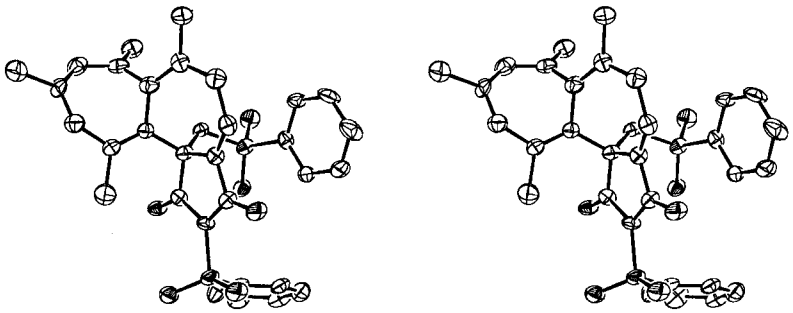


Fig. 1. *Stereoscopic view of the crystal structure of 5,11b-dihydro-3-hydroxy-6,7,9,11-tetramethyl-2-(phenylsulfonyl)-11b-[(phenylsulfonyl)methyl]cyclopenta[*a*]heptalen-1(1*H*)-one* (**9**) (H-atoms omitted)

The yield of benzo[*a*]heptalene **2b** could be still improved to up to 65% when **1′b** was treated with 6 mol-equiv. of $LiCH_2SO_2Ph$, followed by 6 mol-equiv. of BuLi (*cf. Scheme 6* and *Table 2*), whereas more than 6 mol-equiv. of $LiCH_2SO_2Ph$ and BuLi, or the substitution of BuLi by LDA, reduced the yield of **2b** (*cf. Table 2*)[6]). Important was the observation that under optimal conditions (*i.e.*, 6 mol-equiv. of nucleophile and base), compound **9** was recognizable only in traces. Moreover, when **9** was treated with 6 mol-equiv. of BuLi at $-10°$ to room temperature, to restore the optimal reaction conditions for the formation of **1′b**, benzo[*a*]heptalene **2b** was formed in over 60% isolated yield, indicating that compounds of type **9** may represent key intermediates in benzo[*a*]heptalene formation from heptalene-1,2- and heptalene-4,5-dicarboxylates and lithiated methyl sulfonyl compounds under strongly basic conditions. A possible route from **9** to **2b** is depicted in *Scheme 7*.

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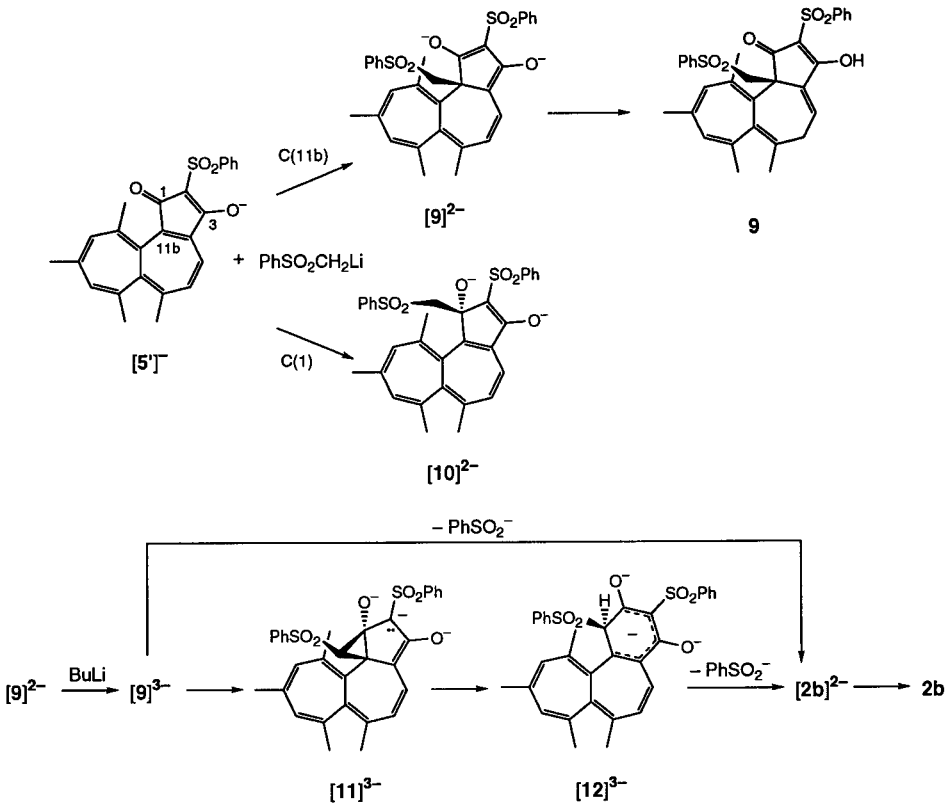
[6]) The quantity of BuLi also seems to play a role because runs of **1′b** with 4 mol-equiv. of $MeSO_2Ph$ and in total 8 mol-equiv. of BuLi gave yields of **2b** in the range of 24 to 50% (*cf. Exper. Part*).

Scheme 7



The precursor of **9** could be the anion $[\mathbf{5}']^-$ of the DBS isomer of **5** which should be present in the reaction mixture, because we started with **1′b**. Anions $[\mathbf{5}]^-$ and those of the same type (*cf.* [1]) do not form benzo[*a*]heptalene-2,4-diols when treated with lithiated methyl sulfonyl compounds, followed by BuLi, since the C=C bonds of the heptalene core are in unfavorable positions for a conjugative attack of lithiated sulfonyl compounds[7]). Their DBS isomers, such as $[\mathbf{5}']^-$, however, should behave like cyclopentadienones prone to conjugative attack at C(11b)[8]). Such an attack will lead to bisanions of type $[\mathbf{9}]^{2-}$ with an optimal conjugative stabilization of both negative charges. On the other hand, an attack on the formal carbonyl group C(1)=O will generate bisanions of type $[\mathbf{10}]^{2-}$ with much less stabilization of both negative charges. Bisanions of type $[\mathbf{9}]^{2-}$, once formed, can further be deprotonated by BuLi at the (sulfonyl)methylene group at C(11b) to give corresponding trisanions, *e.g.*, $[\mathbf{9}]^{3-}$, which

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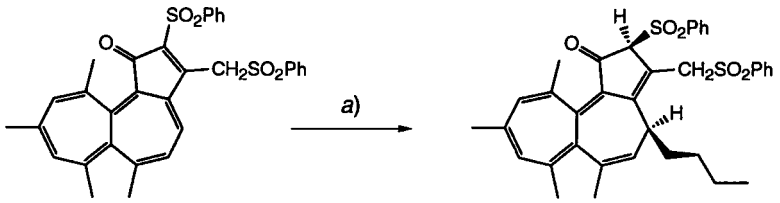
[7]) As we have already reported [6], five-ring-anellated heptalenes with two further *peri*-substituents undergo rapid thermal DBS already below 0°. This would explain why the benzo[*a*]heptalene-2,4-diol formation is also observed with heptalene-4,5-dicarboxylates such as **1a**, showing the 'wrong' starting position of the C=C bonds at the heptalene core (see *Scheme 1*).

[8]) For similar nucleophilic additions to tropone and tropolone derivatives, see [7].

may then rearrange under loss of phenyl sulfinate or equivalent sulfites (*cf.* [1]) to [**2b**]$^{2-}$ as depicted in *Scheme 7*. At the present stage of our investigations (*vide infra*), we favor a stepwise mechanism *via* trisanions such as [**12**]$^{3-}$ and [**13**]$^{3-}$ instead of a more or less one-step process *via* carbenoid transients as discussed in [1].

Another experiment taught us that cyclopenta[*d*]heptalen-1(1*H*)-ones, *i.e.*, the type of intermediates with the 'wrong' position of the core C=C bonds, may also react with nucleophiles in a *Michael*-type addition. When we examined the behavior of **6** under the conditions of benzo[*a*]heptalene formation with $LiCH_2SO_2Ph$ and BuLi, we observed the formation of a new compound in *ca.* 50% yield that crystallized from Et_2O/hexane as yellow needles (*Scheme 8*). An X-ray crystal-structure analysis (*Fig. 2*) showed that **6** had been attacked by BuLi at C(4) to form the adduct **13**.

