Formation of 2-(Phenylsulfonyl)resorcinols (= 2-(Phenylsulfonyl)benzene-1,3-diols) from Symmetrically Substituted Maleic Anhydrides (= Furan-2,5-diones)

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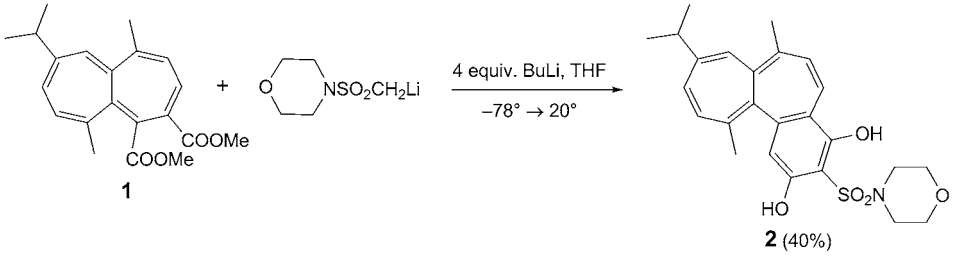
Dedicated to *John Anthony Robinson* on the occasion of his 60th birthday

Treatment of symmetrically substituted maleic anhydrides (= furan-2,5-diones) **6** with lithium (phenylsulfonyl)methanide, followed by methylation of the adduct with MeI/K_2CO_3 in acetone, give the corresponding 4,5-disubstituted 2-methyl-2-(phenylsulfonyl)cyclopent-4-ene-1,3-diones **8** (*Scheme 3*). Reaction of the latter with lithium (phenylsulfonyl)methanide in THF (−78°) and then with 4 mol-equiv. BuLi (−5° to r.t.) leads to 5,6-disubstituted 4-methyl-2-(phenylsulfonyl)benzene-1,3-diols **9** (*Scheme 4*).

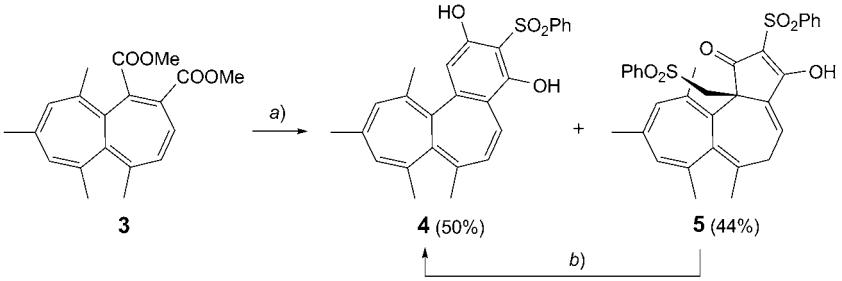
Introduction. – More than 15 years ago, we reported on a 'One-Pot Anellation Method for the Transformation of Heptalene-4,5-dicarboxylates into Benzo[*a*]heptalenes' (see **1** → **2** in *Scheme 1*) [1], which allowed us to envisage and probe a new entrance into the field of colchicinoids starting with azulenes and acetylenedicarboxylates (see, *e.g.*, [2]). At the beginning, we had no clear insight into the mechanism of this new anellation reaction, apart from the experimental facts, which showed that at least two mol-equiv. of the (X-sulfonyl)methanides (X = $N(CH_2CH_2)_2O$, Ph) were necessary, whereby one served as C_1-carrier and the other one obviously as (X-sulfonyl)methine building block. Moreover, we observed that a minimum of 4 mol-equiv. of BuLi or an other alkyllithium reagent were needed for good yields of the benzo[*a*]heptalenediols. Finally, we learnt more about the anellation mechanism when we treated the tetramethylheptalene-1,2-dicarboxylate **3** with 4 mol-equiv. of lithium (phenylsulfonyl)methanide in THF at −78°, followed by slow warming to −10° and then by addition of 4 mol-equiv. of BuLi and stirring for 15 h at room temperature (*Scheme 2*) [3]. Beside the expected benzo[*a*]heptalene-2,4-diol **4**, we found the highly polar 5,11b-dihydro-3-hydroxy-2-(phenylsulfonyl)-11b-[(phenylsulfonyl)methyl]-1*H*-cyclopenta[*a*]heptalen-1-one (**5**), the structure of which was secured by an X-ray crystal-structure analysis. Its treatment with an excess of BuLi in THF led to **4** showing that it was the crucial intermediate in the described benzo-anellation process, which by loss of benzenesulfinate under the strongly basic conditions induced the 5 → 6-ring enlargement.

The C=C bond arrangement of **3** with its 1,2-dicarboxylate partial structure remembered us that simple 2,3-disubstituted maleic acid (= (2*Z*)-but-2-enedioic acid) derivatives may behave similarly to the vicinal heptalenediester and yield 2-(phenyl-

Scheme 1



Scheme 2

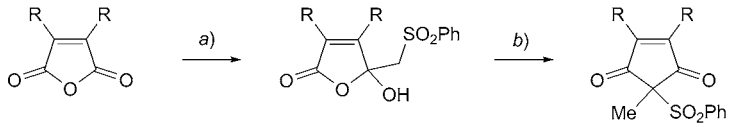


a) 1. 4 mol-equiv. of $LiCH_2SO_2Ph$/THF, $-78°$ (1 h) to $-10°$ (1.5 h); 2. 4 mol-equiv. of BuLi (15 h). *b*) 6 mol-equiv. of BuLi/THF, $-10°$ (20 min) to r.t. (30 min); 61% of cryst. **4**.

sulfonyl)resorcinols (=2-(phenylsulfonyl)benzene-1,3-diols) under the above described treatment. We give in the following part a detailed report on our experiments to verify this idea (see [4] for a preliminary report).

