Formation of 6-Methyl-7,11-diphenylheptaleno[1,2-*c*]furanones

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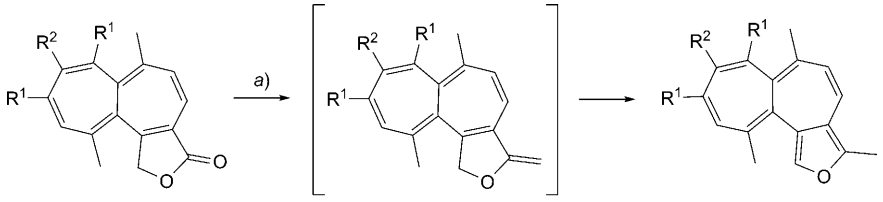
The dehydrogenation reaction of a mixture of heptalene-1,2- and heptalene-4,5-dimethanols **4a** and **4b** with basic MnO_2 in AcOEt at room temperature led to the formation of the corresponding heptaleno[1,2-*c*]furan-1-one **6a** and heptaleno[1,2-*c*]furan-3-one **7a** (*Scheme 2*). Both products can be isolated by chromatography on silica gel. The methylenation of the furan-3-one **7a** with 1 mol-equiv. of *Tebbe*'s reagent at -25 to $-30°$ afforded the 2-isopropenyl-5-methylheptalene-1-methanol **9a**, instead of the expected 3,6-dimethylheptaleno[1,2-*c*]furan **8** (*Scheme 3*). Also, the treatment of **7a** with *Takai*'s reagent did not lead to the formation of **8**. On standing in solution at room temperature, or more rapidly on heating at 60°, heptalene **9a** undergoes a reversible double-bond shift (DBS) to **9b** with an equilibrium ratio of 1:1.

Introduction. – Several years ago, we reported on the dehydrogenation reaction of heptalene-1,2- and heptalene-4,5-dimethanols, which can easily be obtained by $LiAlH_4$ or DIBAH (diisobutylaluminium hydride) reduction of the corresponding heptalenedicarboxylates. Treatment of the heptalenedimethanols with activated MnO_2 in CH_2Cl_2 led to the formation of the corresponding heptaleno[1,2-*c*]furans and heptaleno[1,2-*c*]furan-3-ones **1** and **1′** (*cf.* [1] and lit. cit. therein). We further studied the synthesis of 3-methyl-substituted heptaleno[1,2-*c*]furans **3** and **3′** by the reaction of the corresponding furan-3-ones with 1 mol-equiv. of *Tebbe*'s reagent (= μ-chlorobis(η^5-cyclopenta-2,4-dien-1-yl)(dimethylaluminium)-μ-methylenetitanium) in toluene, respectively (*Scheme 1*). We assumed that, in the first step, the methylene forms **2** and **2′** are formed, and then isomerize under base catalysis to the final products.

Scheme 1

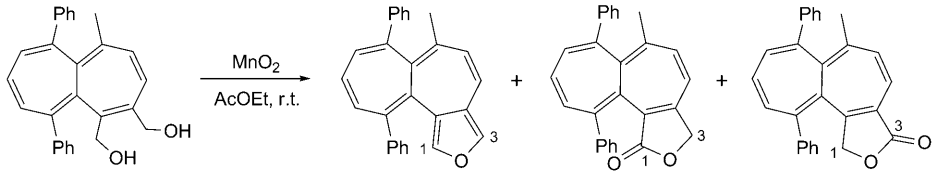


1 R^1 = Me, R^2 = H **2** **3**
1' R^1 = H, R^2 = i-Pr **2'** **3'**

a) 1 Mol-equiv. of *Tebbe*'s reagent (*Aldrich*), 0.5M in toluene [1].

Results. – The starting mixture of the heptalene-1,2- and -4,5-dimethanols **4a** and **4b**, respectively, for this study was obtained by DIBAH reduction of the corresponding heptalene-4,5-dicarboxylate in excellent yield [2]. The thermal equilibrium mixture of **4a** and its DBS isomer **4b** was vigorously stirred in AcOEt at room temperature in the presence of a 20–25-fold amount by weight of MnO_2 for 30–40 min. After removal and extraction of MnO_2 with AcOEt, the product mixture was separated by chromatography (silica gel) leading to heptaleno[1,2-*c*]furan-1-one **6a** and heptaleno[1,2-*c*]furan-3-one **7a** (*Scheme 2*).

Scheme 2



4a[a]) **5** (n.d.)[b]) **6a** (7%) **7a** (87%)[c])

[a]) Thermal 1:2 equilibrium mixture of **4a** and its double-bond-shift (DBS) isomer **4b**. [b]) n.d. = not detectable. [c]) At room temperature, **7a** is in thermal equilibrium with 6% of its DBS isomer **7b** ($CDCl_3$).

In this reaction, heptaleno[1,2-*c*]furan **5** was not found and, instead, the yield of **7a** was up to 87%. Its isomer **6a** was formed in only 7% yield, due to the sterically hindered position of the methanol function at C(5). It is of interest to note that both furanones show quite different UV/VIS spectra in hexane (*Fig. 1*,*a* and *b*). The furan-3-one **7a** displays a clear maximum at 292 nm, whereas the spectrum of the isomeric furan-1-one **6a** possesses only a weak shoulder. On the other hand, the heptalene bands in the long-wavelength region are comparable. Both show a very broad flat maximum at *ca.* 400 nm, which can be attributed to heptalene-band I (see [3] for band assignment). We suppose that the absorption at 292 nm reflects slight differences in the conjugation of the furanone C=O groups with the heptalene chromophore of **6a** and **7a**, which can be attributed to small deviations in the torsion angles of the heptalene perimeter. Indeed, AM1 calculations (*CS Chem3D Pro*®, 2001) of both structures indicate slightly smaller *cisoid* torsion angles at the central heptalene axis (C(6a)–C(11a)) for **7a** in comparison with **6a** (see also [1])[1]).

