Synthesis of Benzo[*a*]heptalenes *via* Benzanellation – Aromatization Sequence

by **Ekaterina A. Ochertyanova** and **Hans-Jürgen Hansen***

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

A novel approach towards the synthesis of functionalized benzo[*a*]heptalenes **9** and **10** *via* a 6π-electrocyclic ring closure – aromatization sequence of corresponding bis[prop-2-enoates] **5** and **6** has been developed (*Scheme 1*). The starting bis[prop-2-enoates] have been prepared from the corresponding dialdehydes **3a** and **4a** in a *Wittig-Horner* reaction, and their UV/VIS properties have also been investigated (*Fig. 1* and *Table 1*). The dehydrogenations of the corresponding diols **1** and **2** to dialdehydes with a number of oxidizing reagents, including MnO_2 in CH_2Cl_2, tetrapropylammonium perruthenate (TPAP), and activated DMSO, have been studied in detail.

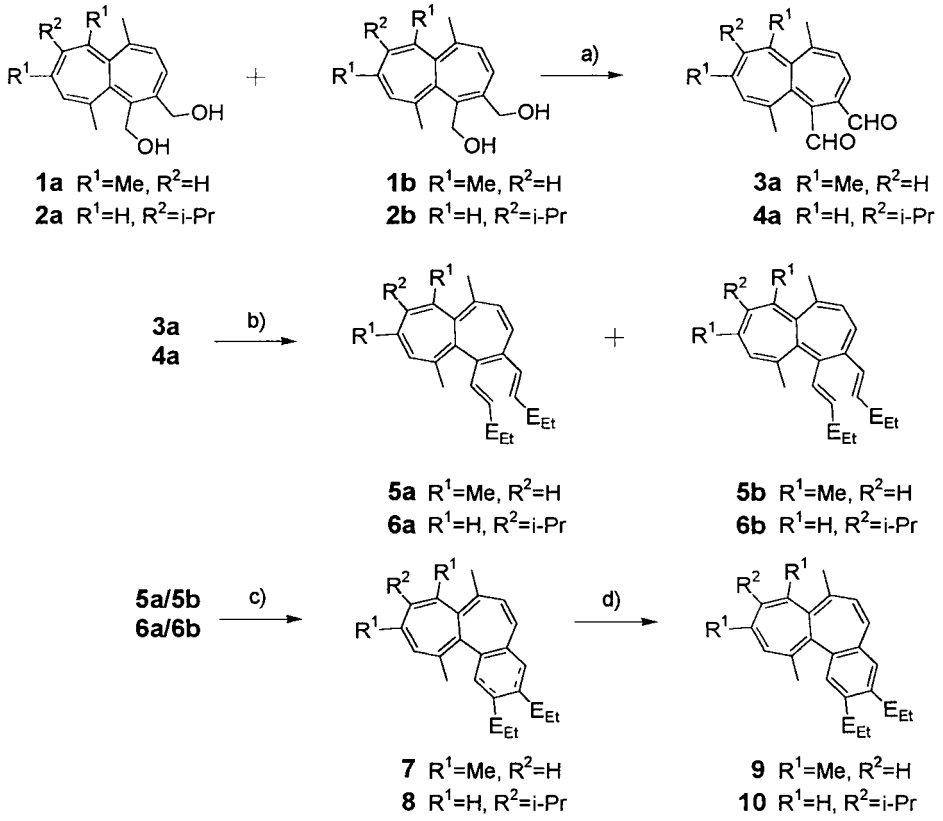
1. Introduction. – So far, benzo[*a*]heptalenes have been synthesized by degradation of colchicinoids [1], by application of *Hafner*'s heptalene synthesis to benz[*a*]azulenes [2][3], or by benzene-ring-forming reaction of heptalene-4,5-dicarboxylates and their derivatives [4][5]. The benzanellation procedures, which have already been tested, are the following: *i*) *Bergman* cyclization of corresponding bis(ethynyl)heptalenes [6] to give benzo[*a*]heptalenes in an overall yield of 6%; *ii*) *Diels-Alder* reaction with heptaleno[1,2-*c*]furans, followed by ring opening of the formed oxabicyclo[2.2.1]heptane substructure [5b][7]; *iii*) 'one-pot' benzanellation procedure, starting directly from heptalene-4,5-dicarboxylates and lithiated methyl sulfones, leading to 3-sulfonyl-substituted benzo[*a*]heptalene-2,4-diols in moderate-to-excellent yields [5].

It has been shown that the thermal electrocyclic ring-closure reaction of azulene-bis[prop-2-enoates] can successfully be applied to the synthesis of benz[*a*]azulenes [8]. We report here on the first results of the utilization of the later benzanellation concept to the synthesis of new functionalized benzo[*a*]heptalenes from the corresponding bis[prop-2-enoates]. A new approach to heptalene-4,5-dicarbaldehydes has also been developed.

2. Results and Discussion. – 2.1. *Synthesis of Heptalene-4,5- and Heptalene-1,2-bis[prop-2-enoates] and Their Conversion to Benzo[*a*]heptalenes.* The starting bis-[prop-2-enoates] **5** and **6** have been obtained from the corresponding dialdehydes **3a** and **4a**, respectively, by a *Wittig-Horner* reaction (*Scheme 1*). The synthesis of the heptalene-4,5-dicarbaldehydes is the key step of the new proposed pathway to benzo[*a*]heptalenes **9** and **10** and will be discussed in *Chapt. 2* in detail. The starting diols **1** and **2** have been obtained by reduction of the corresponding diesters with DIBAH in almost quantitative yields [9].

Reaction of dialdehyde **3a** with diethyl [(ethoxycarbonyl)methyl]phosphonate in THF in the presence of NaH gave the mixture of both double-bond shifted (DBS)

Scheme 1[a])



a) DMSO, $(COCl)_2$, CH_2Cl_2, $-78°$ – r.t. b) $(EtO)_2P(O)CH_2E_{Et}$/NaH in THF, 0–20°. c) 10% Pd/C, decalin, 180–185°, 1 d. d) DDQ, benzene, reflux.

[a]) E_{Et} = COOEt.

isomeric bis[prop-2-enoates] **5a** (8%) and **5b** (86%). The same reaction with **4a** led to the on-state bis[prop-2-enoate] **6a** (23%)[1]). The positions of the C=C bonds in all these bis[prop-2-enoates] have been determined from the observed coupling constants between the H-atoms at adjacent C-atoms in their ^{1}H-NMR spectra, as well as from their distinct UV/VIS properties. For example, the on-state bis[prop-2-enoate] **5a** shows a strong enhancement of the absorption intensity in the region of band III (307 nm) (*Fig. a*, and *Table 1*) as compared to that of the off-state isomer **5b** (*Fig.*, *b*, and *Table 1*). On the other hand, the off-state form **5b** has the maximum of the absorption intensity in the region of band IV (262 nm), where **5a** has a minimum of absorption intensity.

[1]) On-state isomers are represented by structures **a** with conjugation of the two prop-2-enoate side chains with the corresponding heptalene C=C bond, whereas the off-state forms with interrupted conjugation are represented by structures **b**.

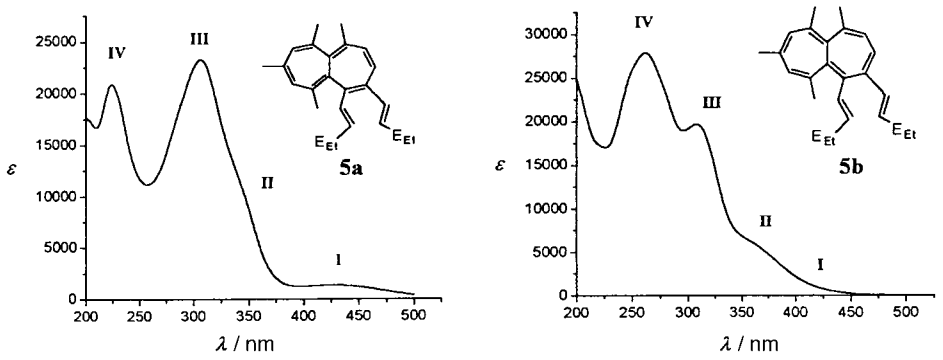


Figure. *UV/VIS Spectra of heptalene-bis[prop-2-enoates]* **5a** *and* **5b**

The opposite situation is observed again in the region of band IV (224 nm). The off-state isomer **5b** exhibits a deep minimum in comparison with the maximum of the absorption intensity of **5a**. The effect of 'through conjugation' is obviously pronounced in the region of band I (400 nm), where the on-state isomer **5a** has a broad and flat absorption maximum (*ca.* 430 nm), while **5b** shows only weak tailing not clearly separated from band II, which appears as a well-recognizable shoulder at 350 nm.