Scheme 8



6 **13** (*ca.* 48%)

a) 1. 4.4 Mol-equiv. of $LiCH_2SO_2Ph$/THF, $-78 \rightarrow -20°$ (0.5 h), 2. 16 mol-equiv. of BuLi/THF, $-20° \rightarrow$ ambient temp. (1 h).

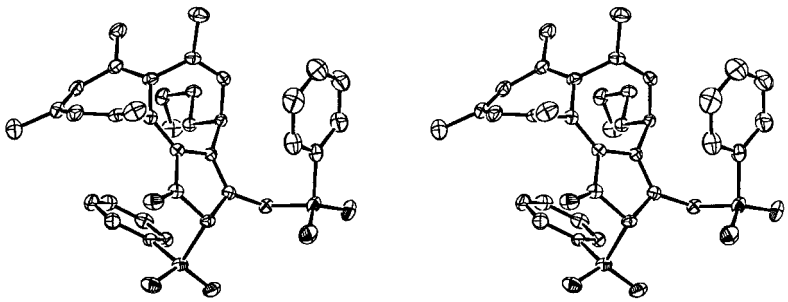
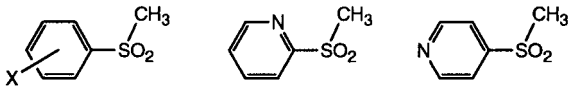


Fig. 2. *Stereoscopic view of the crystal structure of 4-butyl-2,4-dihydro-6,7,9,11-tetramethyl-2-(phenylsulfonyl)-3-[(phenylsulfonyl)methyl]cyclopenta[*a*]heptalen-1(1*H*)-one* (**13**) (H-atoms omitted)

To gain more insight into the electronic effects governing the formation of 3-(arylsulfonyl)benzo[*a*]heptalene-2,4-diols, we reacted heptalene-dicarboxylate **1′b** with a number of methyl X-phenyl sulfones as well as with methyl pyridyl sulfones (*Scheme 9*). The results are compiled in *Table 3*. The sulfones with π-donor and strong σ-acceptor substituents (Cl, MeO) gave moderate yields of the corresponding benzo[*a*]heptalene-2,4-diols, whereby the *o*-Cl substituent was partially replaced, under the standard reaction conditions, by an H-atom through Cl/Li exchange. Even complete metalation was found for the *p*-Br substituent. The yield of **2b** was thereby nearly as good as in the case with $MeSO_2Ph$ itself (*Table 3*). No benzo[*a*]heptalene

formation at all was observed with the sulfone carrying a CN group as a strong π- and σ-acceptor substituent, as well as with the two pyridyl sulfones. TLC Analyses indicated in all three cases that (sulfonyl)methylation had taken place at MeOCO–C(2) and also at both ester functions[9]). The reaction with lithiated methyl *p*-tolyl sulfone and BuLi gave again the corresponding benzo[*a*]heptalene-2,4-diol **2g** in a yield comparable to that with $MeSO_2Ph$. These results allow the assumption that the decisive step in benzo[*a*]heptalene-2,4-diol formation is the conjugative addition reaction of (X-sulfonyl)methanides to anions of type $[\mathbf{5}']^-$ with formation of bisanions of type $[\mathbf{9}]^{2-}$ which then undergo ring enlargement *via* corresponding trisanions, whereby the quality of the phenyl sulfinates (or dialkylamino sulfites [1]) as a leaving group is not critical (*cf. Scheme 7*). Therefore, the formation of carbenoids as transients should not play a role in the discussed reaction sequences to benzo[*a*]heptalene-2,4-diols.

Scheme 9



X=4-Br, 2-Cl, 4-Cl, 4-MeO, 4-CN, 4-Me

Table 3. *Formation of 3-(X-Phenylsulfonyl)benzo[*a*]heptalene-2,4-diols* **2** *from Heptalene-1,2-dicarboxylate* **1′b** *and Lithiated Methyl X-Phenyl Sulfones in the Presence of BuLi*

X in Sulfone	$LiCH_2SO_2C_6H_4X$[a]) [mol-equiv.]	BuLi[b]) [mol-equiv.]	Benzo[*a*]heptalene	
			No.	Yield [%]
H	4	4.5	**2b**	50[c])
H	6	6	**2b**	65[c])
4-Br	6	6	**2b**	56[d])
2-Cl	4	4[e])	**2c**	19[f])
4-Cl	6	6[e])	**2d**	53
4-MeO	4	4[g])	**2e**	30
4-CN	6	6	**2f**	–
4-Me	6	6	**2g**	67

[a]) Addition of **1′b** at $-78°$. [b]) Addition of BuLi at $-10°$ if not otherwise stated. [c]) See *Scheme 6*. [d]) The Br-substituted benzo[*a*]heptalene was not found in the reaction mixture. [e]) Addition of BuLi at $-15°$. [f]) 18% of **2b** was also formed. [g]) Addition of BuLi at $-5°$.

We thank Prof. *M. Hesse* and his co-workers for mass spectra, our NMR Laboratory for specific NMR measurements, and our Analytical Laboratory for elemental analyses. The financial support of this work by the *Swiss National Science Foundation* is gratefully aknowledged.

9) The chromatographic workup procedure showed, in the R_f region of benzo[*a*]heptalene-2,4-diols, other products in small amounts which were neither isolated nor investigated further.

Experimental Part

General. See [1].

1. Heptalene-dicarboxylates 1b and 1′b. 1.1. *Dimethyl 1,6,8,10-Tetramethylheptalene-4,5-dicarboxylate* (**1b**) (*cf.* [4]). *Improved Procedure*. 1,4,6,8-Tetramethylazulene (10.21 g, 55 mmol) and dimethyl acetylenedicarboxylate (20.4 ml = 23.38 g, 165 mmol) were heated in toluene (85 ml) in a closed 150-ml *Schlenk* vessel at 130° for 24 h. The usual workup gave a dark oil that was subjected to CC (silica gel (400 g); hexane/Et_2O 3 : 1). The first yellow-colored fraction yielded, after recrystallization (Et_2O/hexane), pure **1b** (8.42 g, 47%) with m.p. 141° ([4]: 124–125°; [3]: 130°). A second yellow-colored fraction gave, after recrystallization (hexane/Et_2O), pure **1′b** (0.76 g, 4%, see *1.2*). Finally, the blue fraction containing dimethyl 4,6,8-trimethylazulene-1,2-dicarboxylate (4.30 g, 27%; [4]: 39%) was obtained; m.p. 139–140° ([4]: 141–142°).

1.2. *Dimethyl 5,6,8,10-Tetramethylheptalene-1,2-dicarboxylate* (**1′b**) (*cf.* [2]). Pure **1b** (2.00 g, 6.13 mmol) was dissolved in MeCN (650 ml) and irradiated with a Hg high-pressure lamp (150 W) at 17–21°. TLC showed after 3 h the establishment of a photostationary mixture of **1b** and **1′b** (R_f (hexane/Et_2O 1 : 1) 0.42 (**1b**) and 0.57 (**1′b**)). After removal of MeCN, ^{1}H-NMR indicated a composition of 52% of **1b** and 48% of **1′b**. Most of **1b** (0.878 g, 44%) could be removed by crystallization from Et_2O/hexane. The residue of the mother liquor was subjected to CC (silica gel (260 g); hexane/Et_2O 4 : 1) to give pure **1′b** (0.941 g, 47%) and the residual amount of **1b** (0.158 g, 8%). Compound **1′b** was recrystallized from Et_2O/hexane. Orange crystals. M.p. 89–90° ([2]: 91–92°; [3]: 89–91°).