Results and Discussion. – We focused our experiments on symmetrically 2,3-disubstituted maleic acid anhydrides (= 3,4-substituted furan-2,5-diones) **6** (*Scheme 3*), which gave with lithium (phenylsulfonyl)methanide in THF at $-78°$ the corresponding adducts, *i.e.*, 5-hydroxy-5-[(phenylsulfonyl)methyl]furan-2(5*H*)ones **7**. Treatment of

Scheme 3



6a R = Me
6b R = Ph
6c R–R = –$(CH_2)_4$–

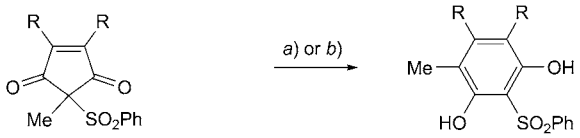
7a R = Me
7b R = Ph
7c R–R = –$(CH_2)_4$–

8a R = Me
8b R = Ph
8c R–R = –$(CH_2)_4$–

a) 2 mol-equiv. of $PhSO_2CH_2Li$/THF, $-78°$ (1 h); **7a** and **7b** 77%; **7c** (74%; with 1,5 mol-equiv. of $PhSO_2CH_2Li$/THF). *b*) MeI, K_2CO_3, acetone, r.t., 8 h; **8a** 89%, **8b** 87%, **8c** 91%.

the latter with MeI and K_2CO_3 in acetone at room temperature led to the symmetrically 4,5-disubstituted 2-methyl-2-(phenylsulfonyl)cyclopent-4-ene-1,3-diones **8** in good yields. The 1,3-diones **8** contained all the necessary structural ingredients for a possible rearrangement into corresponding benzene-1,3-diols by reaction with lithium (phenylsulfonyl)methanide and then with an excess of BuLi as initiator for the $5 \rightarrow 6$-ring enlargement. Indeed, all three 1,3-diones **8** gave under these conditions the 2-(phenylsulfonyl)benzene-1,3-diols **9** (*Scheme 4*).

Scheme 4



8 R = Me, Ph; R–R = –$(CH_2)_4$– **9** R = Me, Ph; R–R = –$(CH_2)_4$–

a) 1. 4 mol-equiv. of $PhSO_2CH_2Li$/THF, $-78°$ to $-5°$ (3 h); 2. 4 mol-equiv. of BuLi, $-5°$ to r.t. (0.5 h), r.t. (15 h); **9a** (R = Me) 11%, **9b** (R = Ph) 71%. *b*) 1. 5 mol-equiv. of $PhSO_2CH_2Li$/THF, $-78°$ to $-5°$ (3 h); 2. 4 mol-equiv. of BuLi/THF, $-5°$ to r.t. (0.5 h), r.t. (3 h); **9c** (R–R = –$(CH_2)_4$) 15%, *endo*-**10c**/*exo*-**10c** 35% (*cf. Scheme 5*).

The structure of the products was evident according to their spectra, in particular, their ^{1}H-NMR spectra in $CDCl_3$. Since 1,3-diol **9a** (R = Me) possesses C_s symmetry, one finds, indeed, for the Me groups two sharp *s* at δ(H) 2.09 and 2.17 in a ratio of 2 : 1. Moreover, the OH group appear as one sharp *s* at δ(H) 8.85 indicating intramolecular H-bonding with one of the O-atoms of the two sulfonyl groups. The other two resorcinols, **9** (R = Ph) and **9** (R – R = –$(CH_2)_4$–), show both two sharp *s* for their OH groups, whereby those of **9b** appear at δ(H) 9.75 and 7.68[1]) and those of **9c** at δ(H) 8.88 and 8.71. The structures of **9a** and **9b** were finally established by an X-ray diffraction analysis of suitable crystals. The found O–H ··· OS distances in the crystals are listed in *Table 1*. In addition, one OH group in molecule A of **9a** forms an intermolecular H-bond with one of the sulfonyl O-atoms of a neighboring molecule B, thereby linking the A and B molecules of **9a** into dimer pairs. Similarly in **9b**, where one OH group forms a weak intermolecular H-bond with a sulfonyl O-atom of a neighboring molecule, thus linking the molecules of **9b** into centrosymmetric dimers.

The formation of 5,6,7,8-tetrahydro-4-methyl-2-(phenylsulfonyl)naphthalene-1,3-diol (**9c**) by the established treatment of 4,5,6,7-tetrahydro-2-methyl-2-(phenylsulfonyl)-1*H*-indene-1,3(2*H*)-dione (**8c**) was accompanied to an appreciable amount by a pair of diastereoisomers (*Schemes 4* and *5*). The main isomer could be purified and crystallized, so that its structure could be characterized as *rel*-(3a*R*,7a*S*,8*R*)-4,5,6,7-tetrahydro-8-methyl-2-(phenylsulfonyl)-3-[(phenylsulfonyl)methyl]-3a,7a-methano-1*H*-inden-1-one (*endo*-**10c**) by an X-ray diffraction analysis (*Fig.*). It is of interest to note that the cyclohexane ring is disordered in that CH_2(5) and CH_2(6) each occupy two positions (*Fig.*, *a* and *b*) representing alternate twist forms of the cyclohexane ring.

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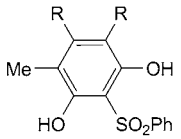
[1]) Responsible for the observed shift difference of the OH signals is without doubt the Ph group in *o*- and *p*-position to the OH groups of **9b**, which shields the signal of *o*-OH and deshields that of *p*-OH.

Table 1. *H-Bonding in the Crystals of* **9a** *and* **9b**[a])



9a R = Me
9b R = Ph

H Bonding (*d* [pm])	**9a**	**9b**
O(1)–H···O(1)S	202(3)	198(3)
O(1)–H···O(1)S′		248(3)
O(3)–H···O(2)S	180(3)	186(3)
O(1)–H···O(1)S′	225(3)	
O′(1)–H···O(1)S′	196(3)	
O′(3)–H···O(2)S′	169(4)	

[a]) Primed atoms refer to the molecule in the following symmetry related position.

The approximate relative site occupation factors of the two conformations are 0.75 : 0.25[2]).

The reaction of **8c** with lithium (phenylsulfonyl)methanide under varying conditions gave some further new products, which cast some light on the reactivity of the reactant (*Scheme 5*). Without the addition of BuLi, we found as sole product the ring-opened form **12c**. Much more interesting was the result of the reaction of **8c** with a minimum excess of the lithium methanide, followed by a reduced amount of BuLi. In this case, we isolated *rel*-(3a*R*,7a*R*)-3a,4,5,6,7,7a-hexahydro-3-hydroxy-2-(phenylsulfonyl)-3a-[(1*S*)-1-(phenylsulfonyl)ethyl]- 1*H*-inden-1-one (**11c**) in a yield of 86%. The structure of **11c** was assigned on the basis of its analytical data (^{1}H- and ^{13}C-NMR, and MS). The weak point is the assignment of the relative configuration of the 1-(phenylsulfonyl)ethyl group at C(3a). However, AM1 calculations showed the indicated *rel*-(1*S*)-configuration to be by 0.9 kcal mol^{-1} more stable in comparison to the rel-(1*R*)-configuration[3]). Therefore, we believe that the side chain at C(3a) is rel-(1*S*)-configured. The similarity of **11c** with the intermediate **5**, which we found in the benzo-anellation reaction of heptalene-1,2-dicarboxylate **3** (*Scheme 2*), gave us the certainty that compounds of type **11c** are the crucial intermediates for the formation of resorcinols **9** from cyclopent-4-ene-1,3-diones **8** on treatment with $PhSO_2CH_2Li$/BuLi (*Scheme 4*). Indeed, the reaction of **11c** with BuLi gave the corresponding tetrahy-