Table 1. *UV/VIS Spectra* (MeCN) *of Heptalene-4,5- and Heptalene-1,2-bis[prop-2-enoates]* **5a**/**5b** *and* **6a**

Compound	λ_{max} [nm]			
	I	II	III	IV
5a	*ca.* 430 (3.14)	347 (sh, 3.97)	306 (4.37)	224 (4.32)
5b	*ca.* 400 (3.33)	350 (sh, 3.83)	307 (4.29)	262 (4.45)
6a	400 (sh, 3.41)	350 (sh, 3.78)	301 (4.07)	220 (4.26)

Heating the off-state bis[prop-2-enoate] **5b** with $PtO_2 \cdot H_2O$ in boiling toluene during 2 h gave the on-state bis[prop-2-enoate] **5a** almost quantitatively (96%), but no other products have been observed. When compound **5a** was heated in decalin at 180–185° in the presence of Pd(10%)/C, electrocyclic ring closure with a subsequent [1,5]-H shift took place, followed by partial dehydrogenation, thus leading to a mixture of dihydrobenzo[*a*]heptalenes **7** (29%) and benzo[*a*]heptalene **9** (51%; *Scheme 1*). The ratio **7**/**9** has been determined by GC/MS measurements. Further aromatization of the mixture **7**/**9** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in boiling benzene gave **9** in 80% yield. It was not possible to separate the mixture **7**/**9** by column chromatography on silica gel, but pure benzo[*a*]heptalene **9** was obtained by preparative MPLC.

The electrocyclic ring closure of bis[prop-2-enoate] **6a** has been achieved in boiling toluene in the presence of Pd/C for 24 h to give again a mixture of dihydrobenzo[*a*]-heptalene **8** (82%) and benzo[*a*]heptalene **10** (17%; *Scheme 1*). The same reaction in decalin at 180–185° gave 71% of **8** and 29% of **10**. Further dehydrogenation of this mixture with DDQ in boiling benzene for 24 h under N_2 gave, after purification by MPLC, **10** in yields of 59–96%. The yield of **10** is strongly depended on the quality of benzene and rather sensitive to the reaction conditions.

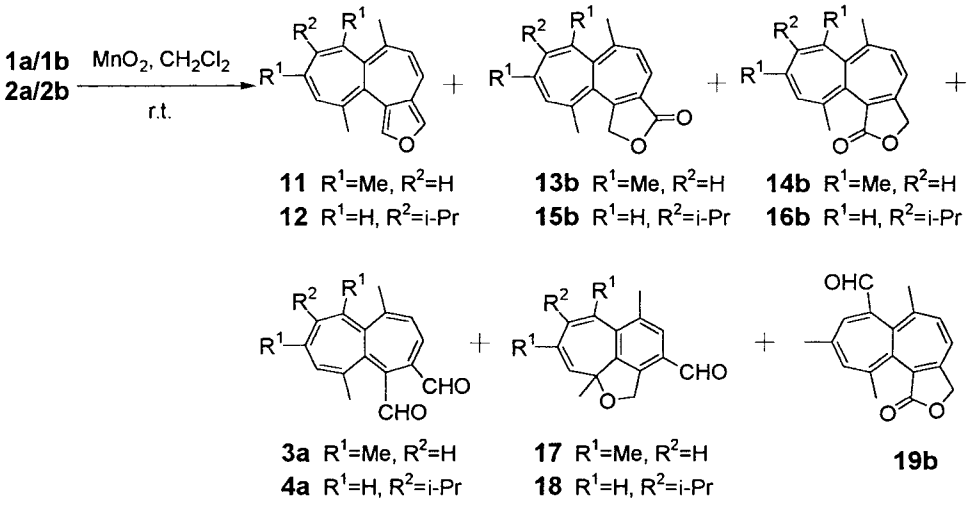
Thus, a novel approach to the synthesis of substituted benzo[*a*]heptalenes *via* thermal electrocyclic ring closure of corresponding bis[prop-2-enoates] followed by aromatization has been developed. The overall yields of benzo[*a*]heptalenes **9** and **10**, obtained from 1,6,8,10-tetramethyl- and 9-isopropyl-1,6-dimethylheptalene-4,5-dicarboxylates in four steps, are 47 and 7%, respectively. The main disadvantage of the novel synthetic pathway is the incomplete dehydrogenation reaction that leads to mixtures of benzo[*a*]heptalenes and their dihydro precursors, which are difficult to separate. This problem may be solved if alkyl substituents are present at C(1) and C(4) of the benzene ring, as has been observed for the dehydrogenation of benz[*a*]azulenes [8]. The synthesis of suitably substituted benzo[*a*]heptalene precursors can be envisaged from the readily available heptalene diesters by MeLi addition, followed by dehydration, and is just under investigation.

2.2. *Synthesis of Heptalene-4,5-dicarbaldehydes.* We have tested the reaction of diols **1** and **2** with some oxidants including MnO_2 in CH_2Cl_2, tetrapropylammonium perruthenate (TPAP), and activated DMSO.

It has been observed [9] that treatment of heptalene-4,5-dimethanol **1a** in CH_2Cl_2 at room temperature with a 20–25-fold amount (by weight) of an old batch of MnO_2 (for details, see [9]) led, after complete conversion of **1a**, to two products, namely the heptaleno[1,2-*c*]furan **11** (45%) and the heptaleno[1,2-*c*]furan-3-one **13b** (53%; *cf. Scheme 2*). The same reaction with the DBS-isomeric heptalene-1,2-dimethanol **1b** gave, in addition to **11** (35%) and **13b** (20%), two other products, namely the heptaleno[1,2-*c*]furan-1-one **14b** (10%) and the heptalene-4,5-dicarbaldehyde **3a** (2%).

We performed the dehydrogenation reaction of **1a** with three types of MnO_2 (A[2]), B[3]), and C[4])) in CH_2Cl_2 for 3–5 h and could isolate all known compounds, as well as

Scheme 2



[2]) Ten-year-old manganese (IV) oxide 'gefällt aktiv', *Merck-Schuchardt.*

[3]) *Ca.* 1–2-year-old manganese (IV) oxide 'gefällt aktiv', *Merck-Schuchardt.*

[4]) *Ca.* 3-year-old manganese (IV) oxide 'gefällt aktiv', *Merck-Schuchardt.*

two new unexpected products **17** and **19b** in each case. The ratio of the products has been determined in case *A* by separation on silica gel, in cases *B* and *C* by GC and GC/MS analyses without separation of each compound from the reaction mixture (*Table 2*). We found that prolongated reaction times lead to the formation of the two new products **17** and **19b**, while the amount of furan **11** strongly decrease (*Table 3*). Also, pure compounds **14b** and **3a** have for the first time been separated and characterized.

Table 2. *Product Composition* [%] *of the Dehydrogenation Reaction of* **1a**/**1b** *with Different Types of* MnO_2[a])

MnO_2	**11**	**13b**	**14b**	**3a**	**17**	**19b**
A	5.2	55.5	8.9	9.1	15.5	4.6
B	4.7	47.5	12	10.2	12.2	13.4
C	3.8	53.2	15.9	10.5	9.9	6.6

[a]) In CH_2Cl_2 at r.t., 3–4 h.