2. Reaction of 1′b with $LiCH_2SO_2Ph$. 2.1. *Formation of Methyl 5,6,8,10-Tetramethyl-2-[(phenylsulfonyl) acetyl]heptalene-1-carboxylate* (**4′**). $MeSO_2Ph$ (0.479 g, 3.07 mmol) was dissolved in freshly distilled THF (20 ml). At −20°, a 1.6M BuLi soln. (2.0 ml, 3.20 mmol) was added dropwise, whereby the temp. raised to −11°. The mixture was stirred for 0.5 h at 0° to complete the lithiation reaction which was accompanied by formation of a colorless, finely dispersed precipitate. After cooling to −78°, a soln. of **1′b** (0.334 g, 1.02 mmol) in THF (5 ml) was added dropwise within 5 min. Stirring was continued for 10 min, and the mixture was poured onto ice. After neutralization with 4N aq. HCl, the org. layer was extracted with Et_2O and washed with a $NaHCO_3$ soln., followed by sat. NaCl soln. After drying ($MgSO_4$), the solvent was distilled off and the residue chromatographed (silica gel (100 g); hexane/Et_2O 1 : 1) to give **4′** (0.382 g, 83%) and its DBS isomer **4** (0.070 g, 15%) (see *Footnote 2* and *2.1.3*). In addition, $MeSO_2Ph$ (0.297 g, 1.90 mmol = 93% of the excess amount) was recovered. Elution of the silica gel column with AcOEt gave a small amount (4.5 mg, 1%) of *3-hydroxy-6,7,9,11-tetramethyl-2-(phenylsulfonyl)cyclopenta[*d*]heptalen-1(1*H*)-one* (**5**; see *2.1.1* as well as *2.1.2*).

Data of **4′**: Yellow crystals. M.p. 111–113°. R_f (hexane/AcOEt 2 : 1) 0.56. IR (KBr): 3060*w*, 2923*s*, 2854*m*, 1756v*s* (C=O), 1723v*s* (C=O), 1659*s*, 1598*m*, 1583*m*, 1563*m*, 1510*m*, 1446*s*, 1378*m*, 1310v*s*, 1267v*s*, 1247*s*, 1216*s*, 1193*s*, 1151v*s*, 1083v*s*, 1024*s*, 980*s*, 949*s*, 924*s*, 891*m*, 869*m*, 841*m*, 804*s*, 782*s*, 766*s*, 745*s*, 690v*s*, 666*m*, 620*w*, 591*m*, 573*m*, 561*s*, 538*s*, 527v*s*, 478*m*. ^{1}H-NMR (300 MHz, $CDCl_3$/(D_8)toluene): 7.98–7.95/7.71 (*m*/*dt*, 2 arom. H, 2 *o*-H of Ph); 7.69–7.55/6.90–6.80 (*m*, 3 arom. H); 6.64 and 6.36/6.49 and 6.24 (*AB*, J_{AB} = 11.7, H–C(3,4)); 6.11/5.91 (br. *s*, H–C(9)); 6.03/5.74 (br. *s*, H–C(7)); 4.59 and 4.56/4.41 and 4.39 (*AB*, J_{AB} = 14.7/14.9, CH_2); 3.63/3.13 (*s*, MeOCO–C(1)); 2.00/1.82 (*d*, ^4J = 1.0, Me–C(6)); 1.98/1.73 (*d*, ^4J = 1.2, Me–C(8)); 1.79/1.50 (*s*, Me–C(5)); 1.59/1.49 (*s*, Me–C(10)). ^{13}C-NMR (75 MHz, $CDCl_3$): 192.78 (*s*, O=*C*–C(2)); 166.44 (*s*, O=*C*–C(1)); 154.61 (*s*, C(10a)); 150.13 (*s*, C(5)); 141.66 (*d*, C(3)); 140.35 (*s*, C(8)); 139.46 (*s*, C(2)); 139.26 (*s*, 1 C of Ph); 134.03 (*d*, 1 C of Ph); 132.93 (*s*, C(6)); 132.58 (*s*, C(10)); 130.22 (*d*, C(7)); 129.92 (*d*, C(9)); 129.13 (*d*, 2 C of Ph); 128.56 (*d*, 2 C of Ph); 124.86 (*d*, C(4)); 122.26 (*s*, C(5a)); 121.42 (*s*, C(1)); 66.62 (*t*, CH_2); 52.67 (*q*, *Me*OCO–C(1)); 25.12 (*q*, Me–C(8)); 22.44 (*q*, Me–C(10)); 17.80 (*q*, Me–C(5)); 17.08 (*q*, Me–C(6)). CI-MS: 468 (100, $[M+NH_4]^+$), 451 (17, $[M+H]^+$), 419 (41, $[M-MeOH]^+$), 174 (28). Anal. calc. for $C_{26}H_{26}O_5S$ (450.55): C 69.31, H 5.82; found: C 69.20, H 5.69.

Data of **4**: Yellow crystals. M.p. 193–196°. R_f (hexane/AcOEt) 0.30. IR (KBr): 2989*m*, 2940*m*, 1746v*s* (C=O), 1723v*s* (C=O), 1662*s*, 1620*w*, 1563*m*, 1531*w*, 1446*s*, 1429*s*, 1384*w*, 1371*m*, 1321*s*, 1310v*s*, 1267v*s*, 1244v*s*, 1219*s*, 1207*s*, 1194*s*, 1155v*s*, 1114*m*, 1098*m*, 1086*s*, 1070*s*, 1014*m*, 981*m*, 860*w*, 840*m*, 805*s*, 786*m*, 763*m*, 733*s*, 718*w*, 690*s*, 604*w*, 592*m*, 528*s*. ^{1}H-NMR (300 MHz, $CDCl_3$/(D_8)toluene: 7.91–7.87/7.65 (*m*/*dt*, 2 arom. H, 2 *o*-H of Ph); 7.66–7.48/6.90–6.80 (*m*, 3 arom. H/H–C(3)); 7.31/– (*dd*, ^3J = 5.9, ^5J = 0.9, H–C(3)); 6.29/5.81 (*dd*, ^3J = 5.9, ^4J = 1.4, H–C(2)); 6.13/5.86 (br. *s*, H–C(9)); 5.99/5.73 (br. *quint.*-like, ^4J = 1.1, H–C(7)); 4.48 and 4.44/3.89 and 3.83 (*AB*, $^2J_{AB}$ = 14.5, CH_2); 3.57/3.30 (*s*, MeOCO–C(5)); 2.03/1.89 (*d*, ^4J = 1.3/1.2, Me–C(1)); 2.02 (*d*, ^4J = 1.2/1.1, Me–C(8)); 1.94/1.69 (*d*, ^4J = 1.2/1.1, Me–C(6)); 1.75/1.50 (*s*, Me–C(10)). ^{1}H-NMR (600 MHz, (D_6)DMSO): 7.87 (*d*, ^3J = 7.4, 2 arom. H); 7.72 (*t*, ^3J = 7.4, 1 arom. H); 7.62 (*t*, ^3J = 7.8, 2 arom. H); 7.51 (*d*, ^3J = 5.8, H–C(3)); 6.37 (*dd*, ^3J = 5.9, ^4J = 1.1, H–C(4)); 6.14 (*s*, H–C(9)); 5.98 (*s*, H–C(7)); 5.12 and 5.08 (*AB*, $^2J_{AB}$ = 15.4, CH_2); 3.39 (*s*, MeOCO–C(5); 1.98 (*s*, Me–C(1)); 1.97 (*s*, Me–C(8)); 1.84 (*s*, Me–C(6)); 1.68

(*s*, Me–C(10)). ^{13}C-NMR (75 MHz, $CDCl_3$): 188.22 (*s*, O=*C*–C(4)); 167.15 (*s*, MeO*C*O–C(5)); 147.67 (*s*, C(5a)); 145.84 (*s*, C(1)); 141.70 (*d*, C(3)); 139.83 (*s*, C(8)); 139.47 (*s*, C(4)); 138.90 (*s*, 1 C of Ph); 133.92 (*d*, 1 C of Ph); 130.83 (*s*, C(10)); 130.31 (*s*, C(6)); 130.04 (*d*, C(9)); 129.01 (*d*, C(7) and 2 C of Ph); 128.67 (*d*, 2 C of Ph); 125.74 (*d*, C(2)); 124.94 (*s*, C(10a)); 121.44 (*s*, C(5)); 63.14 (*t*, CH_2); 51.87 (*q*, *Me*OCO–(5)); 25.01 (*q*, Me–C(8)); 23.74 (*q*, Me–C(6)); 21.90 (*q*, Me–C(1)); 18.48 (*q*, Me–C(10)): EI-MS: 451(27), 450 (100, $M^{+\bullet}$), 309 (26, $[M-PhSO_2]^+$), 277 (20, $[M-(PhSO_2+MeOH)]^+$), 267(11), 262(10), 235(15), 207(15), 185(10), 184(77), 125(25). Anal. calc. for $C_{26}H_{26}O_5S$ (450.55): C 69.31, H 5.82; found: C 69.25; H 5.60.