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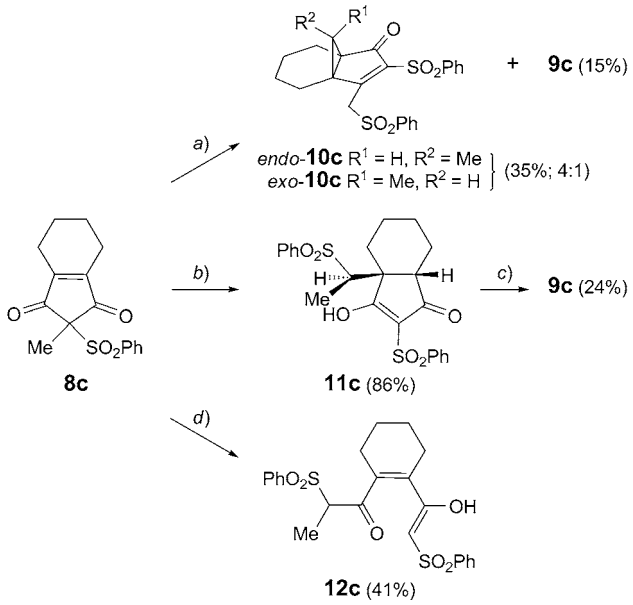
[2]) AM1 Calculations of the basic structure of *endo*-**10c**, *i.e.*, of ((3a*S*,7a*R*,8*S*)-4,5,6,7-tetrahydro-8-methyl-3a,7a-methano-1*H*-inden-1-one, show that the (−)-*sc* conformation at C(5)–C(6) is slightly more stable (−0.10 kcal mol^{-1}) than the (+)-*sc* conformation in contrast to the X-ray crystal structures with the reverse observation (*cf. Fig.*, *a* and *b*).

[3]) We found no relevant indication for the presence of the tautomeric form of **11c**, *i.e.*, of *rel*-(3a*R*,7a*R*)-3a,4,5,6,7,7a-hexahydro-3-hydroxy-2-(phenylsulfonyl)-7a-[(1*S*)-1-(phenylsulfonyl)ethyl]-1*H*-inden-1-one. AM1 Calculations showed this tautomer to be 3.5 kcal mol^{-1} above the ΔH_f^0 value of **11c**.

Scheme 5



a) See *Scheme 4*. *b*) 1. 3 Mol-equiv. of $PhSO_2CH_2Li$/THF, $-78°$ to $-5°$ (2 h); 2. 3 mol-equiv. of BuLi, $-5°$ to r.t. (2 h). *c*) 4 mol-equiv. of BuLi/THF, 0° to 40° (1 h). *d*) 3 mol-equiv. of $PhSO_2CH_2Li$/THF, $-78°$ to 0° (3 h).

dronaphthalene-1,3-diol **9c** (*Scheme 5*), however, in a yield less satisfying as in the case of **5** → **4**[4]).

Taking all results together, it can be said that in the first step of the resorcinol formation, the 1,3-diones **8** are (phenylsulfonyl)methylated at one of their C=O groups (demonstrated by **8c** → **A** in *Scheme 6*). The next step needs BuLi as a strong base for the deprotonation of the introduced (phenylsulfonyl)methyl substituent, which induces ring opening and a new ring closure under formation of **B**. The thus formed 5,5-disubstituted cyclopentadiene substructure undergoes a charge-driven suprafacial [1,5]-C shift of the 1-(phenylsulfonyl)ethyl substituent under formation of dilithium 3a,5,6,7-tetrahydro-2-(phenylsulfonyl)-3a-[1-(phenylsulfonyl)ethyl]-4a*H*-indene-1,3-diolate (**C**). Under the electronic 'pressure' of two olate groups at the cyclopentadiene part, a 5 → 6-ring enlargement takes place under extrusion of benzenesulfinate[5]). The primarily formed cyclohexa-2,5-dien-1-one structure, *i.e.*, lithium 1,4,5,6,7,8-hexahydro-1-methyl-4-oxo-3-(phenylsulfonyl)naphthalen-2-olate, is stabilized by deprotonation to yield the dilithium dianion of **9c** and finally **9c** itself by neutralization (*Scheme 6*).

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[4]) None of the described reactions in this work has systematically been optimized.

[5]) To the utmost, the [1,2]-C shift could be the result of a forgoing carbene formation by loss of benzenesulfinate.