Table 3. *Product Composition of the Dehydrogenation Reaction of* **1a**/**1b** *with* MnO_2 (*A*) *in Dependence of the Reaction Time*

Time [min]	Relative product composition [%]					
	11	**13b**	**14b**	**3a**	**17**	**19b**
9	63	8	3	7	17	0.4
16	47	18	4	10	14	7
25	29	43	3	10	13	0.3
240	5	59	6	15	12	3
300	4	47	8	16	13	4

We had assumed that the initially formed furan **11** would be further transformed to the furan-3-one **13b**. However, the control oxidation reaction of **11** with MnO_2 yielded no **13b**, only decomposition of starting material has been observed.

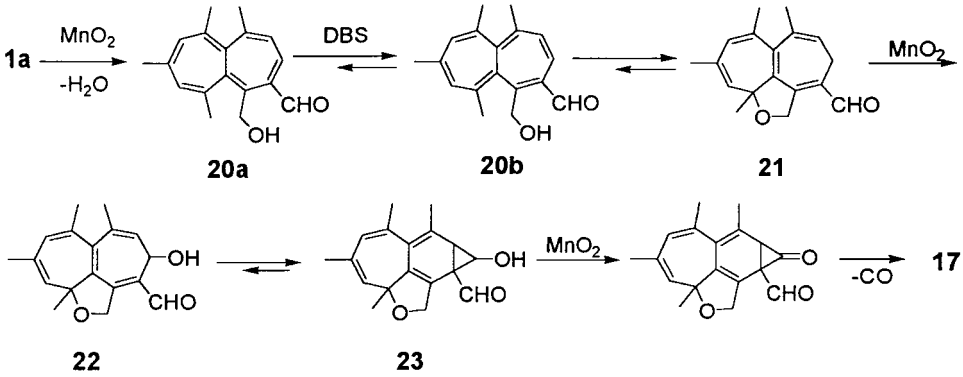
The new compound **19b** exhibited ^{1}H- and ^{13}C-NMR spectra that were closely related with those of **14b**. Extensive ^{1}H-NOE measurements ($CDCl_3$) secured the structure of **19b**, whereby strong reciprocal effects were observed between the signals of Me–C(6) at 1.58 ppm and of the H-atom of the additional CHO group at 9.49 ppm, indicating that Me–C(10) of the starting diol **1a** had been oxidized in the course of the reaction to form the CHO group at C(7) of **19b**.

The structure of the ring-contracted product **17** was mainly deduced from its spectroscopic properties. The mass difference of **17** (*m*/*z* 254) and its precursor **1a** (*m*/*z* 270) indicated the loss of 1 C-atom and 4 H-atoms. The ^{1}H- and ^{13}C-NMR spectra (C_6D_6) revealed the loss of one H–C(sp^2) unit. On the other hand, the presence of one CHO group, as well as a CH_2–O fragment with diastereotropic H-atoms was established by a *s* signal at 9.71 ppm and a *AB* system with $J_{AB} = 14.7$ Hz at 5.59 and 5.54 ppm. The connectivity pattern of **17** followed from a full ^{1}H-NOE analysis (*cf. Exper. Part*) and the observed $^1J(^1H,^{13}C)$ coupling pattern[5]). A possible mechanism for

[5]) The quality of the crystals of **17** was poor. Nevertheless, their X-ray diffraction analysis allowed us at least to secure the basic structure of **17** with an s-*trans* arrangement of the CHO group with respect to C(3)=C(4) bond of the benzene moiety, just as it was revealed by the ^{1}H-NOE measurements in solution. Due to the poor quality of the X-ray results, further details will not be given.

the formation of compound **17** is depicted in *Scheme 3*. Initially, the less-hindered CH_2OH group at C(4) is dehydrogenated by MnO_2 to give the carbaldehyde **20a**, followed by DBS isomerization into **20b**. Then, intramolecular addition of the OH group of CH_2OH at the 'exocyclic' C=C bond of the heptafulvene substructure led to the formation of **21**[6]). Further allylic oxidation would give the cycloheptatrienol **22**, which should be in thermal equilibrium with its bicyclo[4.1.0]hepta-2,4-diene substructure in **23**. The energy requirement for the establishment of such cycloheptatriene-norcardiene equilibria is low [13][14]. Further oxidation of **23** by MnO_2, followed by extrusion of CO, would finally yield the aldehyde **17**.

Scheme 3



To check whether the formation of the unusual aldehyde **17** depends on the substrate and the quality of MnO_2 or not, the dehydrogenation reaction of 9-isopropyl-1,6-dimethylheptalene-4,5-dimethanol (**2a**) with MnO_2 was performed under the same conditions (*Scheme 2*). Dimethanol **2a** reacted with MnO_2 (types *A* and *B*) in CH_2Cl_2 during 4 h to give the new compound **18** as a major product, accompanied by furan **12** and a mixture of furanones **15b** and **16b** with dialdehyde **4a** (*Table 4*). We were not able to isolate any intermediates from the reaction mixture due to their instability or short-

Table 4. *Product Composition of the Dehydrogenation Reaction of* **2a**/**2b** *with* MnO_2 (*A* and *B*) *in Dependence of the Reaction Time*

MnO_2	Product	Reaction time [%]		
		1 h	2 h	4 h
A	**18**	69	58	46
	12	6	2	5
	15b, **16b**, **4a**	16	30	32
B	**18**	69	50	84
	12	8	13	4
	15b, **16b**, **4a**	23	23	7

[6]) A cyclization reaction of this type has already been observed by us (*cf.* Footnote 2 in [12]).

life periods, but we observed the formation of the new aldehyde **18** with the same parent structure as **17** in all cases. Therefore, we have established that electrocyclic ring closure can indeed take place during the dehydrogenation of heptalene-dimethanols with MnO_2, leading to new heptalene carbonyl compounds.

We can conclude that the dehydrogenation reaction of heptalene-1,2- and heptalene-4,5-dimethanols with commercially available MnO_2 for the formation of the corresponding dialdehydes has no synthetic utility because of the large number of products that are formed.

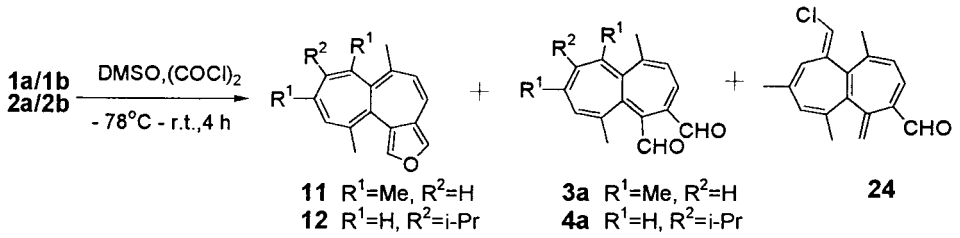
Tetrapropylammonium perruthenate (TPAP) has quite recently been found to be an effective oxidant for alcohols [15]. This reagent is commercially available, catalytic, straightforward to use, and operates at room temperature with good selectivity and without obnoxious or explosive side products. Since the first report in 1987 [16], TPAP has been widely used in synthetic applications, but its full synthetic scope is still developing.

The oxidation of heptalene-4,5-methanol **2a** with TPAP gave furan **12** (6%) and a mixture of furanones **15b** (20%) and **16b** (10%). The latter mixture is rather difficult to separate. We determined the percentage of each furanone on the basis of the integration of characteristic signals in the ^{1}H-NMR spectrum of the crude mixture [17].

Thus, the oxidation of heptalene-4,5-dimethanol **2a** by TPAP did not yield the desired dialdehyde **3a** and led again to a large number of heptalene carbonyl compounds.

The well-known method for dehydrogenation of alcohols to aldehydes with dimethyl sulfoxide (DMSO) activated by oxalyl chloride (*Swern* oxidation [18]) has also been tested for the synthesis of heptalene-4,5-dicarbaldehydes. The reaction of the heptalene-4,5-dimethanol **1a** in a mixture with its DBS isomer **1b** (1 equiv.) with DMSO (4.4 equiv.) activated by oxalyl chloride (2.2 equiv.), followed by treatment with Et_3N (17.8 equiv.) at low temperature yielded the furan **11** (18%) and the desired dialdehyde **3a** (34%; *Scheme 4*).