The structure of **6a** and **7a** could be unequivocally deduced from their NMR spectra. Both compounds exhibit for H–C(4) and H–C(5) an *AB* signal pattern with $^3J_{AB} = 11.3$ and 11.5 Hz for **6a** and **7a**, respectively. Whereas the methylene H-atoms of **7a** display in $CDCl_3$ the expected *AB* signal pattern at δ 4.16 and 3.91, respectively, with $^2J_{AB} = 17.8$ Hz, they appear for **6a** as a more deshielded *s* at δ 4.81 (*cf.* [1]). Moreover, in the ^{1}H-NMR spectrum of **7a**, weak signals of its double-bond-shifted (DBS) isomer **7b**

[1]) Another explanation would be that the clearly defined 292 nm band of heptaleno[1,2-*c*]furan-3-one **7a** reflects a residual conjugation within the partial structure Ph–C(11)=C(11a)–C(11b)=C(3a)–C(3)=O, which is not present in the furan-1-one **6a**. However, the AM1 calculations show for both structures an almost perpendicular Ph–C(11) group with respect to the C(11)=C(11a) bond.

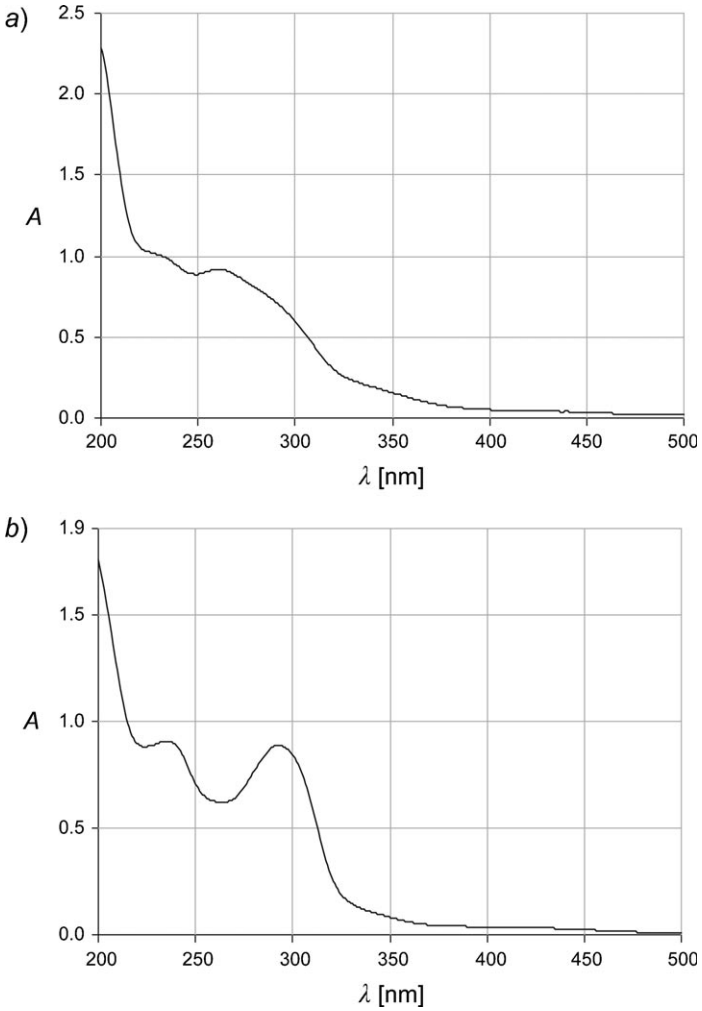


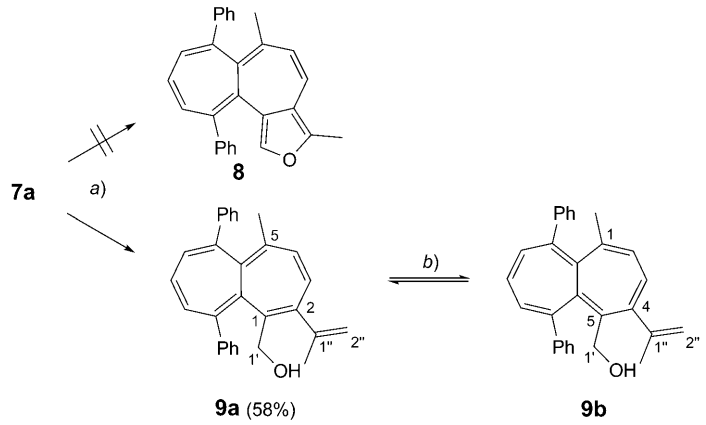
Fig. 1. *UV/VIS Spectra* (hexane) *of* a*)* **6a** *and* b*)* **7a**

could be identified with an *AB* signal pattern for $CH_2(1)$ at δ 4.39 and 3.94, respectively, with $^2J_{AB} = 13.3$ Hz. The reduced ^2J value of **7b** indicates the interrupted hyperconjugation between $CH_2(1)$ and C(3)=O (*cf.* [1]). The DBS isomer of **6a**, *i.e.*, **6b**, was not found in solutions of **6a** (C_6D_6 or $CDCl_3$) at room temperature.

When furanone **7a** was treated in the established way with *Tebbe*'s reagent in toluene at -25 to $-30°$ [1] (see also [4][5]), a single product was formed. However, instead of the expected 3,6-dimethylheptaleno[1,2-*c*]furan **8**, the ring-opened 2-isopropenyl-5-methylheptalene-1-methanol **9a** was isolated (*Scheme 3*). On standing in solution ($CDCl_3$ or C_6D_6), **9a** was converted slowly into its DBS isomer **9b**. The equilibrium mixture **9a**/**9b** in C_6D_6 was rapidly established on heating at 60°, leading to

a 1:1 ratio of **9a**/**9b** (see below). The structures of **9a** and **9b** were unambiguously confirmed by their ^{1}H-NMR spectra in $CDCl_3$ and C_6D_6, respectively. In particular, the ^3J value of H–C(3) and H–C(4) of **9a** (C_6D_6) changed from 11.8 Hz to 6.1 Hz for the equivalent H-atoms H–C(2) and H–C(3) of **9b**. Moreover, the qualitative UV/VIS spectra of **9a** and **9b** in hexane are quite interesting (*Fig. 2*, *a* and *b*). Both isomers show the typical long-wavelength heptalene-band I as a broad shoulder at *ca.* 368 nm with a slightly stronger intensity in the case of **9b**, where the CH_2=C(Me) group is in conjugation with the heptalene fragment Me–C(1)=C(2)–C(3)=C(4). On the other hand, heptalene **9a** displays a much more pronounced absorption band at 286 nm in comparison with that of **9b**, which appears at the same wavelength (*cf. Fig. 2*, *a* and *b*). We believe that this effect is again attributable to the slightly smaller *cisoid* torsion angles at the central σ-bond of the heptalene core of **9a** leading to a better conjugative interaction with the isopropenyl group, as we have already discussed in the case of **7a** (see *Fig. 1*, *b*, and below).