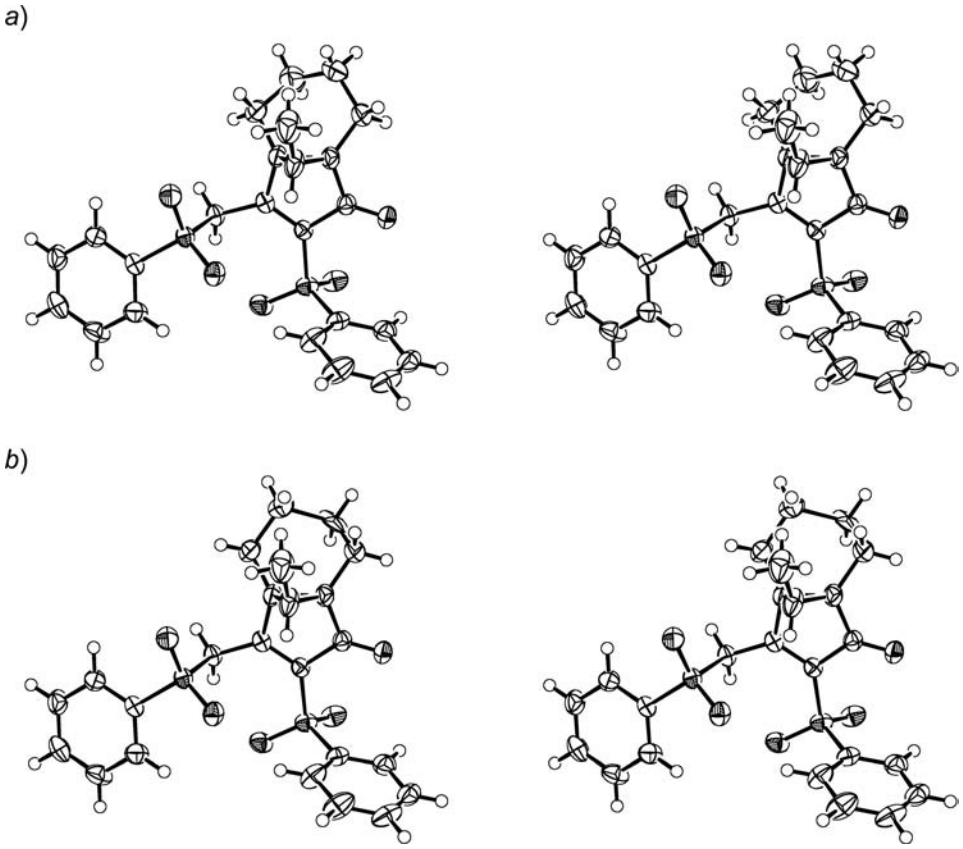
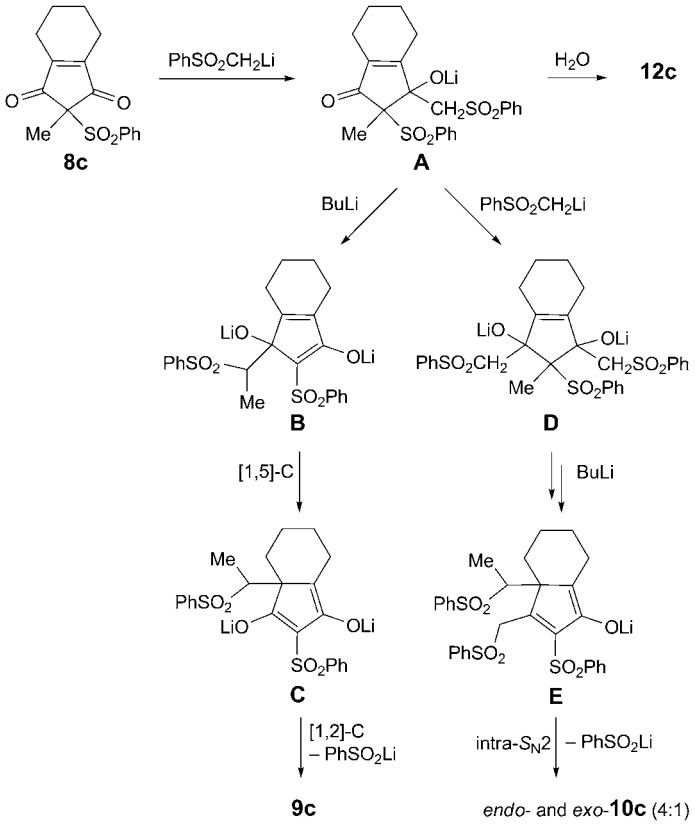


Figure. a) *Stereoscopic view of the X-ray crystal structure of the main conformer* (75%) *of* rel-*(3a*R*,7a*S*,8*R*)-4,5,6,7-tetrahydro-8-methyl-2-(phenylsulfonyl)-3-[(phenylsulfonyl)methyl]-3a,7a-methan-1*H*-inden-1-one* (*endo*-**10c**; 50% probability ellipsoids). b) *Stereoscopic view of the X-ray crystal structure of the minor conformer* (25%) *of* endo-**10c** (50% probability ellipsoids)

Most interesting is the formation of *endo*- and *exo*-**10c**. There is little doubt that their source is the bis[(phenylsulfonyl)methyl]ated intermediate **D**, which rearranges in the presence of BuLi in analogy to **B** → **C** to lithium 3a,5,6,7-tetrahydro-2-(phenylsulfonyl)-3a-(1-(phenylsulfonyl)ethyl)-3-((phenylsulfonyl)methyl)-4a*H*-inden-1-olate (**E**)). In contrast to its analog **C**, **E** carries only one enolate group, but just at the right position to induce the indicated intramolecular nucleophilic three-center substitution reaction yielding *endo*- and *exo*-**10c**. The appearance of both stereoisomers in the reaction mixture indicates that intermediate **E** must also be built in rel-(*R*,*R*)- and rel-(*R*,*S*)-form.

We demonstrated that the benzo-anellation procedure of heptalenedicarboxylates can in a variation also be applied to 2,3-disubstituted maleic anhydrides for the synthesis of correspondingly substituted resorcinols. On the other hand, this new procedure cannot be applied to the cyclic anhydrides of heptalene-1,2- or -4,5-

Scheme 6



dicarboxylic acids, since they exist under thermal conditions as heptaleno[4,5-*c*]furan-1,3-diones, *i.e.*, with a twisted C(4)–C(5) bond [5]. This fact leads to the situation that C(3)=O can indeed preferentially be phenylsulfonylmethylated, however, the further methylation step (MeI/K_2CO_3) causes ring-opening to corresponding methyl 4-[2-(phenylsulfonyl)acetyl]heptalene-5-carboxylates.

We are thankful to Dr. *A. Linden* for the crystal-structure determinations, to our NMR laboratory for 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 [1][6].

1. *Formation of the 4,5-Disubstituted 2-Methyl-2-(phenylsulfonyl)cyclopent-4-ene-1,3-diones* **8**. 1.1. *5-Hydroxy-3,4-dimethyl-5-[(phenylsulfonyl)methyl]furan-2(5*H*)-one* (**7a**). To a soln. of (methylsulfonyl)-benzene (3.472 g, 22.22 mmol) in THF (40 ml) at 0°, 2.5M BuLi in hexane (8.90 ml, 22.22 mmol) was added dropwise, whereby a colorless precipitate of $PhSO_2CH_2Li$ was formed. After 30 min stirring at 0°, the mixture was cooled to −78°, and a soln. of **6a** (1.528 g, 12.12 mmol) in THF (5 ml) was added

dropwise. After some time at $-78°$ to $-60°$, nearly all precipitate of $PhSO_2CH_2Li$ had been dissolved. Then, ice was added, and the org. matter extracted with AcOEt, and the combined AcOEt extract washed once with aq. 2N HCl (100 ml) and then several times with brine, dried (Na_2SO_4), and concentrated. The colorless crystalline residue was washed with Et_2O to remove residual (methylsulfonyl)benzene to yield 1.75 g (77%) of **7a**. Colorless, microcrystalline powder. M.p. 148.0–148.5°. R_f (AcOEt/hexane 3:2) 0.34. ^{1}H-NMR (C*H*Cl$_3$ at δ(H) 7.26): 8.0–7.6 (*m*, $PhSO_2$); 3.74, 3.42 (*AB*, $^2J_{AB}$ = 14.85, CH_2–C(5)); 1.965 (*d*-like, ^5J(Me–C(3),Me–C(4)) = 1.18, Me–C(3)); 1.762 (*d*-like, ^5J(Me–C(4), Me–C(3)) = 1.18, Me–C(4)). ^{13}C-NMR (*C*DCl$_3$ at δ(C) 76.92): 155.52 (C(2)); 139.10 (C(4)); 134.47, 129.21, 128.43 (C_p, C_m, C_o of $PhSO_2$; C_{ipso} not recognizable); 126.54 (C(3)); 101.72 (C(5)); 60.03 (*C*H$_2$–C(5)); 10.52 (*Me*–C(4)); 8.45 (*Me*–C(3)).