Scheme 4



Increasing amounts of *Swern* reagent (15 equiv. of DMSO and 7.5 equiv. of oxalyl chloride) led to a remarkable increase of the yield of aldehyde **3a** (65%) and to the appearance of the new product **24** (15%). However, no furan **11** has been obtained in this case. The structure of the anellated bis(heptafulvene) **24** can be interpreted as a chlorinated follow-up product of the dicarbaldehyde **3a**. It was again deduced from a full analysis of the corresponding spectroscopic data of **19b** (*cf. Exper. Part*). The (*E*)-

configuration at the chloromethylidene group at C(10) was finally established by an X-ray crystal-structure analysis[7]).

The furan **12** (16%) and dicarbaldehyde **4a** (32%) were obtained by oxidation of heptalene-4,5-dimethanol **2a** with the established equivalents of *Swern* reagent (4.4 equiv. of DMSO and 2.2 equiv. of oxalyl chloride; *Scheme 4*).

The oxidation of **2a** with 15 equiv. of DMSO and 7.5 equiv. of oxalyl chloride gave furan **12** and dicarbaldehyde **4a** in yields of 6 and 46–60%, respectively. The yields of the products were determined by GC/MS measurements and will be further improved. Unfortunately, we could not obtain chromatographically pure dicarbaldehyde **4a** because of its decomposition during workup and purification. The reason is the extreme sensitivity of **4a** to traces of acids. The treatment of silica gel by Et_3N or the use of alox instead of silica gel did not improve the chromatographic purification. We could just record the ^{1}H- and ^{13}C-NMR spectra of crude **4a**, in which signals of the two CHO groups were found at 9.89 and 9.46 ppm, and 191.03 and 192.12 ppm, respectively. Nevertheless, we could successfully perform the *Wittig-Horner* reaction with the crude dicarbaldehyde **4a** (see *Sect. 2.1*).

In conclusion, it can be said that the *Swern* oxidation can successfully be applied for the preparation of heptalene-4,5-dialdehydes from the corresponding diols in moderate-to-good yields. The reaction conditions and workup should be optimized in accordance with the chemical sensitivity of the substrates.

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

Experimental Part

General. M.p.: *Büchi FP5* melting-point apparatus; not corrected. CC: silica gel *60* (40–63 μm; *Chemie Uetikon* AG). Prep. MPLC: a MPLC instrument with a *Lichroprep Si 60* (*B*) column. Anal. HPLC: *Waters 911* instrument with a photodiode-array detector (optical resolution: ±1.5 nm) with a *Spherisorb CN* column (ODS 5 μm: length 250, diam. 4.6 mm). UV/VIS Spectra: *Perkin-Elmer Lambda 9* instrument or taken as '*ad hoc*' spectra with the photodiode-array detector of the *Waters* HPLC instrument. IR Spectra: *Perkin-Elmer* spectrophotometer, models *FT-IR 1600* and IR '*Spectrum One*'. NMR Spectra: *Bruker ARX-300* or *Bruker AMX-600* spectrometers; assignments of the signals based on additional COSY, NOESY, and ^{1}H,^{13}C-correlation spectra (HSQC and HMBC techniques). MS: *Varian MAT 112S* (chemical ionization (CI)) and *Finnigan MAT SSQ 700* instruments (electron impact ionization (EI); 70 eV), *m/z* (rel. %).

1. *Synthesis of Heptalene-4,5- and Heptalene-1,2-bis[prop-2-enoates]* **5** *and* **6** (*Scheme 1*) *and Their Aromatization into Benzo[*a*]heptalenes* **9** *and* **10**, *Respectively. General Procedure.* NaH (11.3 mmol) was suspended in THF (50 ml) and cooled to 0°. Diethyl [(ethoxycarbonyl)methyl]phosphonate (13.56 mmol) was added, and the mixture was stirred for 1 h at r.t. Then, the soln. of heptalene-4,5-dicarbaldehyde **3a** or **4a** (1.13 mmol) in THF (25 ml) was slowly added at 0°. The mixture was stirred 36 h at r.t. The mixture was poured into H_2O. The aq. layer was extracted with CH_2Cl_2 and dried ($MgSO_4$). After evaporation under reduced

---

[7]) The quality of the crystals was insufficient for an accurate diffraction analysis. Nevertheless, the data allowed us to secure the parent structure of **24** with the (*E*)-configuration at the *exo*-chloromethylidene group and a s-*trans* arrangement of the CHO group with respect to the C(3)=(4) bond. Moreover, AM1 calculations of the structure of **24** indicated that it may occur in two different combinations of the boat-like conformation of the two heptafulvene substructures. The energetically favorable one ($\Delta\Delta H_f^0 = -1.7$ kcal/mol) shows the two methylidene groups in a global *anti* arrangement, whereas the energetically less favorable one exhibits its two methylidene groups in a *syn* fashion. The crystal structure of **24** shows the energetically relaxed *anti* form. Due to the poor quality of the X-ray results, further details will not be given.

pressure, the residue was subjected to CC (silica gel; 10–15% AcOEt in hexane). Starting with **3a**, a first fraction gave the red 'on-state' compound **5a** (34 mg, 8%) and in a second fraction the yellow 'off-state' compound **5b** (0.39 g, 86%).

Starting from crude dicarbaldehyde **4a**, CC afforded after purification bis[prop-2-enoates] **6a** in yields 20–23%.

Data of Diethyl 5,6,8,10-Tetramethylheptalene-1,2-bis[prop-2-enoate] (**5a**): Orange-red crystals (Et_2O/hexane). M.p. 124–126°. UV/VIS (MeCN): λ_{max} 430 (sh, 3.14), 347 (sh, 3.97), 306 (4.37), 224 (4.32); λ_{min} 257 (4.05). IR (KBr): 3392*w* (br.), 2924*s*, 2855*m*, 1704*s*, 1617*m*, 1439*m*, 1366*w*, 1298*s*, 1260*s*, 1175*s*, 1046*m*, 967*m*, 858*m*, 809*m*, 735*w*, 610*w*. ^{1}H-NMR (300 MHz, $CDCl_3$, $\delta(CHCl_3)$ 7.256): 8.02 (*d*, ^3J = 15.6, H–C(2″)); 7.85 (*d*, ^3J = 15.3, H–C(2′)); 6.64 (*d*, ^3J(3,4) = 11.8, H–C(3)); 6.44 (*d*, ^3J)3,4) = 11.9, H–C(4)); 6.18 (*d*, ^3J = 15.6, H–C(1″)); 6.14 (*s*, H–C(9)); 6.09 (br. *s*, H–C(7)); 5.73 (*d*, ^3J = 15.3, H–C(1′)); 4.26 (*q*, ^3J = 7.2, MeCH_2); 4.19 (*q*, ^3J = 7.2, MeCH_2); 2.00 (*d*, ^3J = 1.1, Me–C(8)); 1.89 (*d*, ^3J = 1.2, Me–C(6)); 1.75 (*s*, Me–C(5)); 1.55 (*s*, Me–C(10)); 1.32, 1.28 (*t*, ^3J = 7.2, 2 *Me*CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.16 (2 Me); 17.45 (Me); 17.88 (Me); 21.39 (Me); 24.99 (Me); 60.38 (CH_2); 60.48 (CH_2); 120.46 (CH); 122.21 (CH); 125.02 (C); 127.72 (CH); 128.69 (C); 129.82 (CH); 130.21 (CH); 130.53 (CH); 132.87 (C); 134.12 (C); 137.71 (C); 137.83 (CH); 138.11 (CH); 138.42 (C); 138.84 (C); 139.47 (CH); 166.55 (C=O); 166.89 (C=O).