Scheme 3



a) 1 Mol-equiv. of *Tebbe*'s reagent (*Fluka*), 0.5M in toluene, at -25 to $-30°$, followed by basic workup at r.t. *b*) On heating at 60° in C_6D_6, **9a** formed a 1:1 equilibrium mixture with its DBS isomer **9b**.

The structure of **9a** was further elucidated by an X-ray crystal-structure analysis (*Fig. 3*). Unfortunately, heptalene **9a** crystallized from hexane/Et_2O as thin plates which showed only very weak diffraction. The poor quality of the available data allowed only the confirmation of the backbone structure of **9a**. Nevertheless, two independent molecules could be identified in the asymmetric unit, which seemed to differ only with respect to the conformation of the primary-alcohol group, relative to the backbone structure (for the X-ray structure, see *Sect. 3* in the *Exper. Part*).

We therefore performed AM1 calculations of **9a** as well as of **9b**. There exist indeed for the two DBS isomers low-energy conformations **A** and **B** with almost the same $\Delta H_f°$ values (*Figs. 4* and *5*). In conformations **A**, the H-atom of the OH group of the primary-alcohol function at C(1) and C(5), respectively, is located close to

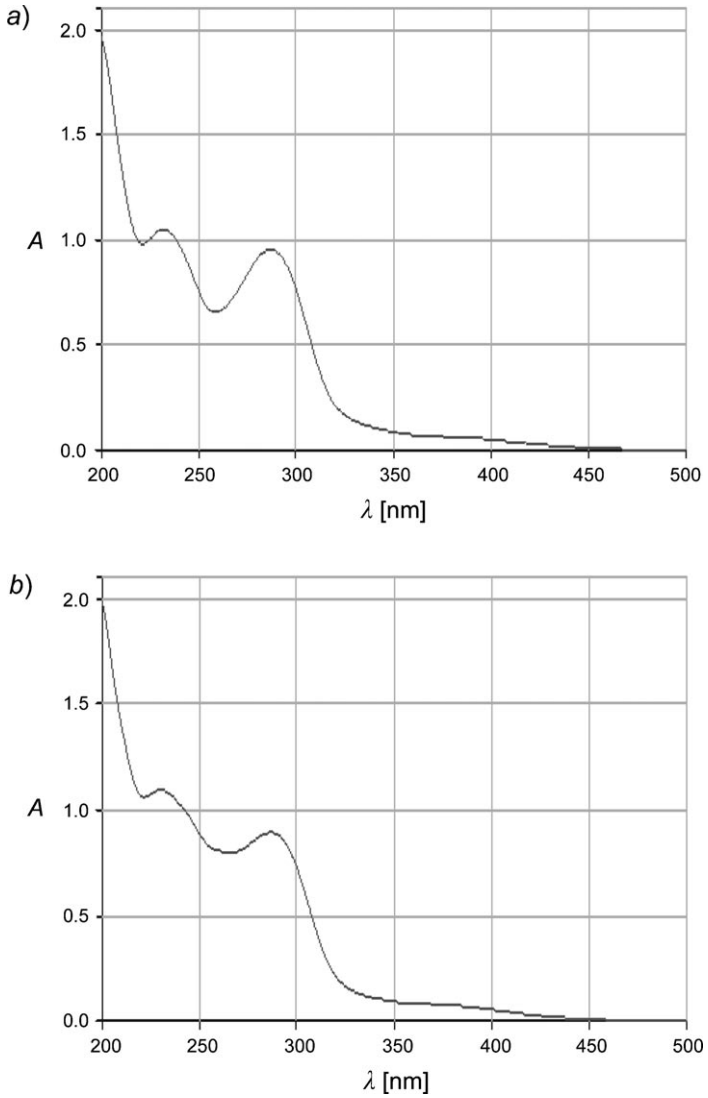


Fig. 2. *UV/VIS Spectra* (hexane) *of* a) **9a** *and* b) **9b**

C(10),C(10a) and C(5a),C(6), respectively. In the **B** conformations, the H-atom of the OH group is pointing toward the C=C bond of the isopropenyl group[2]).

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[2]) There are a number of further conformations of **9a** and **9b** of similar energy and with the O–H bond above the heptalene core or close to the C=C bond of the isopropenyl group. The two of **9a** shown in *Fig. 4* reflect at best the backbone structure of molecules **A** and **B** found in the asymmetric unit of **9a**.

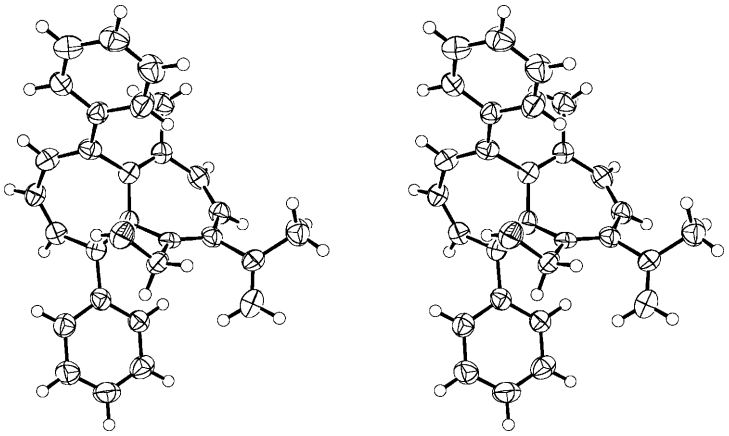


Fig. 3. *Stereoscopic view of the X-ray crystal structure of 2-isopropenyl-5-methyl-6,10-diphenylheptalene-1-methanol* (**9a**)