1.2. *5-Hydroxy-3,4-diphenyl-5-[(phenylsulfonyl)methyl]furan-2(5*H*)-one* (**7b**). As described in *1.1*, with **6b** (2.00 g, 8.00 mmol), (methylsulfonyl)benzene (2.50 g, 16.0 mmol), and 2.5M BuLi (6.4 ml, 16.0 mmol): 2.50 g (77%) **7b**. Colorless powder. M.p. 183–184°. R_f (AcOEt/hexane 3:2) 0.59. ^{1}H-NMR (C*H*Cl$_3$ at δ(H) 7.25): 8.1–7.6 (*m*, $PhSO_2$); 7.5–7.2 (*m*, Ph–C(3), Ph–C(4)); 6.54 (br. *s*, OH–C(5)); 3.66, 3.52 (*AB*, $^2J_{AB}$ = 15.9, CH_2–C(5)). ^{13}C-NMR (*C*DCl$_3$ at δ(C) 76.90): 168.24 (C(2)); 155.03 (C(4)); 139.21, 134.52, 130.38 (C_{ipso}, C_p, C_m of $PhSO_2$; C_o not recognizable); 129.50 (C(3)); 129.34–128.37 (*Ph*–C(3), *Ph*–C(4)); 101.54 (C(5)); 60.70 (*C*H$_2$–C(5)).

1.3. *4,5,6,7-Tetrahydro-3-hydroxy-3-[(phenylsulfonyl)methyl]isobenzofuran-1(3*H*)-one* (**7c**). As described in *1.1*, with **6c** (0.517 g, 3.40 mmol), 1.5 mol-equiv. of (methylsulfonyl)benzene, and 2.5M BuLi: 0.77 g (74%) of **7c**. Colorless powder. R_f (AcOEt/hexane 3:2) 0.36. IR (KBr): 3354*s* (br., OH), 1754*s* (C=O), 1688 (C=C). ^{1}H-NMR (C*H*Cl$_3$ at δ(H) 7.26): 8.05–7.55 (*m*, $PhSO_2$); 5.98 (br. *s*, OH–C(3)); 3.73, 3.46 (*AB*, $^2J_{AB}$ = 14.88, CH_2–C(3)); 2.50–1.55 (*m*, 8 H, CH_2(4) to CH_2(7)).

Treatment of **7c** with HCl/MeOH at r.t. gave the MeO–C(3) derivative of **7c** as colorless powder (89%). R_f (AcOEt/hexane 3:2) 0.58. ^{1}H-NMR (C*H*Cl$_3$ at δ(H) 7.27): 7.9–7.5 (*m*, $PhSO_2$); 3.89, 3.67 (*AB*, $^2J_{AB}$ = 14.98, CH_2–C(3)); 3.04 (*s*, MeO–C(3)); 2.5–1.7 (*m*, 8 H, CH_2(4) to CH_2(7)). ^{13}C-NMR (*C*DCl$_3$ at δ(C) 76.95): 168.88 (C(1)); 158.05 (C(3a)); 139.28, 134.03, 129.22, 127.99 (C_{ipso}, C_p, C_m, C_o of $PhSO_2$); 132.38 (C(7a)); 104.60 (C(3)); 59.44 (*C*H$_2$–C(3)); 49.62 (*Me*O–C(3)); 22.39 (C(7)); 21.19 (C(4)); 21.05 (C(5)); 19.93 (C(6)).

1.4. *2,4,5-Trimethyl-2-(phenylsulfonyl)cyclopent-4-ene-1,3-dione* (**8a**). To a soln. of **7a** (0.200 g, 0.708 mmol) in dry acetone (10 ml), K_2CO_3 (1.0 g, 7.24 mmol) was added. The mixture was stirred for 30 min at 0°, and MeI (1.0 ml, 16.0 mmol) was added. After 2 h, the mixture was replenished with further MeI (1.5 ml, 24.0 mmol) and stirring continued at r.t. for 4 h. Workup as described in 1.1 and crystallization from CH_2Cl_2/Et_2O gave 0.88 g (89%) of **8a**. Colorless crystals.

M.p. 192–193°. R_f (AcOEt/hexane 3:2) 0.60. ^{1}H-NMR (C*H*Cl$_3$ at δ(H) 7.27): 7.77–7.54 (*m*, $PhSO_2$); 2.05 (*s*, Me–C(4), Me–C(5)); 1.53 (*s*, Me–C(2)). ^{13}C-NMR (*C*DCl$_3$ at δ(C) 76.92): 194.73 (C(1),C(3)); 156.85 (C(4),C(5)); 135.13, 134.65, 130.25, 128.88 (C_{ipso}, C_p, C_m, C_o of $PhSO_2$)); 70.23 (C(2)); 13.57 (*Me*–C(2)); 9.69 (*Me*–C(4), *Me*–C(5)). EI-MS: 278 (13, $M^{+\bullet}$), 141 (54, $[M - PhSO_2]^+$), 77 (100, $Ph^{+\bullet}$).

1.5. *2-Methyl-4,5-diphenyl-2-(phenylsulfonyl)cyclopent-4-ene-1,3-dione* (**8b**). As described in *1.4*, with **7b** (0.60 g, 1.48 mmol), acetone (40 ml), K_2CO_3 (4.0 g, 29 mmol), and MeI (5.0 ml, 0.08 mol): **8b** (0.514 g, 87%). Colorless powder. R_f (AcOEt/hexane 1:1) 0.60. ^{1}H-NMR (C*H*Cl$_3$ at δ(H) 7.26): 7.85–7.60 (*m*, $PhSO_2$); 7.42–7.25 (*m*, Ph–C(4), Ph–C(5)); 1.74 (*s*, Me–C(2)). ^{13}C-NMR (*C*DCl$_3$ at δ(C) 76.90): 193.66 (C(1), C(3)); 153.38 (C(4), C(5)); 135.35 (C_{ipso} of $PhSO_2$); 134.68 (C_p of $PhSO_2$); 130.47, 130.19, 129.79, 129.13, 128.43 (*Ph*–C(4), *Ph*–C(5), C_m and C_o of $PhSO_2$); 128.11 (C_{ipso} of Ph–C(4), *Ph*–C(5)); 71.97 (C(2)); 13.38 (*Me*–C(2)).