Data of Diethyl 5,6,8,10-Tetramethylheptalene-4,5-bis[prop-2-enoate] (**5b**): Lemon-colored crystals (Et_2O/hexane). M.p. 131–133°. UV/VIS (MeCN): λ_{max} 350 (sh, 3.83), 307 (4.29), 262 (4.45); λ_{min} 296 (4.28), 226 (4.23). IR (KBr): 3403*w* (br.), 2981*m*, 1713*s*, 1625*s*, 1441*w*, 1366*w*, 1313*s*, 1285*s*, 1168*s*, 1038*m*, 995*m*, 847*w*, 633*w*. ^{1}H-NMR (300 MHz, $CDCl_3$, $\delta(CHCl_3)$ 7.256): 7.41 (*d*, ^3J = 16.2, H–C(2″)); 7.27 (*d*, ^3J = 15.9, H–C(2′)); 6.80 (*d*, ^3J = 5.7, H–C(3)); 6.15 (*d*, ^3J = 5.7, H–C(2)); 6.12 (*s*, H–C(7)); 6.06 (*s*, H–C(9)); 5.72 (*d*, H–C(1′)); 5.67 (*d*, ^3J = 16.2, H–C(1″)); 4.15 (*m*, 2 MeCH_2); 2.04 (*s*, Me–C(8)); 2.02 (*s*, H–C(10)); 1.95 (*s*, Me–C(1)); 1.72 (*s*, Me–C(6)); 1.24 (*m*, 2 *Me*CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 13.94 (Me); 14.11 (Me); 18.33 (Me), 22.75 (Me), 23.45 (Me); 24.71 (Me); 59.97 (CH_2); 60.04 (CH_2); 119.44 (CH); 122.31 (CH); 124.95 (C); 126.05 (CH); 128.94 (C); 129.47 (CH); 129.50 (C); 130.70 (CH); 136.85 (CH); 137.41 (C); 138.48 (C); 140.47 (CH); 145.99 (CH); 146.30 (C); 166.75 (C=O); 166.82 (C=O). EI-MS: 406 (9, $M^{+\bullet}$), 333 (40, $[M - COOEt]^{+\bullet}$), 317 (40), 296 (23), 206 (23), 184 (17), 165 (15), 149 (100).

Data of Diethyl 5,10-Dimethyl-7-(1-methylethyl)heptalene-1,2-bis[prop-2-enoate] (**6a**): Orange crystals (Et_2O/hexane). M.p. 128–130°. UV/VIS (MeCN): λ_{max} 400 (sh, 3.41), 350 (sh, 3.78), 300 (4.05), 220 (4.26). IR (KBr): 3434*m*(br.), 2965*m*, 1715*s*, 1618*w*, 1447*m*, 1369*m*, 1302*m*(br.), 1178*m*, 1132*m*, 1035*m*. ^{1}H-NMR (300 MHz, $CDCl_3$, $\delta(CHCl_3)$ 7.256): 8.00 (*d*, ^3J = 15.8, H–C(2″)); 7.86 (*d*, ^3J = 15.1, H–C(2′)); 6.63 (*d*, ^3J = 11.8, H–C(3)); 6.46 (*d*, ^3J = 11.8, H–C(2)); 6.42 (*AB*, $J_{AB} \approx 12.0$, H–C(7), H–C(8)); 6.17 (*d*, ^3J = 15.8, H–C(1″)); 5.73 (br. *s*, H–C(10)); 5.72 (*d*, ^3J = 15.2, H–C(1′)); 4.26, 4.17 (*2 quint.*, 2 MeCH_2); 2.59 (*sept.*, ^3J = 6.9, Me_2CH); 1.73 (*s*, Me–C(5)); 1.57 (*s*, Me–C(10)); 1.32 (*t*, ^3J = 7.1, *Me*CH_2); 1.26 (*t*, ^3J = 7.2, *Me*CH_2); 1.16, 1.15 (2*d*, ^3J = 6.9, *Me*$_2$CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.11 (Me); 14.18 (Me); 16.53 (Me); 17.23 (Me); 22.71 (Me); 22.93 (Me); 34.89 (CH); 60.27 (CH_2); 60.50 (CH_2); 120.29 (CH); 121.07 (CH); 122.16 (CH); 127.46 (CH); 129.36 (C); 129.77 (C); 131.47 (C); 131.60 (CH); 132.79 (C); 135.25 (C); 135.61 (CH); 137.95 (CH); 138.32 (C); 138.69 (CH); 139.46 (CH); 149.77 (C); 166.53 (C=O); 166.89 (C=O). CI-MS: 421 (30, $[M + 1]^+$), 420 (100, M^+), 380 (14), 352 (16), 347 (34, $[M - COOEt]^+$), 331 (15), 306 (33), 278 (34), 274 (9, $[M - 2$ COOEt]), 259 (20), 231 (26), 215 (41).

2. *Cyclization and Dehydrogenation of* **5** *and* **6**. a) *With* $PtO_2 \cdot H_2O$. The heptalene **5b** (70 mg, 0.17 mmol) and $PtO_2 \cdot H_2O$ (0.04 g) in toluene (10 ml) were heated in a *Schlenk* flask during 2 h under Ar. After cooling to r.t., the solvent was evaporated under reduced pressure. The residue was purified by CC (silica gel; 10% AcOEt in hexane) to give in a first fraction the 'on-state' isomer **5a** (66 mg, 96%) and in a second fraction the starting compound **5b** (4 mg).

b) *With Pd/C. General Procedure.* Compound **5a** in a mixture with its DBS isomer (5%; 85 mg, 0.21 mmol) were heated in decalin (10 ml) at 180–185° during 24 h in the presence of Pd (10%)/C (0.2 g). After cooling to r.t., Pd/C was filtrated. The filtrate was eluted through a silica-gel column first with hexane to remove decalin, and then with 5–10% AcOEt to give in a first fraction benzoheptalene **9** (25.5 mg, 51%) and in a second fraction a mixture of isomers **7** (24.5 mg, 29%).

The same dehydrogenation sequence starting from **6a** gave a mixture of dihydrobenzoheptalene **8** (71%) and benzoheptalene **10** (29%).

c) *Aromatization with DDQ*. The mixture of isomers **7** (17.5 mg, 0.04 mmol) was heated at 58° in dry benzene (5 ml) with DDQ (1.5 equiv.) during 36 h. Then, the solvent was evaporated, and the residue was subjected to CC (silica gel; 10% AcOEt in hexane) to yield **9** (80%) as a first fraction and the starting mixture of **7** as a second fraction (< 10%).

Refluxing the mixture of **8**/**10** in dry benzene during 24 h gave, after separation on MPLC, the benzo[*a*]heptalene **10** in yields of 59–96%.

*Data of Diethyl 7,8,10,12-Tetramethylbenzo[*a*]heptalene-2,3-dicarboxylate* (**9**): Light-yellow crystals (pentane/Et_2O). M.p. 83–85°. UV/VIS (MeCN): λ_{max} 334 (sh, 0.29), 294 (1.37), 249 (sh, 2.06), 225 (2.67); λ_{min} 280 (1.37), 208 (2.28). IR (KBr): 3433*m*, 2981*m*, 2911*m*, 1716*s*, 1598*w*, 1534*w*, 1444*m*, 1369*m*, 1284*s*, 1227*m*, 1175*w*, 1132*m*, 1052*w*, 1025*w*, 929*w*, 847*w*, 786*w*, 742*w*, 608*w*. ^{1}H-NMR (300 MHz, $CDCl_3$, $\delta(CHCl_3)$ 7.256): 7.62 (*s*,H–C(4)); 7.36 (*s*, H–C(1)); 6.85 (*d*, $^3J(5,6) = 11.7$, H–C(5)); 6.35 (*d*, $^3J(5,6) = 11.7$, H–C(6)); 6.18 (*s*, H–C(11)); 6.05 (*s*, H–C(9)); 4.35 (*m*, 2 MeCH_2); 2.03 (*s*, Me–C(10)); 1.92 (*s*, Me–C(8)); 1.74 (*s*, Me–C(7)); 1.60 (*s*, Me–C(12)); 1.37, 1.34 (2*t*, $^3J = 7.2$, 2 *Me*CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.00 (2 Me); 18.04 (Me); 18.79 (Me); 22.87 (Me); 24.89 (Me); 61.38 (CH_2); 61.46 (CH_2); 127.05 (C); 128.84 (CH); 129.38 (CH); 130.43 (CH); 130.49 (CH); 130.80 (C); 131.46 (C); 131.63 (C); 133.75 (C); 134.46 (C); 135.50 (CH); 138.01 (C); 138.86 (C); 139.01 (C); 140.18 (C); 167.10 (C=O); 167.78 (C=O). EI-MS: 405 (33, $[M+1]^{+\bullet}$), 404 (100, $M^{+\bullet}$), 389 (96), 364 (79), 350 (37), 331 (31, $[M-COOEt]^{+\bullet}$), 315 (23), 301 (7), 291 (9). CI-MS: 406 (28, $[M+2]^+$), 405 (100, $[M+1]^+$), 330 (7), 313 (31), 279 (12).