The results of a number of runs with varying mol-equiv. of $LiCH_2SO_2Ph$ and **1′b** are collected in *Table 1*.

2.1.1. *Transformation of* **4′** *into* **5**. $MeSO_2Ph$ (0.061 g, 0.39 mmol) was lithiated with 1.6M BuLi soln. (0.25 ml, 0.40 mmol) as described above. At −30°, ester **4′** (0.120 g, 0.27 mmol) in THF was added dropwise. After 5 h, mainly **4′** was still present. However, after 3 d, TLC showed that all **4′** had been consumed, and **5** was the main product. After usual workup, the residue was chromatographed (silica gel (80 g); hexane/Et_2O 1:1) leading to a fraction (0.071 g) which contained mainly $MeSO_2Ph$ beside small amounts of **4′**, **4**, and **6** (see *2.2*). Elution of the silica gel column with AcOEt gave pure **5** (0.101 g, 93%).

Data of **5**: Yellow crystal powder. M.p. 188.3–189.1° (AcOEt/hexane). R_f (CH_2Cl_2/MeOH 9:1) 0.59. IR (KBr): 3421*w*, 3059*w*, 2942*w*, 2911*w*, 2855*w*, 1644*m*, 1621*m*, 1604*s*, 1595*s*, 1547v*s*, 1480*w*, 1446*m*, 1347v*s*, 1283*s*, 1253*m*, 1181*w*, 1140*s*, 1082*m*, 1044*w*, 1026*w*, 999*w*, 925*w*, 904*w*, 854*m*, 841*w*, 813*w*, 787*w*, 760*m*, 728*m*, 711*w*, 683*m*, 652*w*, 612*m*, 601*m*, 551*m*, 505*w*. ^{1}H-NMR (600 MHz, (D_6)DMSO): 7.87–7.85 (*m*, 2 arom. H); 7.48–7.42 (*m*, 3 arom. H); 6.55 (*d*, ^3J = 6.3, H–C(4)); 6.29 (*dd*, ^3J = 6.3, ^4J = 1.4, H–C(5)); 5.99 (*s*, H–C(8)); 5.93 (*s*, H–C(10)); 2.09 (*s*, Me–C(11)); 1.92 (*s*, Me–C(6)); 1.90 (*s*, Me–C(9)); 1.64 (*s*, Me–C(7)). ^{13}C-NMR (150 MHz, (D_6)DMSO): 183.53 (*s*, C(3)); 181.30 (*s*, C(1)); 145.92 (*s*, 1 C of Ph); 138.70 (*s*, C(3a)); 138.18 (*s*, C(9)); 134.38 (*s*, C(11)); 133.74 (*s*, C(6)); 133.24 (*s*, C(11a)); 131.10 (*d*, 1 C of Ph); 130.05 (*d*, C(8)); 129.54 (*s*, C(11b)); 129.25 (*s*, C(7)); 128.51 (*d*, C(10)); 128.10 (*d*, 2 C of Ph); 127.99 (*s*, C(6a)); 126.30 (*d*, C(5)); 125.82 (*d*, 2 C of Ph); 121.53 (*d*, C(4)); 106.36 (*s*, C(2)); 24.67 (*q*, Me–C(9)); 24.42 (*q*, Me–C(11)); 23.02 (*q*, Me–C(6)); 18.02 (*q*, Me–C(7)). EI-MS: 419 (29, $[M+1]^+$), 417 (100, $[M-1]^+$), 399(24), 377(15), 363(20), 276(43).

2.1.2. *Transformation of* **4** *into* **5**. To a soln. of KOH in MeOH (0.10 g, 1.8 mmol/5 ml) was added **4** (0.10 g, 0.22 mmol) at r.t. After stirring for 30 min, the mixture was poured into ice-water and brought to pH 1 with 20% aq. H_2SO_4. The yellow precipitate was extracted with AcOEt (5 × 20 ml) and the combined extracts washed with brine (50 ml) and dried ($MgSO_4$). The residue of the extracts was recrystallized from CH_2Cl_2/hexane to give pure **5** (0.085 g, 92%) as yellow crystals.

2.1.3. *Equilibrium Mixture of* **4**/**4′** *at 100° in (D$_8$)Toluene.* Yellow crystals of **4** (0.010 g) were dissolved in (D_8)toluene (0.4 ml). ^{1}H-NMR (300 MHz) indicated the presence of *ca.* 3% of **4′**. Irradiation of the soln. with a Hg high-pressure lamp (150 W) for 15 min within the NMR tube resulted in a photostationary state consisting of 23% of **4** and 77% of **4′** (^{1}H-NMR). Heating of this mixture for 2 h at 100° in the NMR tube gave a mixture of 84% of **4** and 16% of **4′**. Additional heating for 2 h at 100° changed the composition only slightly: 88% of **4** and 12% of **4′** (^{1}H-NMR).

2.2. *Formation of 2,3-Dihydro-6,7,9,11-tetramethyl-2-(phenylsulfonyl)-3-[(phenylsulfonyl)methyl]cyclopenta[*d*]heptalen-1(1*H*)-one* (**6**). Lithiation of $MeSO_2Ph$ (0.746 g, 4.84 mmol) was performed, as described, above with 1.6M BuLi (3.1 ml, 4.96 mmol). At −78°, a soln. of **1′b** (0.395 g, 1.21 mmol) in THF (5 ml) was added dropwise. After additional stirring at −78° for 1 h, the temp. was raised within 1 h to −40°. At this stage, TLC showed that all **1′b** had been consumed by formation of **4′** and small amounts of **5**. At temp. > −40°, the formation of two new products, presumably **8′a** and **8′b**, with R_f (hexane/AcOEt 2:1) 0.24 and 0.17 was observed by TLC. The color of their spots on the TLC plate (silica gel) changed in the air after some time from pale-yellow to red. After 3 h, the temp. had slowly increased to 0°, the mixture was poured onto ice. Usual workup and chromatography (silica gel (120 g); hexane/Et_2O 1:1) gave **4′** (0.176 g, 32%), followed by **6** (0.383 g, 57%). Elution of the silica-gel column with AcOEt resulted in the isolation of small amounts of **5** (0.040 g, 8%).

Data of **6**: Yellow crystals. M.p. 259°. R_f (hexane/AcOEt 2:1) 0.33. IR ($CHCl_3$): 3691*w*, 3605*w*, 3030*m*, 2979*m*, 2950*w*, 2916*w*, 1690v*s* (C=O), 1635*m*, 1584*s*, 1547v*s*, 1480*w*, 1448*s*, 1414*w*, 1388*m*, 1372*m*, 1324v*s*, 1178*s*, 1153v*s*, 1086*s*, 1073*s*, 1047*w*, 1025*m*, 999*w*, 902*w*, 869*w*, 844*w*, 686v*s*, 616*m*, 603v*s*, 573v*s*, 562*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 8.25 (*d*, ^3J = 7.6, 2 arom. H); 8.06 (*d*, ^3J = 7.6, 2 arom. H); 7.68 (*dd*, ^3J = 7.6, 1 arom. H); 7.60–7.56 (*m*, 3 arom. H); 7.52 (*dd*, ^3J = 7.8, 2 arom. H); 6.92 (*d*, ^3J = 6.7, H–C(4)); 6.36 (*dd*, ^3J = 6.6, ^4J = 1.3, H–C(5)); 6.20 (br. *s*, H–C(10)); 6.16 (br. *s*, H–C(8)); 5.26, 5.07 (*AB*, $^2J_{AB}$ = 12.6, CH_2); 2.12 (*s*, Me–C(11)); 2.02 (*s*, Me–C(6)); 2.00 (*s*, Me–C(9)); 1.85 (*s*, Me–C(7)). ^{13}C-NMR (150 MHz, $CDCl_3$): 181.45 (*s*, O=C(1)); 153.69 (*s*, C(2)); 145.38 (*s*, C(11a)); 140.28 (*s*, (C(9)); 140.19, 139.56 (2*s*, 2 C of 2 Ph); 139.56 (*s*, C(6)); 137.42 (*s*, C(11b)); 137.37 (*s*, C(3a)); 134.24, 133.68 (2*d*, 2 C of 2 Ph); 133.09 (*s*, C(7)); 132.17 (*s*, C(11)); 131.32