1.6. *4,5,6,7-Tetrahydro-2-methyl-2-(phenylsulfonyl)-1*H*-indene-1,3(2*H*)-dione* (**8c**). As described in 1.4, with **7c** (0.100 g, 0.324 mmol), acetone (5 ml) K_2CO_3 (0.300 g, 2.17 mmol), and MeI (1.0 ml, 16.0 mmol): to yield **8c** (0.90 g, 91%) Colorless crystals. M.p. 201–202° (CH_2Cl_2/Et_2O). R_f (AcOEt/hexane 1:1) 0.47. ^{1}H-NMR (C*H*Cl$_3$ at δ(H) 7.26): 7.8–7.55 (*m*, $PhSO_2$); 2.39 (sym. *m*, CH_2(4),CH_2(7)); 1.70 (sym. *m*, CH_2(5), CH_2(6))); 1.56 (*s*, Me–C(2)). ^{13}C-NMR (*C*DCl$_3$ at δ(C) 76.92): 193.81 (C(1),C(3)); 159.67 (C(3a), C(7a)); 135.38, 134.57, 130.18, 128.91 (C_{ipso}, C_p, C_m, C_o of $PhSO_2$); 71.65 (C(2)); 21.04 (C(4), C(7)); 20.67 (C(5), C(6)); 13.11 (*Me*–C(2)). EI-MS: 304 (11, $M^{+\bullet}$), 179 (21), 163 (23), 141 (53, $[M - PhSO_2]^+$), 77 (100, $Ph^{+\bullet}$).

2. *Formation of the 2-(Phenylsulfonyl)resorcinols* (=*2-(Phenylsulfonyl)benzene-1,3-diols*) **9**. 2.1. *4,5,6-Trimethyl-2-(phenylsulfonyl)benzene-1,3-diol* (**9a**). As described in *1.1*, $PhSO_2CH_2Li$ was prepared from (methylsulfonyl)benzene (0.180 g, 1.15 mmol) at $-5°$ in THF (4 ml). At $-78°$, **8a** (0.080 g, 0.287 mmol) was added, followed by 2M BuLi (0.574 ml, 1.435 mmol). The temp. was raised to r.t., and stirring was continued for 12 h. After usual workup, the residue of the AcOEt extracts was subjected to CC (silica gel, AcOEt/hexane 3:2): **9a** (9 mg, 11%). Colorless powder. M.p. 168–171.3° (after CC without recryst.). R_f (AcOEt/hexane 1:1) 0.79. ^{1}H-NMR (300 MHz, $CDCl_3$; C*H*Cl_3 at δ(H) 7.26): 8.85 (*s*, OH–C(1), OH–(3)); 7.94 (*d*-like, $J_o = 8$, H_o of $PhSO_2$); 7.62 (*t*-like, $J_o \approx 7.5$, H_p of $PhSO_2$); 7.53 (*t*-like, $J_o = 8$, H_m of $PhSO_2$); 2.17 (*s*, Me–C(5)); 2.09 (*s*, Me–C(4), Me–(6)).

The structure of **9a** was finally established by an X-ray crystal-structure analysis of a suitable crystal obtained from Et_2O (*Tables 1* and *2*).

2.2. *4-Methyl-5,6-diphenyl-2-(phenylsulfonyl)benzene-1,3-diol* (=*6′-Methyl-4′-(phenylsulfonyl)-[1,1′:2′,1″-terphenyl]-3′,5′-diol*; **9b**). As described in *2.1* (same molar amounts): **9b** (0.074 g, 71%) after crystallization from CH_2Cl_2/Et_2O. Colorless crystals. M.p. 173.5–174.2°. R_f (AcOEt/hexane 1:1) 0.68. ^{1}H-NMR (300 MHz, $CDCl_3$; C*H*Cl_3 at δ(H) 7.25): 9.75, 7.68 (2*s*, OH–C(3′), OH–C(5′)); 8.05 (*d*-like, $J_o = 8$, H_o of $PhSO_2$); 7.67 (*t*-like, $J_o = 7$, H_p of $PhSO_2$); 7.56 (*t*-like, $J_o = 7$, H_m of $PhSO_2$); 7.17–7.06 (*m*, 6 H, Ph–C(1′), Ph–C(2′)); 6.95–6.87 (*m*, 4 H, Ph–C(1′), Ph–C(2′)); 1.93 (*s*, Me–C(6′)); most probable: 6.93 (*d* with f.s., $J_o = 7.8$, H_o of Ph–C(1′)); 6.89 (*d* with f.s., $J_o = 7.8$, Ph–C(2′)). ^{13}C-NMR ($CDCl_3$; *C*DCl_3 at δ(C) 76.90): 153.61 (C(5′)); 150.02 (C(3′)); 141.55 (C_{ipso} of $PhSO_2$); 138.70 (C_{ipso} of Ph–C(1′)); 134.73 (C_{ipso} of Ph–C(2″)); 133.90 (C_p of $PhSO_2$); 131.02–126.72 (CH of $PhSO_2$, Ph–C(1′), Ph–C(2′)); 121.92 (C(2′)); 117.58 (C(6′)); 108.42 (C(4′)); 13.17 *Me*–C(6′)).

The structure of **9b** was finally established by an X-ray crystal-structure analysis (*Tables 1* and *2*).

2.3. *5,6,7,8-Tetrahydro-4-methyl-2-(phenylsulfonyl)naphthalene-1,3-diol* (**9c**). As described in *2.1*, with **8c** (0.076 g, 0.25 mmol) and $PhSO_2CH_2Li$ (generated from (methylsulfonyl)benzene (0.156 g, 1.0 mmol) at $-78°$ and 2M Buli (0.375 ml, 1.0 mmol)) in THF (15 ml) at $-5°$ to r.t. then, additional 2M BuLi (0.375 ml, 1.0 mmol) was added and the temp. finally brought to r.t. After 15 h stirring and usual workup, CC (silica gel, AcOEt/hexane 3:2) gave **9c** as colorless powder (12 mg, 15%) and *endo*-**10c**/*exo*-**10c** 4:1, from which pure *endo*-**10c** (0.031g, 28%) was obtained by crystallization (CH_2Cl_2/Et_2O).

Data of **9c**: M.p. 183–186.5° (after CC without recryst.). R_f (AcOEt/hexane 1:1) 0.78. ^{1}H-NMR (300 MHz, $CDCl_3$; C*H*Cl_3 at δ(H) 7.26): 8.88, 8.71 (2*s*, OH–C(1), OH–C(3)); 7.93 (*d*-like, $J_o = 7.2$, H_o of $PhSO_2$); 7.52 (*t*-like, H_m of $PhSO_2$); 7.44 (*t*-like, H_p of $PhSO_2$); 2.57 (*t*-like, CH_2(5), CH_2(8)); 2.01 (*s*, Me–C(4)); 1.72 (*q*-like, CH_2(6),CH_2(7)).