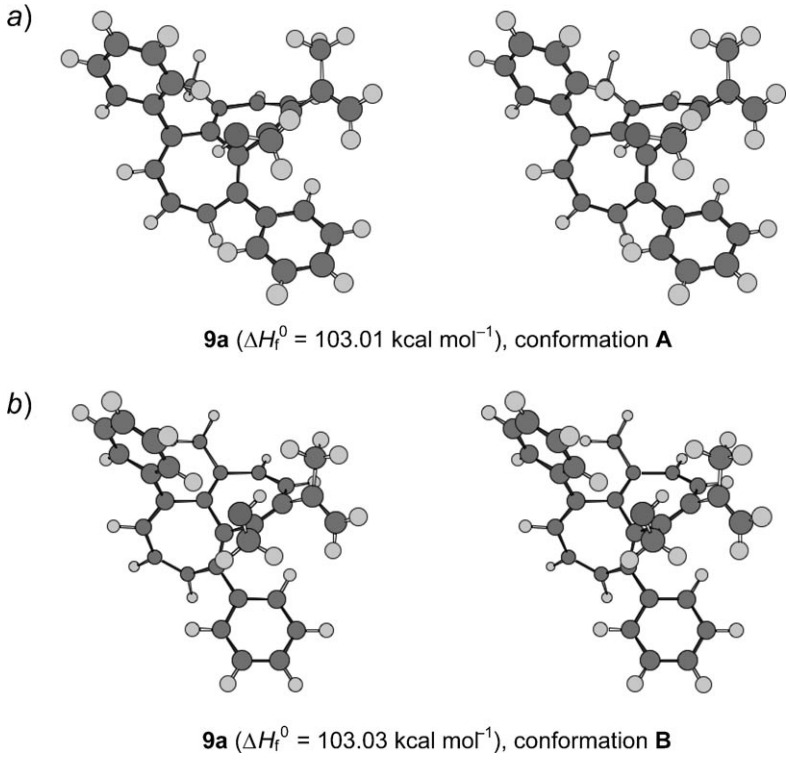


Fig. 4. *Stereoscopic view of the AM1-calculated structure of* **9a** *with the O–H bond oriented* a*) toward the heptalene core and* b*) toward the isopropenyl group*

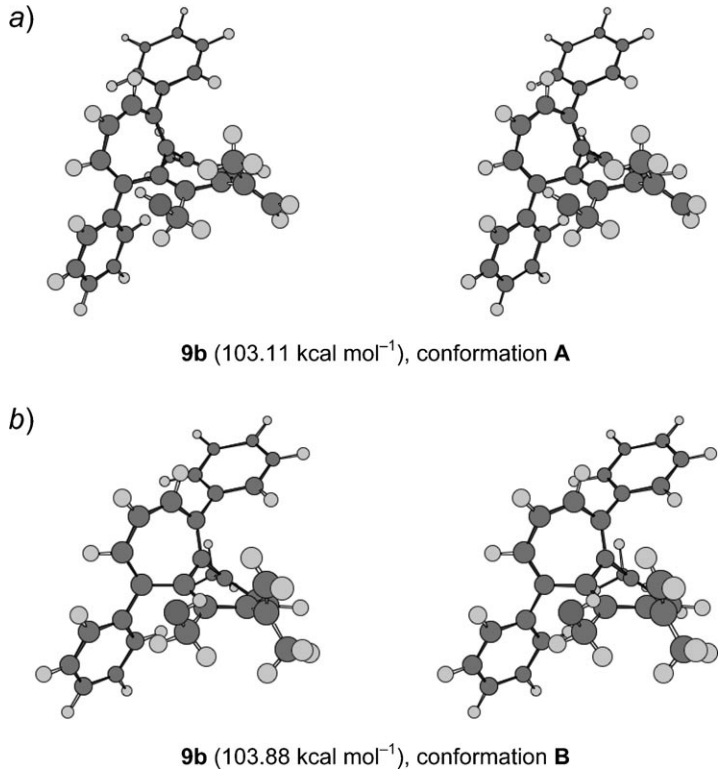


Fig. 5. *Stereoscopic view of the AM1-calculated structure of* **9b** *with the O–H bond oriented* a*) toward the heptalene core and* b*) the isopropenyl group*

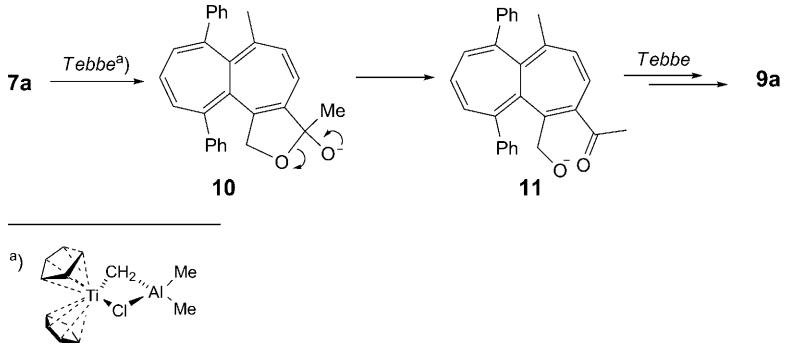
In agreement with the calculated structures for **9a** and **9b** is the fact that both form an 1:1 equilibrium mixture at 60° and both exhibit chemical shifts of the H-atom of the OH group of **9a** and **9b**, which appear in $CDCl_3$ as well as C_6D_6 around δ 1.0 (*cf. Exper. Part*), speaking for intramolecular shielding of the hydroxy H-atom by the surrounding π-systems. Moreover, the above-mentioned *cisoid* torsion angles at the central σ-bond are slightly larger for **9a** than for **9b**, which explains the stronger conjugation of the isopropenyl group with the heptalene core of **9b** in comparison with **9a**.

Regarding the formation of **9a** from furanone **7a** and *Tebbe*'s reagent (*Scheme 3*), it is of interest to note that a Me group must have been transferred from the reagent to the C=O group of the fused lactone, followed, after ring opening, by normal methylenation of the formed MeCO group (*Scheme 4*).