*Data of Diethyl 7,12-Dimethyl-9-(1-methylethyl)benzo[*a*]heptalene-2,3-dicarboxylate* (**10**): ^{1}H-NMR (300 MHz, $CDCl_3$, $\delta(CHCl_3)$ 7.256): 7.60 (*s*, H–C(4)); 7.35 (*s*, H–C(1)); 6.83 (*d*, $^3J(5,6) = 11.9$, H–C(5)); 6.43 (H–C(11), H–C(10)); 6.35 (*d*, $^3J(5,6) = 11.7$, H–C(6)); 5.71 (*s*, H–C(8)); 4.38–4.33 (*m*, 2 MeCH_2); 2.56 (*sept.*, $^3J = 6.9$, Me_2CH); 1.71 (*s*, Me–C(7)); 1.62 (*s*, Me–C(12)); 1.36 (*m*, 2 *Me*CH_2); 1.16, 1.14 (2*d*, $^3J = 6.9$, Me_2CH). CI-MS: 420 (11, $[M+2]^+$), 419 (100, $[M+1]^+$), 391 (28), 313 (11), 279 (15). EI-MS: 420 (7, $[M+2]^+$), 419 (23, $[M+1]^+$), 418 (72, M), 403 (16), 378 (41), 350 (21), 345 (13).

2.1. *Dehydrogenation of Heptalene-4,5-dimethanols* **1** *and* **2** *with* MnO_2 (*Scheme 2*). The starting heptalene-4,5-dimethanols **1a** and **2a** in a mixture with their DBS isomers were synthesized according to the procedure in [9] with yields of 94–96%.

General Procedure. Heptalene-dimethanol **1a** (1.65 g, 6.1 mmol) was dissolved in CH_2Cl_2 (200 ml), and then MnO_2 (42 g; type *A*) was added. The mixture was stirred vigorously during 3–5 h at r.t. MnO_2 was removed by filtration over *Celite* and washed with CH_2Cl_2. The solvent was evaporated, and the residue was purified by FC (silica gel; 10% Et_2O in hexane) to give in a first fraction compound **17** (0.20 g, 13%). A second fraction contained *6,7,9,11-tetramethylheptaleno[1,2-*c*]furan-3-one* (**13b**; 0.76 g, 47%; see data in [9]). A third fraction delivered *1,6,8,10-tetramethylheptalene-4,5-dicarbaldehyde* (**3a**; 0.26 g, 16%) and a forth *6,7,9,11-tetramethylheptaleno[1,2-*c*]furan* (**11**; 0.06 g, 4%; see data in [9]). The fifth fraction yielded *6,7,9,11-tetramethylheptaleno[1,2-*c*]furan-1-one* (**14b**; 0.13 g, 8%) and a last fraction *7-formyl-1,3-dihydro-6,9,11-trimethylheptaleno[1,2-*c*]furan-1-one* (**19b**; 0.07 g, 4%). The ratio of the products was also determined in the course of the reaction by GC/MS measurements (*Tables 2* and *3*).

The same procedure with heptalene-4,5-dimethanol **2** and MnO_2 (*A* and *B*) gave after CC (silica gel; 15–20% Et_2O in hexane) *1,2a-dihydro-2a,7-dimethyl-5-(1-methylethyl)cyclohepta[*bc*][2]benzofuran-9-carbaldehyde* (**18**) in a first fraction, *6,11-dimethyl-8-(1-methylethyl)heptaleno[1,2-*c*]furan* (**12**; see data in [9]) in a second fraction and a mixture of isomeric *6,11-dimethyl-8-(1-methylethyl)heptaleno[1,2-*c*]furan-3-* and *-1-one* (**15b** and **16b**, resp.; see data in [9][17]) in a third fraction. The yields of all products are presented in *Table 4* (GC/MS measurements).

Data of **14b**: Orange-red crystals (Et_2O/hexane). M.p. 184–186°. ^{1}H-NMR (300 MHz, $CDCl_3$, $\delta(CHCl_3)$ 7.26): 6.70 (*d*, $^3J(4,5) = 11.4$, H–C(4)); 6.34 (*d*, $^3J(4,5) = 11.4$, H–C(5)); 6.12 (*s*, H–C(10)); 6.00 (*s*, H–C(8)); 4.94, 4.80 (*AB*, $^3J_{AB} = 16.8$, 2 H–C(3)); 1.98 (*d*, $^3J(10,Me–C(9)) = 1.1$, Me–C(9)); 1.96 (*d*, $^3J(10, Me–C(11)) = 1.3$, Me–C(11)); 1.77 (*s*, Me–C(6)); 1.68 (*s*, Me–C(7)). ^{13}C-NMR (75 MHz, $CDCl_3$): 18.32 (Me); 18.76 (Me); 22.68 (Me); 69.53 (CH_2); 118.70 (C); 120.97 (CH); 122.79 (C); 129.42 (C); 130.47 (CH); 131.04 (CH); 132.20 (C); 133.89 (C); 140.08 (C); 140.49 (C); 143.35 (CH); 159.08 (C); 170.54 (CO). EI-MS: 266 (100, $M^{+\bullet}$), 251 (47, $[M-Me]^{+\bullet}$), 226 (60), 212 (94), 178 (30), 165 (43).

Data of **3a**: Light-orange crystals (Et_2O). M.p. 139–141°. UV/VIS (MeCN): λ_{max} 352 (sh, 3.25), 300 (sh, 3.70), 267 (4.08), 235 (4.12); λ_{min} 254 (4.05), 227 (4.12). ^{1}H-NMR (300 MHz, $CDCl_3$, $\delta(CHCl_3)$ 7.27): 9.92, 9.49 (2*s*, 2 CHO); 7.28 (*d*, $^3J2,3) = 5.8$, H–C(3)); 6.39 (*dd*, $^3J(2,3) = 5.7$, ^3J(Me–C(1),2) = 1.4, H–C(2)); 6.20 (*s*, H–C(9)); 6.17 (*s*, H–C(7)); 2.15 (*d*, $^3J(7,Me–C(6)) = 1.2$, Me–C(6)); 2.06 (*s*, Me–C(8)); 2.05 (*s*, Me–C(1)); 1.79 (*s*, Me–C(10)). ^{13}C-NMR (75 MHz, $CDCl_3$): 18.39 (Me); 23.51 (Me); 24.75 (Me); 25.26 (Me); 125.99 (C); 126.33 (CH); 126.88 (C); 127.43 (C); 130.46 (CH); 130.95 (C); 131.08 (CH); 138.47 (C); 139.42 (C); 143.95 (C); 144.45 (CH); 154.16 (C); 190.32 (CHO); 191.33 (CHO). CI-MS: 284 (9, $[M+NH_4^+]$), 268 (18, $[M+2]^+$), 267 (100, $[M+1]^+$).