Data of rel-*(3a*R*,7a*S*,8*R*)-4,5,6,7-Tetrahydro-8-methyl-2-(phenylsulfonyl)-3-[(phenylsulfonyl)-methyl]-3a,7a-methano-1*H*-inden-1-one* (*endo*-**10c**): ^{1}H-NMR (300 MHz, $CDCl_3$; C*H*Cl_3 at δ(H) 7.27): 8.15–7.50 (*m*, H of 2 $PhSO_2$); 5.90, 4.25 (*AB*, $^2J_{AB} = 12.3$, $PhSO_2CH_2$–C(1)); 2.4–2.2 (*m*, 3 H); 1.69 (*q*, $^3J = 6.6$, H–C(8)); 1.65–1.20 (*m*, 5 H); 1.16 (*d*, $^3J = 6.5$, Me–C(8)).

The structure of *endo*-**10c** was finally established by an X-ray crystal-structure analysis (*Fig.*, *Table 2*).

Data of rel-*(3a*R*,7a*S*,8*S*)*-4,5,6,7-Tetrahydro-*8-methyl-2-(phenylsulfonyl)-3-[(phenylsulfonyl)-methyl]-3a,7a-methano-1*H*-inden-1-one* (*exo*-**10c**): ^{1}H-NMR (300 MHz, $CDCl_3$; in the presence of 80% *endo*-**10c**; recognizable signals): 8.25 (*d*-like, $J_o = 7.2$, H_o of $PhSO_2$–C(2)); 5.88, 4.22 (*AB*, $^2J_{AB} = 12.0$, $PhSO_2CH_2$–C(1)); 0.94 (*d*, $^3J = 6.5$, Me–C(8)).

3. *Experiments with 4,5,6,7-Tetrahydro-2-methyl-2-(phenylsulfonyl)-1*H*-indene-1,3(2*H*)-dione* (**8c**). 3.1. *1-{2-[(1*Z*)-1-Hydroxy-2-(phenylsulfonyl)ethenyl]}cyclohex-1-en-1-yl}-2-(phenylsulfonyl)propan-1-one* (**12c**). A soln. of **8c** (0.130 g, 0.43 mmol) in THF (15 ml), cooled to $-78°$, was treated with $PhSO_2CH_2Li$ (generated from (methylsulfonyl)benzene (0.200 g, 1.28 mmol) and 2.5M BuLi (0.70 ml, 1.67 mmol) in the usual manner (*cf.* 1.1)). The mixture was warmed to 0° and stirred for 3 h.

The formed white precipitate was filtered off and washed with Et_2O (20 ml). Evaporation of the Et_2O filtrate delivered **12c** (0.055g, 41%). Colorless powder. R_f (AcOEt/hexane 3:2) 0.43. ^{1}H-NMR (C*H*Cl_3 at δ(H) 7.26): 8.0–7.5 (2 $PhSO_2$); 4.75 (*s*, H–C(2″)); 4.56 (*s*, OH–C(1″)); 3.62 (*q*, ^3J(H–C(2′),Me–C(2′)) = 7.0, H–C(2′)); 2.50 (*qt*-like, CH_2(3)); 2.14 (sym. *m*, CH_2(6)); 1.80–1.57 (*m*, CH_2(4), CH_2(5)); 1.47 (*d*, ^3J(Me–C(2′),H–C(2′)) = 7.0, Me–C(2′)). ^{13}C-NMR (*C*DCl_3 at δ(C) 76.90): 191.77 (C(1′)); 171.99 (C(1″)); 141.08 (C(2)); 138.16, 138.04 (C_{ipso} of $PhSO_2$–C(2′,2″)); 134.21, 134.07 (C_p of $PhSO_2$–C(2′), $PhSO_2$–C(2″)); 129.39, 129.29 (C_m of $PhSO_2$–C(2′), $PhSO_2$(2″)); 128.84, 128.38 (C_o of

$PhSO_2$–C(2′) and $PhSO_2$(2″)); 80.42 (C(1)); 70.87 (C(2′)); 63.14 (C(2″)); 23.32, 21.51, 20.58, 20.00 (C(3) to C(6)); 11.89 (*Me*–C(2′)). EI-MS: 460 (21, $M^{+\bullet}$), 443 (32, $[M-OH]^+$), 442 (18, $[M-H_2O]^{+\bullet}$), 396 (100, $[M-SO_2]^{+\bullet}$), 332 (30, $[M-2\ SO_2]^{+\bullet}$). CI-MS: 478 (100, $[M+NH_4]^+$), 460 (8, $M^{+\bullet}$).

3.2. rel-*(3a*R*,7aR)-3a,4,5,6,7,7a-Hexahydro-3-hydroxy-2-(phenylsulfonyl)-3a-((1*S*)-1-(phenylsulfonyl)ethyl)-1*H*-inden-1-one* (**11c**). $PhSO_2CH_2Li$ was formed at 0° from (methylsulfonyl)benzene (0.308 g, 1.98 mmol) in THF (15 ml) with 2.5M BuLi (1.05 ml, 2.65 mmol). After cooling to −78°, a soln. of **8c** (0.200 g, 0.66 mmol) in THF (15 ml) was added dropwise. Stirring of the mixture was continued for 3 h, and the temp. increased again to 0°. Then 2.5M BuLi (0.79 ml, 1.98 mmol) was added dropwise, (yellow mixture → dark orange). After 1 h stirring, the mixture became turbid and a white precipitation was formed. Ice was added, followed by the usual workup procedure with CH_2Cl_2 for the extraction. The thus obtained residue was crystallized from CH_2Cl_2/Et_2O: Colorless crystals. **11c** (0.261 g, 86%). M.p. 174.3–175.2°. R_f (AcOEt/hexane 3:2) 0.0. ^{1}H-NMR (300 MHz, $CDCl_3$; C*H*Cl_3 at δ(H) 7.26): 11.25 (OH–C(3)); 8.01 (*d*-like, J_o = 8.1, H_o of $PhSO_2$–C(2)); 7.81 (*d*-like, J_o = 7.9, H_o of *Ph*SO_2CH-(Me)–C(3a)); 7.68–7.63 (*m*, H_p of both $PhSO_2$)); 7.58–7.51 (*m*, H_m of both $PhSO_2$)); 3.75 (*t*-like, ^3J = 4.6 and 3.3, H–C(7a)); 3.35 (*q*, ^3J(H, Me) = 7.0, $PhSO_2$C*H*(Me)–C(3a)); 2.65 (*td*, $^3J(H_{ax}$–C(7), H_{ax} – C(6)) ≈ $^2J(H_{eq}$ – C(7),H_{ax}–C(7)) = 13.8, $^3J(H_{ax}$–C(7),H–C(7a)) = 4.6, H_{ax}–C(7)); 2.3–2.1 (*m*, 2 H); 1.73–1.40 (*m*, 3 H)); 1.40–1.20 (*m*, 1 H); 0.98–0.80 (*m*, 1 H); 0.72 (*d*, ^3J((Me, H) = 7.0, $PhSO_2$CH-(*Me*)–C(3a)). ^{13}C-NMR (75 MHz, $CDCl_3$; CDCl_3 at δ(C) 76.91): 198.89 (C(1)); 195.37 (C(3)); 139.45 (C_{ipso} of $PhSO_2$–C(2)); 139.10 (C_{ipso} of $PhSO_2$CH(Me)–C(3a)); 134.18 (C_p of $PhSO_2$–C(2)); 133.73 (C_p of $PhSO_2$CH(Me)–C(3a)); 129.16, 129.10 (C_m of both $PhSO_2$); 128.16 (C_o of $PhSO_2$–C(2)); 127.45 (C_o of $PhSO_2$CH(Me)–C(3a)); 115.36 (C(2)); 62.68 ($PhSO_2$C*H*(Me)–C(3a)); 53.14 (C(3a)); 41.38 (C(7)); 24.48 (C(4)); 20.37 (C(7)); 16.80 (C(5)); 16.33 (C(6)); 11.47 ($PhSO_2$CH(*Me*)–C(3a)). EI-MS: 460 (1.8, M^+), 396 (6.6, $[M-SO_2]^+$), 319 (64, $[M-PhSO_2]^+$), 291 (12, $[M-PhSO_2CH(Me)]^+$), 246 (10), 231 (5.0), 177 (9.6); (100, $Ph^{+\bullet}$).