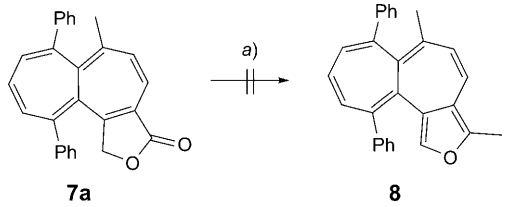
Later on, we also tested the reaction of furan-3-one **7a** with 1 mol-equiv. of *Takai*'s reagent [6] (see *Exper. Part*), which did not lead to the desired 3-methylheptaleno[1,2-*c*]furan **8** either (*Scheme 5*).

We thank our MS department for mass spectra and our NMR department for NMR support and 2D-NMR measurements. The financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Scheme 4



Scheme 5



a) 1 Mol-equiv. of *Takai*'s reagent in 0.5M solution in toluene, r.t., followed by basic workup [6].

Experimental Part

1. *General.* See [1][2]. Compound **4** was available from our previous work [2].

2. *Heptaleno[1,2-c]furans and Heptaleno[1,2-c]furanones.* 2.1. *6-Methyl-7,11-diphenyl-heptaleno[1,2-c]furan-1(3H)-one* (**6a**) *and 6-Methyl-7,11-diphenyl-heptaleno[1,2-c]furan-3(1H)-one* (**7a**). The basic MnO_2 was prepared according to [7]. The thermal 1:2 equilibrium mixture of **4a** and its DBS isomer **4b** (56 mg, 0.147 mmol) was dissolved in AcOEt (100 ml), and a 20–25-fold amount by weight of MnO_2 was added within 30–40 min. After the addition, the mixture was stirred vigorously during 30 min at r.t. (TLC: no dimethanols left). The MnO_2 was filtered off over *Celite* and washed with AcOEt. To the filtrate was added TsOH (15 mg), and stirring was continued overnight. The soln. was washed with a sat. aq. $NaHCO_3$ soln. and dried ($MgSO_4$). CC (silica gel, hexane/Et_2O 1:1) gave two yellow products, **6a** (4 mg, 7%) and **7a** (48 mg, 87%). The products were recrystallized from hexane/Et_2O 1:1 and acetone, resp.

Data of **6a**: M.p. 197–198° (hexane/Et_2O). R_f (hexane/Et_2O 1:1) 0.16. UV/VIS (hexane; *Fig. 1,a*): max. 231 (sh, 1.00), 260 (0.86); min. 249 (0.84), 289 (sh, 0.64). IR (KBr): 3438*w*, 3054*w*, 3018*m*, 2923*m*, 2853*m*, 1757*s*, 1684*m*, 1595*m*, 1491*m*, 1443*m*, 1335*m*, 1243*w*, 1153*m*, 1108*m*, 1076*m*, 1036*m*, 901*w*, 839*w*, 803*w*, 761*m*, 720*m*, 699*s*, 533*w*, 494*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.30 (*d* with f.s., ^3J = 7.2, 2 arom. H); 7.18–7.14 (*m*, 5 arom. H); 7.11 (*t*-like, ^3J = 7.2, 7.4, 1 arom. H); 6.99 (2*d*, ^3J = 7.2, 8.0, 2 arom. H); 6.81 (*d*, ^3J(5,4) = 11.3, H–C(5)); 6.80 (*d*, ^3J(8,9) = 6.2, H–C(8)); 6.63 (*dd*, ^3J(9,10) = 11.4, ^3J(9,8) = 6.3, H–C(9)); 6.49 (*d*, ^3J(4,5) = 11.3, H–C(4)); 6.46 (*d*, ^3J(10,9) = 11.4, H–C(10)); 4.81 (*s*, CH_2(3)); 1.44 (*s*, Me–C(6)). EI-MS (GC): 377, 376, and 375 (9, 31, and 12, $M^{+\bullet}$), 281 (11), 274 (35), 239 (10), 209 (14), 208 (20), 207 (100), 198 (33), 191 (13), 151 (38), 150 (20), 138 (12), 105 (17), 96 (32), 91 (15), 73(22).

Data of **7a**: M.p. 157–158° (acetone). R_f (hexane/Et_2O 1:1) 0.37. UV/VIS (hexane, $c = 0.361 \cdot 10^{-4}$ M; *Fig. 1,b*): max. 234 (0.91), 292 (0.88); min. 223 (0.87), 263 (0.63), 310 (sh, 0.53). IR (KBr): 3486*w*, 3018*w*, 2914*w*, 2861*w*, 1752*s*, 1640*w*, 1596*w*, 1490*m*, 1442*m*, 1374*w*, 1330*m*, 1284*w*, 1270*w*, 1240*w*, 1189*w*, 1144*w*, 1101*w*, 1074*w*, 1048*m*, 1029*s*, 1003*m*, 924*w*, 876*w*, 814*w*, 790*m*, 769*m*, 753*w*, 738*m*, 721*m*,

703*m*, 675*w*, 633*w*, 616*w*, 567*w*, 538*w*, 503*w*, 473*w*. ^{1}H-NMR (600 MHz, $CDCl_3$; in thermal equilibrium with 6% of **7b**): 7.30 (*d* with f.s., $^3J = 7.2$, 2 arom. H); 7.23–7.19 (*m*, 5 arom. H); 7.16 (*t*-like, $^3J = 7.2$, 1 arom. H); 6.97–6.96 (*m*, 2 arom. H); 6.86 (*d*, $^3J(8,9) = 6.2$, H–C(8)); 6.75 (*dd*, $^5J = 0.7$, $^3J(4,5) = 11.3$, H–C(4)); 6.88 (*dd*, $^3J(9,10) = 11.5$, $^3J(9,8) = 6.2$, H–C(9)); 6.69 (*d*, $^3J(5,4) = 11.5$, H–C(5)); 6.42 (*d*, $^3J(10,9) = 11.5$, H–C(10)); 4.16 (*d*, *A* of *AB*, $^2J_{AB} = 17.8$, 1 H, CH_2(1)); 3.91 (*d* with f.s., *B* of *AB*, $^2J_{AB} = 17.8$, 1 H, CH_2(1)); 1.44 (*s*, Me–C(6)). ^{13}C-NMR (125 MHz, $CDCl_3$): 171.81 (*s*); 153.50 (*s*); 139.22 (*d*); 139.31 (*s*); 139.20 (*s*); 138.82 (*s*); 137.76 (*s*); 135.78 (*s*); 134.05 (*d*); 133.52 (*d*); 130.26 (*s*); 129.51 (*s*); 129.31 (*d*, 2 arom. C); 129.27 (*d*, 2 arom. C); 128.90 (*d*, 2 arom. C); 128.62 (*d*); 127.98 (*d*); 127.31 (*d*); 126.17 (*d*, 2 arom. C); 125.20 (*s*); 122.22 (*s*); 68.69 (*t*); 19.36 (*q*). EI-MS (GC): 377, 376, and 375 (17, 57, and 13, $M^{+\bullet}$), 361 (52), 317 (18), 303 (20), 302 (29), 289 (16), 275 (19), 274 (88), 246 (9), 245 (41), 239 (26), 215 (32), 207 (59), 202 (68), 198 (88), 158 (21), 157 (38), 151 (100), 145 (60), 138 (36), 132 (22), 91 (25), 77(14).