*Data of 1,2a-Dihydro-2a,4,6,7-tetramethylcyclohepta[*bc*][2]benzofuran-9-carbaldehyde* (**17**): Light-orange crystals (Et_2O/pentane). M.p. 118–120°. ^{1}H-NMR (600 MHz, C_6D_6): 9.71 (*s*, CHO); 6.96 (*s*, H–C(8)); 6.01

(*s*, H–C(5)); 5.92 (*s*, H–C(3)); 5.59 (*d*, $^3J_{AB}$ = 14.7, H_{endo}–C(1)); 5.54 (*d*, $^3J_{AB}$ = 14.7, H_{exo}–C(1)); 2.10 (*s*, Me–C(7)); 1.97 (*d*, ^3J = 1.3, Me–C(6)); 1.55 (*d*, ^3J = 1.3, Me–C(4)); 1.42 (*s*, Me–C(2a)). ^{1}H-NOE (600 MHz, C_6D_6): 9.71 (CHO) → 6.96 (*s*, H–C(8)); 5.59, 5.54 (*AB*, 2 H–C(1)); 6.96 (H–C(4)) → 9.71 (CHO); 2.10 (*s*, Me–C(7)); 2.10 (Me–C(7)) → 6.96 (*s*, H–C(8)); 1.97 (*d*, Me–C(6)); 1.97 (Me–C(6)) → 1.42 (*s*, Me–C(2a)); 2.10 (*s*, Me–C(7)); 6.01 (*s*, H–C(5)); 1.42 (Me–C(2a)) → 5.54 (*d*, H_{exo}–C(1)); 1.97 (*d*, Me–C(6)); 5.92 (H–C(3)); 5.54 (*d*, H_{exo}–C(1)) → 1.42 (*s*, Me–C(2a)); 9.71 (*s*, CHO); 5.59 (*d*, H_{endo}–C(1)) → 9.71 (*s*, CHO); 5.92 (H–C(3)) → 1.42 (*s*, Me–C(2a)); 1.55 (*d*, Me–C(4)); 1.55 (Me–C(4)) → 5.92 (*s*, H–C(3)); 6.01 (*s*, H–C(5)); 6.01 (H–C(5)) → 1.55 (*d*, Me–C(4)); 1.97 (*d*, Me–C(6)). ^{13}C-NMR (75 MHz, C_6D_6): 20.78 (Me); 21.97 (Me); 22.07 (Me); 24.28 (Me); 71.17 (CH_2); 84.96 (C); 128.73 (C); 129.76 (C); 133.82 (CH); 134.30 (CH); 134.92 (C); 135.31 (C); 136.55 (C); 136.61 (C); 136.99 (CH); 146.95 (C); 191.09 (CHO). CI-MS: 272 (21, $[M+NH_4]^+$), 256 (17, $[M+2]^+$), 255 (100, $[M+1]^+$). EI-MS: 254 (5, M^+), 239 (24, $[M-Me]^+$), 211 (100, $[M-(Me+CO)]^+$), 183 (25), 168 (22).

Data of 1,3-Dihydro-6,9,11-trimethyl-1-oxoheptaleno[1,2-c]furan-7-carbaldehyde (**19b**): Red oil. IR (KBr): 3428*w*, 2974*m*, 2926*m*, 2850*m*, 1686*s*, 1591*m*, 1448*m*, 1361*w*, 1206*w*, 1142*m*, 1082*m*, 1049*m*, 880*m*, 849*m*, 754*m*, 599*w*, 547*w*, 528*w*. ^{1}H-NMR (300 MHz, $CDCl_3$, $\delta(CHCl_3)$ 7.26): 9.49 (*s*, CHO); 7.05 (*s*, H–C(8)); 6.74 (*d*, ^3J(4,5) = 11.4, H–C(5)); 6.50 (*s*, H–C(10)); 6.42 (*d*, ^3J(4,5) = 11.4, H–C(4)); 4.94, 4.86 (*AB*, $^3J_{AB}$ = 17.0, H–C(3)); 2.16 (*d*, ^3J(10,Me–C(9)) = 1.2, Me–C(9)); 1.73 (*s*, Me–C(11)); 1.58 (*s*, Me–C(6)). ^{1}H-NOE (600 MHz, $CDCl_3$): 9.49 (CHO) → 1.58 (*s*, Me–C(6)); 7.05 (*s*, H–C(8)); 7.05 (H–C(8)) → 2.16 (*d*, Me–C(9)); 9.49 (*s*, CHO); 6.74 (H–C(5)) → 1.58 (*s*, Me–C(6)); 6.42 (*d*, H–C(4)); 6.42 (H–C(4)) → 4.94 (*d*, 2 H–C(3)); 6.74 (*d*, H–C(5)); 6.50 (H–C(10)) → 1.73 (*s*, Me–C(11)); 2.16 (*d*, Me–C(9)); 4.94, 4.86 (*AB*, 2 H–C(3)) → 6.42 (*d*, H–C(4)); 2.16 (Me–C(9)) → 7.05 (*s*, H–C(8)); 6.50 (*s*, H–C(10)); 1.73 (Me–C(11)) → 6.50 (*s*, H–C(10)); 1.58 (Me–C(6)) → 9.49 (*s*, CHO); 6.74 (*d*, H–C(5)). ^{13}C-NMR (75 MHz, $CDCl_3$): 18.95 (Me–C(6)); 18.97 (Me–C(11)); 24.12 (Me–C(9)); 69.66 (CH_2); 122.10 (C(4)); 123.14 (C); 124.18 (C); 128.39 (C); 130.08 (C); 133.88 (C); 134.23 (C); 135.24 (C); 138.16 (C(10)); 142.81 (C(5)); 151.43 (C(8)); 159.78 (C); 170.15 (CO); 190.04 (CHO). EI-MS: 280 (14, $M^{+\cdot}$), 265 (31, $[M-Me]^{+\cdot}$), 239 (11), 223 (9, $[M-(CO+CHO)]^{+\cdot}$).

Data of **18**: Light-yellow crystals (Et_2O/pentane). M.p. 92–94°. ^{1}H-NMR (300 MHz, C_6D_6; $\delta(C_6D_5H)$ 7.16): 9.71 (*s*, CHO); 7.03 (*d*, ^3J(8,Me–C(7)) = 0.6, H–C(8)); 6.67 (*d*, ^3J(6,Me–C(7)) = 0.8, H–C(6)); 6.15 (*dd*, ^3J(3,4) = 11.3, ^3J(3,Me–C(2a)) = 0.6, H–C(3)); 5.82 (*d*, ^3J(3,4) = 11.2, H–C(4)); 5.61, 5.50 (*AB*, $^3J_{AB}$ = 15.0, 2 H–C(1)); 2.32 (*sept.*, ^3J = 6.9, Me_2CH); 2.13 (*d*, ^3J(8,Me–C(7)) = 0.8, Me–C(7)); 1.27 (*s*, Me–C(2a)); 1.02, 1.00 (2*s*, Me_2CH). ^{13}C-NMR (75 MHz, C_6D_6): 19.26 (Me); 21.43 (Me); 21.66 (Me); 22.52 (Me); 37.50 (CH); 71.43 (CH_2); 84.56 (C); 120.78 (CH); 121.73 (CH); 130.10 (C); 132.48 (CH); 133.22 (C); 134.63 (C); 137.46 (C); 139.93 (CH); 142.28 (C); 149.52 (C); 190.84 (CHO). CI-MS: 286 (31, $[M+NH_4]^+$), 272 (11, $[M+3]^+$), 270 (19, $[M+1]^+$), 269 (100, M^+), 255 (16).

2.2. *Oxidation of Heptalene-4,5-dimethanol* **2a** *by Tetrapropylammonium Perruthenate* (*TPAP*). *General Procedure* [16]. Solid TPAP (0.03 g, 0.09 mmol) was added in one portion to a stirred mixture of **2a** (0.5 g, 1.76 mmol) with 4-methylmorpholine 4-oxide (NMO) (0.36 g, 2.64 mmol) and powdered 4-Å molecular sieves (500 mg/mmol) in CH_2Cl_2 (5 ml) at r.t. under Ar. After 40 min, the mixture was filtered through a short pad of silica gel and eluted with CH_2Cl_2. Then, the filtrate was evaporated, and the residue was purified by FC (silica gel; 5–10% Et_2O in hexane) to give **12** (25 mg, 6%) and a mixture (0.15 g) of **15b** (20%) and **16b** (10%).