(*d*, C(4)); 130.63 (*d*, C(8)); 130.39 (*d*, C(10)); 129.41, 129.25, 128.65, 128.45 (4*d*, 8 C of 2 Ph); 126.92 (*d*, C(5)); 126.00 (*s*, C(6a)); 124.57 (*s*, C(3)); 52.51 (*t*, CH_2); 25.01 (*q*, Me–C(11)); 24.20 (*q*, Me–C(6)); 23.64 (*q*, Me–C(9)); 19.88 (*q*, Me–C(7)). EI-MS: 557(19), 556 (49, $M^{+\cdot}$), 417(12), 416(32), 415 (100, $[M-PhSO_2]^+$), 275(35), 260(11), 259(19), 216(11), 215(17), 77 (18, $[Ph]^+$). Anal. calc. for $C_{32}H_{28}O_5S_2$ (556.70): C 69.04, H 5.07, S 11.52; found: C 68.71, H 5.08, S 11.25.

2.2.1. *Formation of 4-Butyl-2,4-dihydro-6,7,9,11-tetramethyl-2-(phenylsulfonyl)-3-[(phenylsulfonyl)methyl]cyclopenta[a]heptalen-1(1*H*)-one* (**13**) *from* **6** *in the Presence of BuLi.* $MeSO_2Ph$ (0.034 g, 0.22 mmol) was lithiated in THF as described above. At −78°, **6** (0.028 g, 0.05 mmol) was added. After 30 min stirring at −20°, 1.6M BuLi soln. (0.5 ml, 0.80 mmol) was added, followed by 1 h stirring at ambient temp. Usual workup, followed by chromatography (silica gel (30 g); hexane/Et_2O 2 : 1), led to a mixture (0.064 g) of $MeSO_2Ph$ and **13** with a content of *ca.* 25% of the latter. The mixture was chromatographed anew, and **13** was further purified by recrystallization from Et_2O/hexane (0.015 g, 48%).

Data of **13**: Yellow needles. M.p. 231°. R_f (AcOEt/hexane 1:2) 0.38. IR (KBr): 3407*w*, 3059*w*, 2961*m*, 2923*m*, 2857*w*, 1711v*s* (C=O), 1627*w*, 1570*s*, 1462*w*, 1446*s*, 1404*w*, 1378*w*, 1308v*s*, 1242*m*, 1187*s*, 1146v*s*, 1132*s*, 1082*s*, 1023*w*, 999*w*, 938*w*, 885*w*, 843*m*, 809*w*, 774*m*, 762*m*, 739*w*, 714*w*, 704*m*, 687*s*, 645*w*, 622*w*, 596*m*, 552*s*, 522*w*, 510*w*, 498*w*, 453*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.97–7.95 (*m*, 2 arom. H); 7.72 (*t*, $^3J = 7.5$, 1 arom. H); 7.62 (*t*, $^3J = 7.8$, 2 arom. H); 7.55–7.53 (*m*, 2 arom. H); 7.50–7.47 (*m*, 1 arom. H); 7.29–7.27 (*m*, 3 arom. H); 6.18 (*s*, H–C(10)); 6.08 (*s*, H–C(8)); 5.46 (*dd*, $^3J = 8.3$, $^4J = 1.2$, H–C(5)); 4.94, 4.18 (*AB*, $^2J_{AB} = 14.1$, $PhSO_2CH_2$); 4.50 (*s*, H–C(2)); 3.27–3.22 (*m*, H–C(4)); 2.11 (*s*, Me–C(11)); 2.10 (*s*, Me–C(9)); 1.89 (*s*, Me–C(7)); 1.70 (*d*, $^4J = 1.2$, Me–C(6)); 1.35–1.15 (*m*, 5 H of Bu); 0.89 (*t*, $^3J = 6.9$, Me of Bu); 0.78–0.72 (*m*, 1 H of Bu). ^{13}C-NMR (150 MHz, $CDCl_3$): 190.05 (*s*, C=O); 154.67 (*s*, C(3a)); 146.93 (*s*, C(11a)); 139.44 (*s*, 1 C-atom of Ph); 139.29 (*s*, C(6)); 138.69 (*d*, C(9)); 136.52 (*s*, 1 C of Ph); 134.07 (*d*, 1 C of Ph); 133.58 (*d*, 1 C of Ph); 132.37 (*d*, C(7)); 132.32 (*s*, C(11a)); 129.40 (*d*, 2 C of Ph); 129.34 (*d*, C(8)); 129.32 (*s*, C(6a)); 129.20 (*d*, 2 C of Ph); 128.52 (*d*, 2 C of Ph); 128.31 (*d*, 2 C of Ph); 127.80 (*s*, C(11b)); 127.04 (*s*, C(10)); 126.27 (*d*, C(5)); 115.73 (*s*, C(11)); 73.91 (*d*, C(2)); 54.05 (*s*, C(3)); 36.92 (*d*, C(4)); 33.27 (*t*, $PhSO_2CH_2$); 30.01 (*t*, $MeCH_2(CH_2)_2$); 24.60 (*q*, Me–C(9)); 23.35 (*q*, Me–C(11)); 23.30 (*q*, Me–C(6)); 22.77 (*t*, $MeCH_2(CH_2)_2$); 20.90 (*q*, Me–C(7)); 14.00 (*q*, $MeCH_2(CH_2)_2$). Anal. calc. for $C_{36}H_{38}O_5S_2$ (614.82): C 70.33, H 6.23; found: C 70.38, H 6.18.

The structure of **13** was finally established by an X-ray crystal-structure analysis (see *Fig. 2* as well as *Sect. 4*).

2.3. *Formation of 7,8,10,12-Tetramethyl-3-(phenylsulfonyl)benzo[a]heptalene-2,4-diol* (**2b**) *and 5,11b-Dihydro-3-hydroxy-6,7,9,11-tetramethyl-2-(phenylsulfonyl)-11b-[(phenylsulfonyl)methyl]cyclopenta[a]heptalen-1(1*H*)-one* (**9**). $MeSO_2Ph$ (0.681 g, 4.36 mmol) in THF (20 ml) was lithiated at −10° with 1.6M BuLi (2.7 ml, 4.36 mmol) and stirred for 0.5 h. Then, at −78°, a soln. of **1′b** (0.356 g, 1.09 mmol) was added dropwise. After 1 h stirring at −78°, the temp. was raised within 1.5 h to −10°. TLC control showed that all **1′b** as well as its monosubstitution product **4′** had been consumed. Further 1.6M BuLi (2.7 ml, 4.36 mmol) was added within 5 min whereby the color of the mixture changed from orange *via* dark-red to dark-yellow. Cooling was removed, and the mixture stirred for 15 h at r.t. Usual workup led to a residue that was chromatographed (silica gel (120 g); hexane/Et_2O 2 : 1). The first fraction delivered **2b** (0.235 g, 50%) as yellow crystals. A second fraction (0.314 g, *ca.* 44%) contained **9**, which was recrystallized from CH_2Cl_2/Et_2O/hexane to give **9** as yellow prisms which readily lost solvent molecules on standing in the air and changed to a beige-colored powder (*cf. Footnote 5*).

Data of **2b**. Yellow crystals. M.p. 203–204° ([1]: 198–199°). For all other spectral data, see [1] as well as *Tables 4–6*. Anal. calc. for $C_{26}H_{24}O_4S$ (432.54): C 72.20, H 5.59; found: C 72.19, H 5.85.