*Data of 6-Methyl-7,11-diphenylheptaleno[4,5-*c*]furan-3(1*H*)-one* (**7b**): ^{1}H-NMR (600 MHz, $CDCl_3$; 6% **7b** in the thermal equilibrium mixture with **7a**): identified signals: 6.82 (*d*, $^3J(10,9) = 6.5$, H–C(10)); 6.51 (*dd*, $^3J(9,8) = 11.6$, $^3J(9,10) = 6.5$, H–C(9)); 6.45 (*dq*-like, $^3J(5,4) = 6.8$, $^4J(5,\text{Me–C}(6)) = 1.4$, H–C(5)); 6.42 (*d*, $^3J(8,9) = 11.6$, H–C(8)); 4.39 (*d*, *A* of *AB*, $^2J_{AB} = 13.3$, 1 H, CH_2(1)); 3.94 (*d*, *B* of *AB*, $^2J_{AB} = 13.3$, 1 H, CH_2(1)); 1.70 (*d*-like, $^4J(\text{Me–C}(6),5) \approx 1.3$, Me–C(6)).

2.2. *Methylenation of Heptaleno[1,2-*c*]furan-3-one* **7a** *with* Tebbe*'s Reagent.* Furanone **7a** (25 mg, 0.066 mmol) was dissolved in dry THF (10 ml) and treated with *Tebbe*'s reagent (*Fluka*®; 0.2 ml of a 0.5M soln. in toluene) as described in Exper. 3.1 of [1]. Purification by CC (silica gel, hexane/Et_2O 4:1) gave pure **9a** (15 mg, 58%). When its solution was exposed to daylight for 2 days, the ^{1}H-NMR showed, besides **9a**, the presence of **9b** (*cf. Scheme 3*). The molar ratio **9a**/**9b** was 61:39 in C_6D_6 and 71:29 in $CDCl_3$. The equilibrium mixture **9a**/**9b** in C_6D_6 was rapidly established on heating at 60° for 10 h, leading to a 1:1 ratio of **9a**/**9b**. Both isomers were isolated by CC (silica gel, hexane/Et_2O 4:1).

Data of 5-Methyl-2-(1-methylethenyl)-6,10-diphenylheptalene-1-methanol (**9a**): Yellow crystals. M.p. 112–113° (hexane/Et_2O). R_f (hexane/Et_2O 4:1) 0.18. UV/VIS (hexane; *Fig. 2*,*a*): max. 231 (1.05), 286 (0.95); min. 221 (0.98), 258 (0.65). ^{1}H-NMR (600 MHz, C_6D_6; present with 39% of **9b**): 7.65 (*d* with f.s., $J_o = 8.4$, H_o of Ph–C(6)); 7.28 (*d* with f.s., $J_o = 8.4$, H_o of Ph–C(10)); 7.15–7.03 (arom. H); 7.01 (*tt*, $J_o = 7.4$, $J_m = 1.0$, H_p of Ph–C(10)); 6.82 (*d*, $^3J(7,8) = 6.1$, H–C(7)); 6.56 (*d*, $^3J(9,8) = 11.4$, H–C(9)); 6.51 (*dd*, $^3J(8,9) = 11.5$, $^3J(8,7) = 6.2$, H–C(8)); 6.47 (br. *d*, $^3J(3,4) = 11.8$, H–C(3)); 6.37 (*d*, $^3J(4,3) = 11.7$, H–C(4)); 4.94 (*t*-like, $J = 1.8$, H_{trans} of CH_2=C(Me)–C(2)); 4.86 (*t*-like, $^5J = 1.0$, H_{cis} of CH_2=C(Me)–C(2)); 4.16 (*dd*, *A* of *ABX*, $^2J_{AB} = 12.8$, $^3J_{AX} = 5.5$, 1 H, HOCH_2–C(1)); 3.57 (*dd*, *B* of *ABX*, $^2J_{AB} = 12.8$, $^3J_{BX} = 2.6$, 1 H, HOCH_2–C(1)); 1.82 (*s*, CH_2=C(*Me*)–C(2)); 1.52 (*s*, Me–C(5)); 1.03 (*t*-like, partially covered, $J \approx 5.8$, *H*OCH_2–C(1)). ^{1}H-NMR (600 MHz, $CDCl_3$; present with 29% of its DBS isomer **9b**): 7.47 (*d* with f.s., $J_o = 7.4$, H_o of Ph–C(6)); 7.21 (*t*-like, partially covered, H_m of Ph–C(6)); 7.20–7.15 (arom. H); 7.11 (*d*, superimposed by *d* of **9b**, H_o of Ph–C(10)); 6.94 (*d*, $^3J(7,8) = 6.3$, H–C(7)); 6.63 (*dd*, $^3J(8,9) = 11.6$, $^3J(8,7) = 6.4$, H–C(8)); 6.47 (*d*, $^3J(9,8) = 11.4$, H–C(9)); 6.46 (*s*, $^3J(3,4) \approx 12$, H–C(3,4)); 5.00 (*t*-like, $J = 1.6$, H_{trans} of CH_2=C(Me)–C(2)); 4.67 (*d*-like, $J = 0.9$, H_{cis} of CH_2=C(Me)–C(2)); 3.93 (*dd*, *A* of *ABX*, $^2J_{AB} = 12.7$, $^2J_{AX} = 6.3$, 1 H, HOCH_2–C(1)); 3.33 (*dd*, *B* of *ABX*, $^2J_{AB} = 12.9$, $^2J_{BX} = 4.0$, 1 H, HOCH_2–C(1)); 1.86 (*s*, CH_2=C(*Me*)–C(2)); 1.45 (*s*, Me–C(5)); 0.96 (br. *t*, $J \approx 6$, *H*OCH_2–C(1)). ^{13}C-NMR (125 MHz, C_6D_6; present with 76% of its DBS isomer **9b**): not assigned signals: 134.52 (*d*); 132.86 (*d*); 131.21 (*d*); 130.27, 128.91, 127.51, 127.25, 125.78 (5 × 2 C); assigned signals: 145.19 (*s*, C(1)); 143.35 (*s*, C(2)); 140.66 (*s*, 1 arom. C); 139.80 (*s*, 1 arom. C); 136.75 (*s*, C(6)); 136.37 (*s*, C(10)); 133.51 (*s*, CH_2=*C*(Me)–C(2)); 132.10 (*s*, C(5a)); 131.68 (*s*, C(5)); 115.14 (*t*, *C*H_2=C(Me)–C(2)); 60.36 (*t*, HO*C*H_2–C(1)); 23.60 (*q*, CH_2=C(*Me*)–C(2)); 22.23 (*q*, *Me*–C(5)). EI-MS (GC): 391 and 390 (24 and 75, $M^{+\bullet}$), 375 (20, $[M - \text{Me}]^+$), 331 (19), 317 (27), 289 (16), 273 (69), 252 (18), 239 (40), 215 (34), 212 (47), 202 (17), 197 (100), 165 (21), 164 (29), 163 (46), 151 (53), 145 (30), 138 (22), 115 (20), 92 (30), 91 (92), 77 (19), 57 (21).