2.3. *Oxidation of Heptalene-1,2- and Heptalene-4,5-dimethanols* **1** *and* **2** *with activated DMSO* (*Scheme 3*). *General Procedure* [18]. Oxalyl chloride (0.35 ml, 4.07 mmol) was added to CH_2Cl_2 (5 ml) in a dry flask under Ar. The stirred soln. was cooled to −78°, and then a soln. of DMSO (0.65 ml, 8.4 mmol) in CH_2Cl_2 (1.3 ml) was added dropwise. The soln. was stirred for 3–5 min, and **1a** (0.5 g, 1.85 mmol) soln. in CH_2Cl_2/DMSO mixture 2:1 (15 ml) was added dropwise. The reaction was allowed to continue for 30 min, and then Et_3N (4.9 ml, 33.7 mmol) was slowly added at −78°. The mixture was stirred for 10 min at −78° and then slowly warmed during 1 h to r.t. After stirring during 3.5 h at r.t., ice-cold H_2O (5 ml) was added, and the aq. layer was extracted with CH_2Cl_2 and dried ($MgSO_4$). The purification by CC (silica gel; 5–20% AcOEt in hexane) gave **3a** (0.17 g, 34%) in a first fraction and heptaleno[1,2-*c*]furan **11** in a second fraction (0.08 g, 18%).

The same reaction with an excess of oxidizing reagents (15 equiv. of DMSO, 7.5 equiv. of oxalyl chloride) led to **3a** (65%) and compound **24** (15%).

Data of 10-(Chloromethylidene)-6,10-dihydro-5-methylidene-1,6,8-trimethylheptalene-4-carbaldehyde (**24**): Limon-yellow crystals (Et_2O/hexane). M.p. 178–180°. UV/VIS (MeCN): λ_{max} 376 (3.46), 299 (3.63), 245 (4.15), 209 (4.19); λ_{min} 342 (3.39), 287 (3.62), 229 (4.07). ^{1}H-NMR (300 MHz, $CDCl_3$, $\delta(CHCl_3)$ 7.26): 9.57 (*s*, CHO); 6.84 (*d*, ^3J(2,3) = 6.07, H–C(3)); 6.48 (*d*, ^3J(2,3) = 6.09, H–C(2)); 6.27 (*s*, H–C(7)); 5.98 (*s*, H–C(9)); 5.54 (*d*, ^3J = 2.1, CH=C(10)); 5.10 (*d*, ^3J = 0.8, 1 H, CH_2=C(5)); 5.08 (*s*, 1 H, CH_2=C(5)); 2.14 (*d*, ^3J = 0.9,

Me–C(1)); 2.04 (d, ^3J = 1.2, Me–C(6)); 2.00 (d, ^3J = 0.7, Me–C(8)). ^{1}H-NOE (600 MHz, $CDCl_3$): 9.57 (CHO) → 6.84 (d, H–C(3)); 6.84 (H–C(3)) → 9.57 (s, CHO), 6.48 (d, H–C(2)); 6.48 (H–C(2)) → 6.84 (d, H–C(3)); 2.14 (d, Me–C(1)); 2.14 (Me–C(1)) → 6.48 (d, H–C(2)); 5.54 (d, CH=C(10)); 5.54 (CH=C(10)) → 2.14 (d, Me–C(1)); 5.10 (1 H, CH_2=C(5)) → 5.08 (s, 1 H, CH_2=C(5)); 5.08 (1 H, CH_2=C(5)) → 5.10 (d, 1 H, CH_2=C(5)), 2.04 (d, Me–C(6)); 2.04 (Me–C(6)) → 5.08 (s, 1 H, CH_2=C(5)), 6.27 (s, H–C(7)); 6.27 (H–C(7)) → 2.04 (d, Me–C(6)), 2.00 (d, Me–C(8)). ^{13}C-NMR (75 MHz, $CDCl_3$): 22.57 (Me–C(8)); 24.24 (Me–C(6)); 26.03 (Me–C(1)); 117.74 (*C*H=C(10)); 121.84 (*C*H_2=C(5)); 123.01 (C(9)); 127.18 (C(2)); 133.62 (C(7)); 135.60 (C(1a)); 136.46 (C(5)); 136.61 (C(8)); 136.77 (C(10)); 138.49 (C(6)); 138.94 (C(4)); 141.44 (C(6a)); 142.21 (C(3)); 147.82 (C(1)); 190.07 (CHO). EI-MS: 286/284 (4/12, $M^{+\cdot}$), 249 (100, $[M - Cl]^+$), 221 (23), 206 (98), 189 (50).

Swern oxidation of **2a**/**2b** afforded, after elution from a small pad (5 cm) of alox, **12** (16%) and **2a** (32%). Dialdehyde **4a** was very unstable. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.89, 9.46 ppm (2*s*, 2 CHO; *cf.* **3a**: 9.92 and 9.49 ppm). ^{13}C-NMR (75 MHz, $CDCl_3$): 192.12, 191.03 ppm (2*s*, 2 CHO; *cf.* **3a**: 191.33 and 190.32 ppm).

REFERENCES

[1] P. Kouroupis, H.-J. Hansen, *Helv. Chim. Acta* **1995**, *78*, 1247.

[2] a) A. J. Rippert, H.-J. Hansen, *Helv. Chim. Acta* **1993**, *76*, 2906; A. Linden, M. Meyer, P. Mohler, A. J. Rippert, H.-J. Hansen, *Helv. Chim. Acta* **1999**, *82*, 2274; b) R. Hunziker, D. Sperandino, H.-J. Hansen, *Helv. Chim. Acta* **1995**, *78*, 772; c) J. Guspanovà, R. Knecht, M. Lagana, C. Weymuth, H.-J. Hansen, *Helv. Chim. Acta* **1997**, *80*, 1375.

[3] M. Yasunami, T. Sato, M. Yoshifuji, *Tetrahedron Lett*. **1995**, *36*, 103.

[4] M. Lutz, A. Linden, K. Abou-Hadeed, H.-J. Hansen, *Helv. Chim. Acta* **1999**, *82*, 372.

[5] a) K. Abou-Hadeed, H.-J. Hansen, *Helv. Chim. Acta* **1997**, *80*, 2535; b) M. Meyer, K. Abou-Hadeed, H.-J. Hansen, *Helv. Chim. Acta* **2000**, *83*, 2383.

[6] K. Abou-Hadeed, *Chimia* **2000**, *54*, 763.

[7] P. Uebelhart, unpublished results.

[8] R.-A. Fallahpour, H.-J. Hansen, *Helv. Chim. Acta* **1995**, *78*, 231.

[9] P. Uebelhart, P. Mohler, R.-A. Fallahpour, H.-J. Hansen, *Helv. Chim. Acta* **1995**, *78*, 1437.

[10] R.-A. Fallahpour, R. Sigrist, H.-J. Hansen, *Helv. Chim. Acta* **1995**, *78*, 1408.

[11] 'Vogel's Textbook of Practical Organic Chemistry', 4th edn., Longman Scientific & Technical, Essex, 1987, p. 302.

[12] P. Uebelhart, A. Linden, H.-J. Hansen, Yu. A. Ustynyuk, O. I. Trifonova, N. G. Akhmedov, V. I. Mstislavsky, *Helv. Chim. Acta* **1999**, *82*, 1930.

[13] G. Maier, *Angew. Chem*. **1967**, *79*, 446; *Angew. Chem.*, *Int. Ed.* **1967**, *6*, 402.

[14] M. Görlitz, H. Günther, *Tetrahedron* **1969**, *25*, 4467.

[15] S. V. Ley, J. Norman, W. P. Griffith, S. P. Marsden, *Synthesis* **1994**, 639.

[16] W. P. Griffith, S. V. Ley, G. P. Whitcombe, A. D. White, *J. Chem. Soc., Chem. Commun*. **1987**, 1625.

[17] J. Guspanovà, Dissertation, University of Zürich, 1999.

[18] a) K. Omura, A. K. Sharma, D. Swern, *J. Org. Chem*. **1976**, *41*, 957; **1976**, *41*, 3329; b) K. Omura, D. Swern, *Tetrahedron* **1978**, *34*, 1651; c) A. J. Mancuso, D. Swern, *Synthesis* **1981**, 165.

Received December 17, 2001