Data of **9**: Yellow prisms. M.p. 271° (dec.); R_f (CH_2Cl_2/MeOH 9 : 1) 0.66. IR (KBr): 3240*w*, 3061*w*, 2922*m*, 2855*m*, 1703*s*, 1670*m*, 1625*w*, 1584*m*, 1548v*s*, 1447*s*, 1388*m*, 1307v*s*, 1266*s*, 1212*s*, 1144v*s*, 1085*s*, 1024*m*, 998*w*, 844*m*, 831*w*, 784*m*, 739*s*, 720*s*, 687*s*, 610*m*, 598*s*, 579*s*, 556*s*, 526*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.12 (*d*, $J_o = 7.4$, 2 arom. H); 7.65–7.45 (*m*, 8 arom. H); 6.50 (br. *s*, H–C(4)); 5.84 (*s*, H–C(10)); 5.72 (*s*, H–C(8)); 4.21 (br. *d*, $J_{AB} = 14.3$, *A* of *AB*; $PhSO_2CH_2$); 3.69 (*d*, $J_{AB} = 14.3$, *B* of *AB*, $PhSO_2H_2$); 3.10 (*dd*, $J_{gem} = 25.4$, $J_{vic} = 5.4$, 1 H of CH_2(5)); 2.73 (br. *d*, $J_{gem} = 25.5$, 1 H of CH_2(5)); 1.95 (br. *s*, Me–C(7)); 1.84 (br. *s*, Me–C(9)); 1.56 (*s*, Me–C(11)); 1.30 (very br. *s*, Me–C(6)). The broadened signals of atoms or groups at or around C(5) indicate that a slow inversion of the boat conformation of ring B (see *Fig. 1* as well as *Sect. 4*) takes place in soln. at 30°. ^{13}C-NMR (75 MHz, $CDCl_3$): 180.09 (C(1)=O); 140.56–125.70 ($C(sp^2)$; 17 signals of 20 are registered); 63.78 ($PhSO_2CH_2$); 55.69 (C(11b)); 24.46, 21.71, 19.93 (Me–C(7,9,11)); 21.40 (br., Me–C(6)). EI-MS: 574 (16, $M^{+\cdot}$), 434(21), 433 (71, $[M-PhSO_2]^+$), 432(24), 419 (22, $[M-PhSO_2CH_2]^+$), 418(17), 417(57), 405(16), 403(24), 292(18), 291 (60, $[M-2\,PhSO_2]^{+\cdot}$), 277 (11, $[M-(PhSO_2+PhSO_2CH_2)]^{+\cdot}$), 276(11), 275(11), 265(35), 263 (11, $[M-2\,PhSO_2CH_2]^{+\cdot}$), 261(12), 249(14), 207(18), 193(11), 189(10), 184(27),

Table 4. *UV Spectra* (EtOH) *of 3-(X-Phenylsulfonyl)benzo[*a*]heptalene-2,4-diols* **2**

Heptalene	λ_{max} [nm] (log ε)					λ_{min} [nm] (log ε)[a])			
2a	218 (4.50)	245 (4.41)	263 (4.45)	313 (4.03)	344 (sh, 3.74)	206 (4.46)	233 (4.39)	249 (4.41)	302 (4.01)
2b	219 (4.46)	239 (4.40)	259 (4.44)	310 (4.08)	354 (sh, 3.52)	206 (4.40)	233 (4.39)	246 (4.39)	296 (4.04)
2c	221 (4.54)	242 (4.38)	261 (4.45)	310 (4.12)	341 (sh, 3.73)	212 (4.51)	237 (4.39)	245 (4.38)	296 (4.07)
					378 (sh, 3.29)				
2d	224 (4.48)	246 (4.32)	260 (4.45)	310 (4.07)	348 (sh, 3.61)	*209 (4.29)*	239 (4.41)	248 (4.32)	297 (4.04)
2e	227 (4.46)	250 (4.49)	263 (4.50)	309 (4.13)	346 (sh, 3.71)	*209 (4.29)*	237 (4.42)	254 (4.49)	299 (4.11)
			273 (sh, 4.47)						
2g	223 (4.45)	242 (4.42)	260 (4.45)	310 (4.09)	346 (sh, 3.62)	209 (4.39)	234 (4.41)	249 (4.41)	297 (4.04)
2h[b])	219 (4.50)	–	259 (4.47)	317 (4.11)	346 (sh, 3.78)	208 (4.46)	239 (4.41)	–	298 (4.01)

[a]) Values given in italics are estimated. [b]) 8,10,12-Trimethyl derivative [1].

Table 5. *^{1}H-NMR Shifts* (δ [ppm]) *of 3-(X-Phenylsulfonyl)benzo[*a*]heptalene-2,4-diols* **2**[a])

H-Atom	**2b**	**2c**	**2d**	**2e**	**2g**
H–C(1)	6.18	6.16	6.16	6.18	6.17
HO–C(2)	8.65	8.19	8.65	8.68	8.67
HO–C(4)	9.24	8.69	9.25	9.30	9.26
H–C(5)[b])	7.02	6.98	7.02	7.05	7.03
H–C(6)[b])	6.21	6.21	6.21	6.20	6.20
H–C(9)	5.99	6.00	5.99	5.99	5.99
H–C(11)	6.13	6.13	6.12	6.12	6.12
Me–C(7)	1.70	1.71	1.70	1.69	1.70
Me–C(8)[c])	1.89	1.91	1.89	1.87	1.89
Me–C(10)[d])	2.00	2.01	2.00	1.99	2.00
Me–C(12)	1.63	1.64	1.63	1.63	1.63
X-Ph[e])					
H–C(2,6)	7.96	8.24 (6)	7.91	7.87	7.86
H–C(3,5)	7.7–7.5	7.52 (3); 7.50 (5)	7.50	6.92	7.34
H–C(4)	7.7–7.5	7.58	–	–	–
R	–	–	–	3.80	2.43

[a]) Spectra in $CDCl_3$ at 300 or 600 MHz; C*H*Cl_3 at 7.26 ppm. [b]) *AB* System with $J_{AB} = 11.9–12.0$ Hz. [c]) *d* with $^4J = 0.8–1.2$ Hz. [d]) *d* with $^4J = 1.1–1.2$ Hz. [e]) $J_o = 7.5–8.0$, $J_m = 1.5–1.6$ (**2c**), $J_p \approx 0.8$ Hz (**2c**).

183 (19), 169 (16), 165 (13), 142 (33), 141 (14, $[PhSO_2]^+$), 125 (20), 94 (15), 78 (36), 77 (100, $[Ph]^+$), 57 (13), 51 (28), 43 (10).

The structure of compound **9** was further established by an X-ray crystal-structure analysis (see *Fig. 1* as well as *Sect. 4*).

2.3.1. *Optimized Formation of* **2b**. A repetition of the reaction described in *2.3*, however, applying 6 mol-equiv. of $LiCH_2SO_2Ph$ upon **1′b** (0.356 g, 1.09 mmol), followed by further 6 mol-equiv. of 2.5M BuLi at $-10°$, resulted in the formation of 65% of **2b** and only traces of **9**. For further runs with **1′b**, see *Table 2*.

2.3.2. *Rearrangement of* **9** *into* **2b**. 2.5M BuLi (0.042 ml, 0.104 mmol) was added to a soln. of **9** (0.010 g, 0.0174 mmol) in THF (5 ml) at $-10°$. The mixture was allowed to warm up to ambient temp. within 20 min. Stirring at r.t. was continued for 30 min. Usual workup led to 4.6 mg (61%) of pure **2b**.

3. Reaction of 1′b with Lithiomethyl X-Phenyl Sulfones. – 3.1. *4-Bromophenyl Methyl Sulfone.* The sulfone (0.897 g, 3.81 mmol) was lithiated with 2.5M BuLi (1.7 ml, 4.25 mmol) in THF in the usual manner. Heptalene-1,2-dicarboxylate **1′b** (0.203 g, 0.62 mmol) was added at $-78°$. At $-10°$, additional 2.5M BuLi (1.7 ml, 4.25 mmol) was added. Finally, **2b** (0.151 g, 56%) was isolated.