Data of 1-Methyl-4-(1-methylethenyl)-6,10-diphenylheptalene-5-methanol (**9b**): Yellow oil. R_f (hexane/Et_2O 4:1) 0.10. UV/VIS (hexane; *Fig. 2*,*b*): max. 229 (1.09), 286 (0.89); min. 221 (1.06), 266 (0.80). ^{1}H-NMR (600 MHz, C_6D_6; present with 61% of its DBS isomer **9a**): 7.60 (*d* with f.s., $J_o = 8.4$, $J_m = 1.3$, H_o of Ph–C(6)); 7.33 (*d* with f.s., $J_o = 8.2$, $J_m = 1.3$, H_o of Ph–C(10)); 7.15–7.03 (arom. H); 6.97 (*tt*, $J_o = 7.3$, $J_m = 1.5$, H_p of Ph–C(6)); 6.71 (*d*, $^3J(7,8) = 6.0$, H–C(7)); 6.67 (*dq*-like, $^3J(3,2) = 6.1$,

^5J(3,Me−C(1)) = 0.7, H−C(3)); 6.58 (*d*, ^3J(9,8) = 11.4, H−C(9)); 6.51 (*dd*, ^3J(8,9) = 11.5, ^3J(8,7) = 6.3, H−C(8)); 6.08 (*dq*-like, ^3J(2,3) = 6.1, ^4J(2,Me−C(1)) = 1.4, H−C(2)); 5.10 (*d*-like, *J* = 1.5, H_{cis} of CH_2=C(Me)−C(4)); 4.94 (*t*-like, *J* = 1.8, H_{trans} of CH_2=C(Me)−C(4)); 4.28 (*dd*, *A* of *ABX*, $^2J_{AB}$ = 12.4, $^3J_{AX}$ = 4.2, 1 H, HOCH_2−C(5)); 4.24 (*dd*, *B* of *ABX*, $^2J_{AB}$ = 12.4, $^3J_{BX}$ = 5.0, 1 H, HOCH_2−C(5)); 1.92 (*s*, CH_2=C(*Me*)−C(4)); 1.55 (*s*, Me−C(1)); 1.02 (*t*-like, partially covered, *J* ≈ 6, *H*OCH_2−C(5)). ^{1}H-NMR (600 MHz, $CDCl_3$, present with 71% of its DBS isomer **9a**): 7.52 (*d* with f.s., J_o = 7.4, H_o of Ph−C(6)); 7.23 (*t*-like, J_o = 7.4, 7.9, H_m of Ph−C(6)); 7.20–7.15 (arom. H); 7.13 (*d*, superimposed by *d* of **9a**, H_o of Ph−C(10)); 6.85 (*d*, ^3J(9,8) = 6.1, H−C(9)); 6.64 (*dd*, ^3J(8,7) = 11.2, ^3J(8,9) = 6.2, H−C(8)); 6.61 (br. *d*, partially covered, ^3J(3,4) ≈ 6, H−C(3)); 6.48 (*d*, ^3J(7,8) = 11.4, H−C(7)); 6.20 (*dq*-like, ^3J(2,3) = 6.0, ^4J(2,Me−C(1)) = 1.3, H−C(2)); 4.96 (*qunit.*-like, *J* = 1.5, H_{trans} of CH_2=C(Me)−C(4)); 4.91 (br. *d*-like, *J* = 1.7, H_{cis} of CH_2=C(Me)−C(4)); 3.97, 3.94 (*AB* of *ABX*, $^2J_{AB}$ = 12.2, $^3J_{AX} \approx {}^3J_{BX}$ = 5, HOCH_2−C(5)); 1.88 (*s*, CH_2=C(*Me*)−C(4)); 1.49 (*s*, Me−C(1)); 0.91 (br. *t*-like, *J* ≈ 6.7, *H*OCH_2−C(5)). ^{13}C-NMR (125 MHz, C_6D_6; present with 24% of its DBS isomer **9a**): 147.94 (*s*, C(4)); 146.44 (*s*, C(5)); 140.42 (*s*, 1 arom. C); 139.54 (*s*, 1 arom. C); 137.61 (*s*, C(1)); 136.26 (*s*, C(10)); 134.95 (*s*, CH_2=*C*(Me)−C(4)); 134.45 (*d*, C(9)); 134.29 (*s*, C(6)); 134.18 (*s*, C(10a)); 132.75 (*s*, C(5a)); 131.47 (*d*, C(8)); 129.89 (*d*, 2 arom. C); 129.42 (*d*, C(3)); 129.17 (*d*, 2 arom. C); 129.02 (*d*, C(2)); 128.33 (*d*, 2 arom. C); 127.95 (*d*, 1 arom. C); 127.76 (*d*, 1 arom. C); 126.47 (*d*, 2 arom. C); 125.71 (*d*, C(7)); 114.83 (*t*, *C*H_2=C(Me)−C(4)); 60.32 (*t*, HO*C*H_2−C(5)); 23.42 (*q*, CH_2=C(*Me*)−C(4)); 22.23 (*q*, *Me*−C(1)). EI-MS (GC): 391 and 390 (5 and 16, $M^{+\bullet}$), 373 (17), 372 (53), 357 (22), 313 (10), 295 (11), 279 (19), 270 (45), 256 (40), 239 (41), 215 (14), 202 (13), 194 (100), 179 (35), 164 (40), 163 (65), 157 (39), 151 (36), 138 (28), 132 (18), 92 (29), 91 (78), 84 (47), 77 (12), 57 (18).