3.2.1. *Rearrangement of* **11c**. A soln. of **11c** (0.030 g, 0.065 mmol) in THF (5 ml) was cooled to 0°. 2.5M BuLi (0.13 ml, 0.325 mmol) was added. Under stirring, the temp. was increased within 1h to 40°. The usual workup delivered **9c** (5 mg, 24%).

4. *Crystal-Structure Determinations of* **9a**, **9b**, *and* endo-**10c** (*Tables 1* and *2*, *Fig.*, *a* and *b*)[6]). All measurements were made with a *Rigaku AFC5R* diffractometer with graphite-monochromated MoK_α radiation (λ 0.71069 Å) and a rotating anode generator. All three structures were solved and refined successfully with no unusual features.

Benzene-1,3-diol **9a**: There are two symmetry-independent molecules in the asymmetric unit, however, there are no significant conformational differences between the molecules. Each OH group in each symmetry-independent molecule forms an intramolecular H-bond with an adjacent sulfonyl O-atom. In addition, one OH group in molecule A forms an intermolecular H-bond with one of the sulfonyl O-atoms of a neighboring molecule B, thereby linking the A and B molecules into dimeric pairs (*Table 1*).

Benzene-1,3-diol **9b**: Similar by to **9a**, each OH group forms an intramolecular H-bond with one of the adjacent sulfonyl O-atoms. Additionally, one OH group forms a weak intermolecular H-bond with a sulfonyl O-atom of a neighboring molecule, thus linking molecules into centrosymmetric dimers (*Table 1*).

Tricyclic endo-**10c**: Since the space group is centrosymmetric, the crystals are racemic. The cyclopropane ring is fused to the common bond between the cyclohexane and cyclopentene rings. The cyclohexane ring is disordered in that two adjacent methylene C-atoms each occupy two positions representing alternate twist forms of the ring (*Fig.*, *a* and *b*). The disordered sites were successfully resolved and refined satisfactorily. The approximate relative site occupation factors of the two conformations are 0.75:0.25[2]). Due to the relative small amount of the minor conformer, the geometry of the minor conformation is less than ideal, and the corresponding geometric parameters have large standards uncertainties.

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[6]) CCDC-941510–941512 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from *the Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data request/cif.

Table 2. *Crystallographic Data for Compounds* **9a**, **9b**, *and* endo-**10c**

	9a	**9b**	*endo*-**10c**
Crystallized from	Et_2O	Et_2O	CH_2Cl_2/Et_2O
Empirical formula	$C_{15}H_{16}O_4S$	$C_{25}H_{20}O_4S$	$C_{24}H_{24}O_5S_2$
M_r	292.35	416.49	456.57
Crystal color, habit	colorless, prism	colorless, prism	pale yellow, prism
Crystal dimensions [mm]	$0.20 \times 0.20 \times 0.55$	$0.18 \times 0.32 \times 0.38$	$0.40 \times 0.43 \times 0.60$
Temperature [K]	173(1)	173(1)	173(1)
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
Z	4[a])	4	4
Reflections for cell determination	25	25	25
2θ Range for cell determination [°]	24 – 26	24 – 26	24 – 26
Unit cell parameters:			
a [Å]	10.559(2)	11.953(3)	11.219(2)
b [Å]	16.713(2)	9.411(4)	10.158(2)
c [Å]	7.679(2)	18.058(4)	19.178(3)
α [°]	93.65(1)	90	90
β [°]	66.44(2)	97.52(2)	98.10(2)
γ [°]	89.39(1)	90	90
V [Å^3]	1343.9(4)	2014(1)	2163.7(7)
$F(000)$	616	872	960
D_x [g/cm^{-3}]	1.445	1.373	1.401
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	0.251	0.191	0.280
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{(\max)}$ [°]	55	50	50
Total reflections measured	6499	3969	4262
Symmetry-indepedent reflections	6166	3538	3807
R_{int}	0.022	0.038	0.028
Reflections used ($I > 2\sigma(I)$)	4819	2683	3188
Parameters refined	378	279	298
Reflection/parameter ratio	12.7	9.62	10.7
Final R	0.0527	0.0418	0.0454
wR	0.0560	0.0420	0.0478
Weights[b])	0.005	0.005	0.005
Goodness of fit	2.601	1.991	2.699
Secondary extinction coefficient	$3.0(7) \cdot 10^{-7}$		
Final $\Delta_{\max}/\sigma$	0.0002	0.0003	0.0003
$\Delta\rho$ (max; min) [e Å^{-3}]	0.63; −0.47	0.24; −0.31	0.70; −0.38
$\sigma(d_{(\mathrm{C-C})})$ [Å]	0.003 – 0.005	0.003 – 0.004	0.004 – 0.03

[a]) Two formula units per asymmetric unit. [b]) p in $w = [\sigma^2(F_o) + (pF_o)^2]^{-1}$.

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