3.2. *2-Chlorophenyl Methyl Sulfone.* The sulfone (m.p. 90–91°; 0.726 g, 3.81 mmol), prepared together with 4-chlorophenyl methyl sulfone according to [8], was lithiated with 1.6M BuLi (2.7 ml, 4.28 mmol) and further reacted with **1′b** (0.311 g, 0.95 mmol), followed by addition of 1.6M BuLi (2.7 ml, 4.28 mmol) at $-10°$.

Table 6. *^{13}C-NMR Data of 3-(X-Phenylsulfonyl)benzo[a]heptalene-2,4-diols* **2**[a])

C-Atoms	**2b**	**2c**	**2d**	**2e**	**2g**
C(1)	109.06	108.87	108.97	108.82	108.97
C(2)	156.38	157.36	156.26	156.03	156.28
C(3)	107.70	106.44	107.59	108.66	108.17
C(4)	153.36	154.12	153.39	153.00	153.25
C(4a)	119.55	119.39	119.63	119.38	119.47
C(5)	124.85	124.61	124.73	124.92	124.92
C(6)	132.27	132.32	132.39	132.07	132.16
C(7)	127.81	127.81	127.82	127.68	127.76
C(7a)	136.12	136.15	136.10	136.00	136.07
C(8)	134.31	134.32	134.21	134.13	134.24
C(9)	128.56	128.56	128.57	128.49	128.53
C(10)	139.02	139.04	139.05	138.82	138.94
C(11)	130.35	130.35	130.32	130.32	130.36
C(12)	130.76	130.75	130.76	130.59	130.68
C(12a)	129.59	129.41	129.32	129.41	129.47
C(12b)	146.93	147.28	147.06	146.37	146.68
Me–C(7)	17.87	17.89	17.85	17.80	17.86
Me–C(8)	22.78	22.79	22.75	22.69	22.76
Me–C(10)	25.01	25.01	24.99	24.92	24.99
Me–C(12)	19.30	19.30	19.27	19.22	19.29
X-Phenyl					
C(1)	141.28	138.28	139.74	132.57	138.36
C(2)	126.21	133.48	127.82	128.49	126.27
C(3)	129.59	132.43	129.79	114.63	130.16
C(4)	134.31	134.93	140.99	164.15	145.55
C(5)	129.59	127.13	129.79	114.63	130.16
C(6)	126.21	130.54	127.82	128.49	126.27
R	–	–	–	55.68	21.65

[a]) Spectra in $CDCl_3$ at 75.5 MHz, *C*DCl_3 at 77.00 ppm.

Chromatography (silica gel (120 g); hexane/Et_2O 2:1) gave, as a first fraction, pure **2b** (0.075 g, 18%) and, as a second fraction, pure *3-[(2-chlorophenyl)sulfonyl]-7,8,10,12-tetramethylbenzo[a]heptalene-2,4-diol* (**2c**; 0.086 g, 19%).

Data of **2c**: Yellow crystals. M.p. 130–140° (Et_2O/hexane; partial melting); 250–251° (re-melting). R_f (hexane/AcOEt 2:1) 0.45. UV: see *Table 4*. IR (KBr): 3380*w*, 3242*m*, 2976*m*, 2936*m*, 2911*m*, 2857*w*, 1600*s*, 1565*m*, 1491*w*, 1453*s*, 1437*s*, 1361*m*, 1304*m*, 1265*m*, 1234*m*, 1204*w*, 1144*s*, 1122*m*, 1037*m*, 948*w*, 916*w*, 887*w*, 793*w*, 752*m*, 708*m*, 671*m*, 628*s*, 569*s*, 555*m*, 508*w*, 469*w*. ^{1}H-NMR: see *Table 5*. ^{13}C-NMR: see *Table 6*. EI-MS: 468/466 (11/30, $M^{+\bullet}$), 467(6), 453/451 (7/20), 452(5), 426(9), 412(5), 233(10), 232(8), 207(9), 203(17), 202(24), 189(23), 178(18), 165(22), 112(100), 77(33), 75(53).

3.3. *4-Chlorophenyl Methyl Sulfone*. The sulfone (m.p. 95–96°; 0.352 g, 1.84 mmol) was lithiated with 2.5M BuLi (0.75 ml, 1.88 mmol) and further reacted with **1′b** (0.100 g, 0.31 mmol), followed by additional 2.5M BuLi (0.75 ml, 1.88 mmol) at –15°. Chromatography (silica gel (120 g); hexane/Et_2O 2:1) gave pure *3-[(4-chlorophenyl)sulfonyl]-7,8,10,12-tetramethylbenzo[a]heptalene-2,4-diol* (**2d**; 0.076 g, 53%).

Data of **2d**: Yellow crystals. M.p. 155° (Et_2O/hexane; partial melting); 203–204° (re-melting). R_f (hexane/AcOEt 2:1) 0.51. UV: see *Table 4*. UV (0.1N KOH/EtOH): λ_{max} 227 (4.50), 247(4.37), 270 (sh, 4.27), 340(3.95), 423 (sh, 3.61); λ_{min} 244(4.36), 322(3.93). IR (KBr): 3420*w*, 3188*m*, 2953*w*, 2934*m*, 2912*m*, 1597*s*, 1552*s*, 1476*w*, 1435*s*, 1388v*s*, 1294*m*, 1261v*s*, 1208*m*, 1187*s*, 1140*s*, 1126*s*, 1092*s*, 1061*m*, 1014*m*, 992*w*, 886*w*, 856*w*, 832*m*, 817*w*, 790*m*, 771*m*, 756*s*, 729*m*, 706*m*, 660*m*, 638*s*, 592*m*, 556*s*, 469*w*. ^{1}H-NMR: see *Table 5*. ^{13}C-NMR: see *Table 6*. EI-MS: 468/466 (37/100, $M^{+\bullet}$), 467(24), 453(17), 452(12), 451(4), 126(19), 125(76, $[ClC_6H_4SO_2]^+$), 81(12). Anal. calc. for $C_{26}H_{23}ClO_4S$ (466.98): C 66.87, H 4.98; found: C 66.90, H 5.18.

3.4. *4-Methoxyphenyl Methyl Sulfone.* The sulfone (0.802 g, 4.31 mmol), prepared by oxidation of 4-(Methylthio)phenyl methyl ether with *m*-chloroperbenzoic acid (m.p. 121°), was lithiated with 2.5M BuLi (1.95 ml, 4.88 mmol) and further reacted with **1′b** (0.345 g, 1.06 mmol), followed by additional 2.5M BuLi (1.95 ml, 4.88 mmol) at −5°. Chromatography (silica gel (120 g); hexane/Et_2O 3:1) gave pure *3-[(4-methoxyphenyl)sulfonyl]-7,8,10,12-tetramethylbenzo[a]-heptalene-2,4-diol* (**2e**; 0.143 g, 30%).

Data of **2e**: Yellow crystals. M.p. 112–113° (Et_2O/hexane; partial melting); 214–215° (re-melting). R_f (hexane/AcOEt 2:1) 0.42. UV: see *Table 4*. UV (0.1N KOH/EtOH): λ_{max} 222 (4.53), 231 (4.52), 269 (sh, 4.37), 344 (3.98), 377 (sh, 3.88), 426 (sh, 3.59); λ_{min} 227 (4.51), 320 (3.91). IR (KBr): 3439*w*, 3243*m*, 3014*w*, 2972*m*, 2964*w*, 2955*m*, 2908*m*, 1762*w*, 1596v*s*, 1498*m*, 1438*m*, 1357*m*, 1300*m*, 1263*s*, 1178*m*, 1124v*s*, 1090*s*, 1024*m*, 991*w*, 886*w*, 830*m*, 803*m*, 733*m*, 714*w*, 674*m*, 651*w*, 620*m*, 553*s*, 468*w*. ^{1}H-NMR: see *Table 5*. ^{13}C-NMR: see *Table 6*. EI-MS: 463 (28), 462 (100, $M^{+\cdot}$), 448 (18), 447 (59), 422 (28), 408 (13), 276 (11), 275 (22), 250 (13), 202 (8), 179 (4).