2.3. *Methylenation of Heptaleno[1,2-c]furan-3-one* **7a** *with* Takai*'s Reagent*. The *Takai*'s reagent was prepared as described in [6]. A soln. of $TiCl_4$ (1.0M, 0.4 mmol) in CH_2Cl_2 was diluted with THF (10 ml) at 0°, then *N,N,N′,N′*-tetramethylethylenediamine (= N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine; TMEDA; 0.12 ml, 0.8 mol) and zinc dust (59 mg, 0.9 mmol) were added. After 30 min stirring at 25°, a soln. of furanone **7a** (37.6 mg, 0.1 mmol) and CH_2Br_2 (54 mg, 0.22 mmol) in THF (1 ml) were added. After 3 h, the reaction was quenched with 2M NaOH, the mixture filtered over *Celite*, and the filtrate dried ($MgSO_4$). The solvent was distilled off and the residue subjected to CC (silica gel, hexane/Et_2O 1:1). The results indicated that compound **8** was not formed.

3. *X-Ray Crystal-Structure Determination of Compound* **9a** (*cf. Table* and *Fig. 3*)[3]). All measurements were made with a *Nonius-KappaCCD* area-detector diffractometer [8], graphite-monochromated MoK_α radiation (λ 0.71073 Å), and an *Oxford-Cryosystems-Cryostream-700* cooler. The data collection and refinement parameters are given in the *Table*. Data reduction was performed with HKL DENZO and SCALEPACK [9]. The intensities were corrected for *Lorentz* and polarization effects but not for absorption. The structure was solved by direct methods with SHELXS97 [10], which revealed the positions of all non-H-atoms. There are two symmetry-independent molecules in the asymmetric unit. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher-symmetry space group with the program PLATON [11], but none could be found. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined with a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent atom (1.5 U_{eq} for the Me groups). Refinement of the structure was carried out on F^2 by full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o| - |F_c|)^2$. A correction for secondary extinction was not applied. One reflection, whose intensity was considered to be an extreme outlier, was omitted from the final refinement.

Neutral-atom scattering factors for non-H-atoms were taken from [12a], and the scattering factors for H-atoms were taken from [13]. Anomalous dispersion effects were included in F_c [14]; the values for *f′*and *f″* were those of [12b]. The values of the mass attenuation coefficients are those of [12c]. All calculations were performed with SHELXL97 [15].

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[3]) CCDC-758044 contains the supplementary crystallographic data for this work. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

Table. *Crystallographic Data of* **9a**

Crystallized from	hexane/Et_2O	$F(000)$	832
Empirical formula	$C_{29}H_{26}O$	D_x [g cm^{-3}]	1.179
M_r	390.52	μ(MoK_a) [mm^{-1}]	0.0694
Crystal color, habit	yellow, plate	Scan type	ω
Crystal dimensions [mm]	$0.02 \times 0.12 \times 0.30$	2θ ($_{max}$) [°]	50
Temperature [K]	160(1)	Total reflections measured	26048
Crystal system	monoclinic	Symmetry-independent reflections	4171
Space group	$P2_1$	R_{int}	0.134
Z	4	Reflections with $I > 2\sigma(I)$	2711
Reflections for cell determination	4136	Reflections used in refinement	4170
2θ Range for cell determination [°]	4–50	Parameters refined; restraints	545; 1
Unit cell parameters:		Final $R(F)$ ($I > 2\sigma(I)$ reflections)	0.0788
a [Å]	13.471(1)	$wR(F^2)$ (all data)	0.1758
b [Å]	8.1778(7)	Weights	[a])
c [Å]	20.812(2)	Goodness of fit	1.129
α [°]	90	Final Δ_{max}/σ	0.001
β [°]	106.278(6)	$\Delta\rho$ (max; min) [e Å^{-3}]	0.27; –0.21
γ [°]	90	σ (d (C–C)) [Å]	0.008–0.01
V [Å^3]	2200.8(3)		

[a]) $w = [\sigma^2 (F_o)^2 + (0.0491\ P)^2 + 0.5479\ P]^{-1}$, where $P = (F_o^2 + 2\ F_c^2)/3$.

The diffraction data of **9a** are poor due to very weak diffraction of the available thin-plate crystals and do not allow the structure to be confirmed unambiguously. There are two independent molecules in the asymmetric unit. Molecule A looks to have the expected structure, but molecule B leaves some doubt about the nature of the hydroxymethyl substituent, because the displacement parameters for the hydroxy O-atom are too large, but a disordered model cannot be refined successfully either, leaving doubt about whether the hydroxy O-atom is really an O-atom. The space group permits the compound in the crystal to be enantiomerically pure, but the absolute configuration of the molecules was assigned arbitrarily. The two independent molecules have the same axial chirality. The two independent molecules have similar conformations, except for the 1-methylethenyl substituents which differ by a small twist of *ca.* 33° about the C(2)–C(1″) bond.

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