3.5. *4-(Methylsulfonyl)benzonitrile.* The benzonitrile (0.321 g, 1.77 mmol), prepared by oxidation of 4-(methylthio)benzonitrile with $KMnO_4$ (m.p. 139–140°), was lithiated with 2.5M BuLi (0.7 ml, 2.13 mmol) and further reacted with **1′b** (0.096 g, 0.295 mmol). TLC control showed the formation of mono- and disubstituted products of **1′b**. However, the addition of further 2.5M BuLi (0.7 ml, 2.13 mmol) led not to the formation of the expected *[(2,4-dihydroxy)-7,8,10,12-tetramethylbenzo[a]heptalen-3-yl)sulfonyl]benzonitrile* (**2f**) according to TLC. However, we cannot exclude that **2f** had been formed and then reacted further in the presence of the excess of BuLi to unknown products.

3.6. *Methyl 4-Methylphenyl Sulfone.* The sulfone (0.157 g, 0.92 mmol) was lithiated with 2.5M BuLi (0.38 ml, 0.95 mmol) and further reacted with **1′b** (0.050 g, 0.153 mmol), followed by additional 2.5M BuLi (0.38 ml, 0.95 mmol) at −10°. Chromatography (silica gel (100 g); hexane/Et_2O 2:1) gave pure *7,8,10,12-tetramethyl-3-[(4-methylphenyl)sulfonyl]benzo[a]heptalene-2,4-diol* (**2g**; 0.046 g, 67%).

Data of **2g**: Yellow crystals. M.p. 211–212° (Et_2O). R_f (hexane/EtOAc 2:1) 0.55. UV: see *Table 4*. IR (KBr): 3228*m*, 2975*m*, 2906*w*, 1599v*s*, 1560*w*, 1508*w*, 1491*w*, 1437*s*, 1362*m*, 1262*s*, 1140*s*, 1122v*s*, 1091*s*, 1066*s*, 1041*w*, 992*w*, 844*w*, 796*m*, 735v*s*, 705*s*, 669*s*, 621*m*. ^{1}H-NMR: see *Table 5*. ^{13}C-NMR: see *Table 6*. EI-MS: 446 (100, $M^{+\cdot}$), 431 (84), 406 (49), 392 (32), 275 (37), 189 (41). Anal. calc. for $C_{27}H_{26}O_4S$ (446.57): S 7.18; found: S 7.00.

3.7. *Further Sulfones and Sulfone-Related Compounds.* No benzo[*a*]heptalene-2,4-diol formation was observed with methyl 2-pyridyl and methyl 4-pyridyl sulfone as well as methyl 2-pyrimidyl sulfone (base in all cases: LDA) and **1′b**. Similarly, no type-**2** compounds were formed with MeSOPh or $MeSO_3H$ acid and **1′b**. In the latter case, two compounds of unknown structure, one yellow, the other orange, were isolated. Already decomposition of the Li salts of the methyl sulfones with the following second substituents was observed: 4-(methoxycarbonyl)phenyl, 3-nitrophenyl, and 2-methyl-5-nitrophenyl.

4. X-Ray Crystal-Structure Determinations of Compound 9 and 13[10]. – All measurements were conducted on a *Rigaku AFC5R* diffractometer using graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å) and a 12-kW rotating anode generator. Three standard reflections, which were measured after every 150 reflections, remained stable throughout each data collection. The intensities were corrected for *Lorentz* and polarization effects. All refinements were carried out on *F* using full-matrix least-squares procedures which minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$. The data collection and refinement parameters for each compound are listed in *Table 7*. Neutral atom scattering factors for non-H-atoms were taken from [9a] and the scattering factors for H-atoms from [10]. Anomalous dispersion effects were included in F_c [11]; the values for f' and f'' were taken from [9b]. All calculations were performed using the TEXSAN [12] crystallographic software package and the figures were produced with ORTEPII [13].

The crystals of **9** were of relatively low quality and weakly diffracting. They also lost solvent rapidly upon exposure to air. Therefore, it was necessary to immerse a crystal in polyether oil in order to stabilize it during the low-temperature measurement. An absorption correction based on ψ-scans [14] was applied to the intensities. The structure was solved by direct methods using SHELXS86 [15]. In addition to the org. molecule, the asymmetric unit contains one half of a molecule of CH_2Cl_2, in which the Cl-atoms are disordered over two equally occupied positions, and four sites which were assumed to be partially occupied by H_2O molecules. Three

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[10]) Crystallographic data (excluding structure factors) for the structures of compounds **9** and **13** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication no. CCDC-113860 and 113861, respectively. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Table 7. *Crystallographic Data for Compounds* **9** *and* **13**

Compound	**9**	**13**
Crystallised from	CH_2Cl_2/Et_2O/hexane	Et_2O/hexane
Empirical formula	$C_{32}H_{30}O_6S_2 \cdot 1/2\ CH_2Cl_2 \cdot 1.75\,H_2O$	$C_{36}H_{38}O_5S_2$
Formula weight [g mol^{-1}]	648.70	614.81
Crystal colour, habit	yellow, prism	yellow, plate
Crystal dimensions [mm]	$0.18 \times 0.30 \times 0.38$	$0.16 \times 0.43 \times 0.45$
Temperature [K]	173(1)	173(1)
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	$P2_1/n$
Z	8	4
Reflections for cell determination	25	25
2θ range for cell determination [°]	32 – 39	36 – 40
Unit cell parameters *a* [Å]	31.318(4)	10.985(4)
b [Å]	12.900(3)	13.902(4)
c [Å]	23.734(4)	20.930(4)
β [°]	135.349(4)	96.80(3)
V [Å^3]	6739(2)	3174(2)
$D_{calc.}$ [g cm^{-3}]	1.279	1.287
$\mu(MoK_\alpha)$ [mm^{-1}]	0.283	0.210
Scan type	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{(max)}$ [°]	50	55
Transmission factors (min; max)	0.850; 1.000	–
Total reflections measured	6334	7958
Symmetry-independent reflections	5924	7267
Reflections used [$I > 2\sigma(I)$]	2614	4646
Parameters refined	397	541
R	0.0796	0.0477
wR	0.0655	0.0419
Goodness of fit *s*	2.290	1.631
Secondary extinction coefficient	–	$1.0(2) \times 10^{-7}$
Final Δ_{max}/σ	0.0005	0.0004
$\Delta\rho$ (max; min) [e Å^{-3}]	0.54; −0.46	0.35; −0.36
$\sigma(d(C-C))$ [Å]	0.01	0.003 – 0.005

of the H_2O molecules were assigned site occupation factors of 0.5 and the fourth was assigned with 0.25 occupation. Further evidence for the solvent molecules was found by using the SQUEEZE routine of the program PLATON [16], which attempts to remove the solvent contribution from the reflection data. After accounting for the org. molecule, the unit cell contains two holes, each of 874 Å^3, which are presumably filled with solvent molecules. The electron count in these holes was 84 e. The model used for the refinement provides a total of 87 e from the solvent molecules, so it is believed that the model used for the solvent region is a reasonable approximation of the true situation. The non-H-atoms were refined anisotropically, except for the atoms of the solvent molecules, which were refined only isotropically. All of the H-atoms, except those of the OH group and the solvent molecules, were fixed in geometrically calculated positions ($d(C-H) = 0.95$ Å). The OH H-atom was fixed in the position indicated by a difference electron-density map. Each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of the atom to which it was bonded. The solvent H-atoms were not included in the model. The final refinement results are of lower than normal accuracy, which is partially due to crystal quality and partly due to the difficulties with adequately modelling the solvent molecules.

The intensities for **13** were not corrected for absorption. The structure was solved by the *Patterson* method and the difference *Fourier* expansion technique of DIRDIF 92 [17]. The non-H-atoms were refined anisotropically. All of the H-atoms were located in a difference electron-density map and their positions were allowed to refine together with individual isotropic displacement parameters. A correction for secondary extinction was applied.

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