176. New Anellation Methods for the Synthesis of 8*H*-Heptaleno[1,10-*bc*]furans, -pyrroles, and -thiophenes

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Dedicated to *Wolfgang Pfleiderer* on the occasion of his 70th birthday

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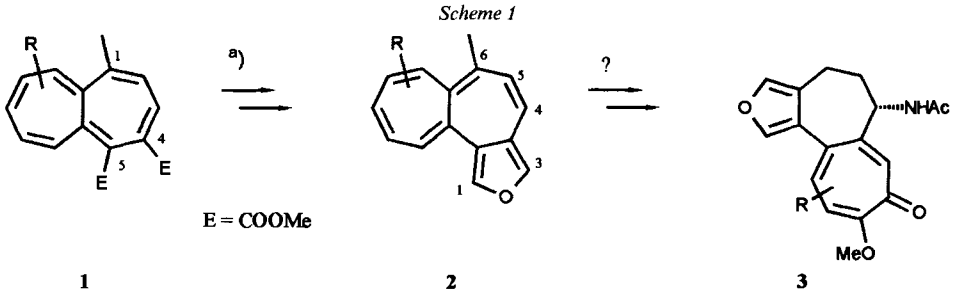
Heptaleno[1,2-*c*]furan-6-carbaldehydes such as **8** or their thiocarbaldehyde or iminomethyl derivatives easily undergo thermal cyclization, followed by a [1,5]-H shift, to give the corresponding heptalenodifurans, thienoheptalenofurans, as well as furoheptalenopyrroles (*cf. Schemes 2* and *3*). Generation of the 6-acetyl derivative of **8** from the corresponding secondary alcohol **15** with 1-hydroxy-1,2-benziodoxol-3(1*H*)-one 1-oxide (IBX) at 0° (*cf. Scheme 4*) leads directly to the formation of the cyclization product **16** which, upon standing at room temperature, undergoes the [1,5]-sigmatropic H-shift to the final difuran **17**. 1-Formylheptalene-4,5-dicarboxylates such as **9** can also be cyclized thermally, followed by the [1,5]-H shift, to the corresponding 8*H*-heptaleno[1,10-*bc*]furan-5,6-dicarboxylate **11**. On thiation with *Lawesson*'s reagent, **9** yields directly the corresponding heptalenothiophene **13** (*cf. Scheme 3*).

1. Introduction. – In the course of our investigations on the formation of heptaleno[1,2-*c*]furans **2** [1], we were interested in their transformation into furano analogues **3** of colchicines (*Scheme 1*). Starting materials for the synthesis of **2** are the corresponding heptalene-4,5-dicarboxylates **1** [1]. Therefore, we aimed at the transformation of the Me group at C(1) of **1** into an aldehyde, acyl, or carboxylic-acid function in order to convert these functional groups into an amino group by standard methods such as *Beckmann*, *Hofmann*, *Lossen*, and *Curtius* rearrangement, or *Schmidt* reaction.

Here, we describe the transformation of the Me group at C(1) of dimethyl 9-isopropyl-1,6-dimethylheptalene-4,5-dicarboxylate (**1**; R = 9-i-Pr and 6-Me) into an aldehyde or Ac function under concomitant conversion of the adjacent ester groups into a

Scheme 1



1 **2** **3**

[a]) See [1].

furano moiety. However, these types of compounds are quite reactive, as we found, since they easily rearrange into heptaleno[1,2-*c*:6,5-*b'c'*]difurans, a reaction that can also be applied for the synthesis of corresponding thienofurans as well as furopyrroles. We report on these syntheses below and will return to the transformation of **2** and **3** in a later publication.

2. Results. – We chose the 1-(chloromethyl)heptalene-4,5-dicarboxylate **4**, which can easily be obtained by base-induced chlorination of the corresponding heptalene **1** [2], as starting material for the introduction of an aldehyde function at C(1). The exchange of the Cl substituent by an AcO group is realized by reaction of **4** with 2 mol-equiv. of AcOK in dimethylsulfoxide (DMSO) at room temperature (*Scheme 2*). The reductive cleavage of the AcO function of **5** takes place smoothly at room temperature in tetrahydrofuran (THF) in the presence of 1.2 mol-equiv. of $Na[BH(OMe)_3]$ to give the corresponding heptalene-1-methanol **6**. On the other hand, when diisobutylaluminum hydride (DIBAH) in hexane/THF at 0° is applied as reducing agent, the heptalene-1,4,5-trimethanol **7** is formed in good yield.

Recently, 1-hydroxy-1,2-benziodoxol-3(1*H*)-one 1-oxide (IBX [3]) has turned out to be an excellent oxidizing agent for the dehydrogenation of primary and secondary alcohols (see [4] and lit. cit. therein). In addition, it has been found that IBX converts 1,4-diols smoothly into corresponding lactols [5], which, in the case of (*Z*)-but-2-ene-1,4-diols as starting materials, lose H_2O to yield directly furans [4]. Indeed, when we treated the trimethanol **7** with 3 mol-equiv. of IBX we killed two birds with one stone that we obtained, in excellent yield, the heptaleno[1,2-*c*]furan-6-carbaldehyde **8** (*Scheme 2*)[1]). The 1-(hydroxymethyl)heptalene-4,5-dicarboxylate **6** gave, when reacted with 1.5 mol-equiv. of IBX, the expected 1-formylheptalene-4,5-dicarboxylate **9**, also in fair yield.

We were surprised when we found that the orange-colored **8**, on standing in solution at room temperature, was slowly transformed into a new, yellow compound. Heating **8** in toluene solution at 130° for 3 h gave, in an almost quantitative yield, the new compound which crystallized in irregular yellow prisms. The new compound, which proved to be the 2*H*-heptaleno[1,2-*c*:6,5-*b'c'*]difuran **10**, displayed a characteristic ^{1}H-NMR spectrum (C_6D_6) with signals of 3 H-atoms in the region of 7 ppm, indicating furano moieties (*cf.* [1]). A just discernible *AB* system at 6.17 ppm with $\delta_A \approx \delta_B$ and $J_{AB} = 11.5$ Hz indicated the presence of two adjacent H-atoms at a heptalene C=C bond. Quite typical was a *triplet* of an olefinic H-atom at 5.37 ppm with $^3J = 6.9$ Hz which was coupled to an *AB* system at 2.48 and 2.31 ppm with poorly resolved coupling patterns. A *singlet* at 1.92 ppm for a Me group and two *doublets* at 1.14 and 1.05 ppm, again with bad resolution and $^3J \approx 6$ Hz, for an i-Pr group with diastereotopic Me residues completed the spectrum. The habitus of the ^{1}H-NMR spectrum revealed an exchange process of diastereotopic sites of the molecule which was still slow at the normal temperature of measurement. Indeed, heating of an NMR probe of **10** in ($^2H_8$)toluene led to a coales-

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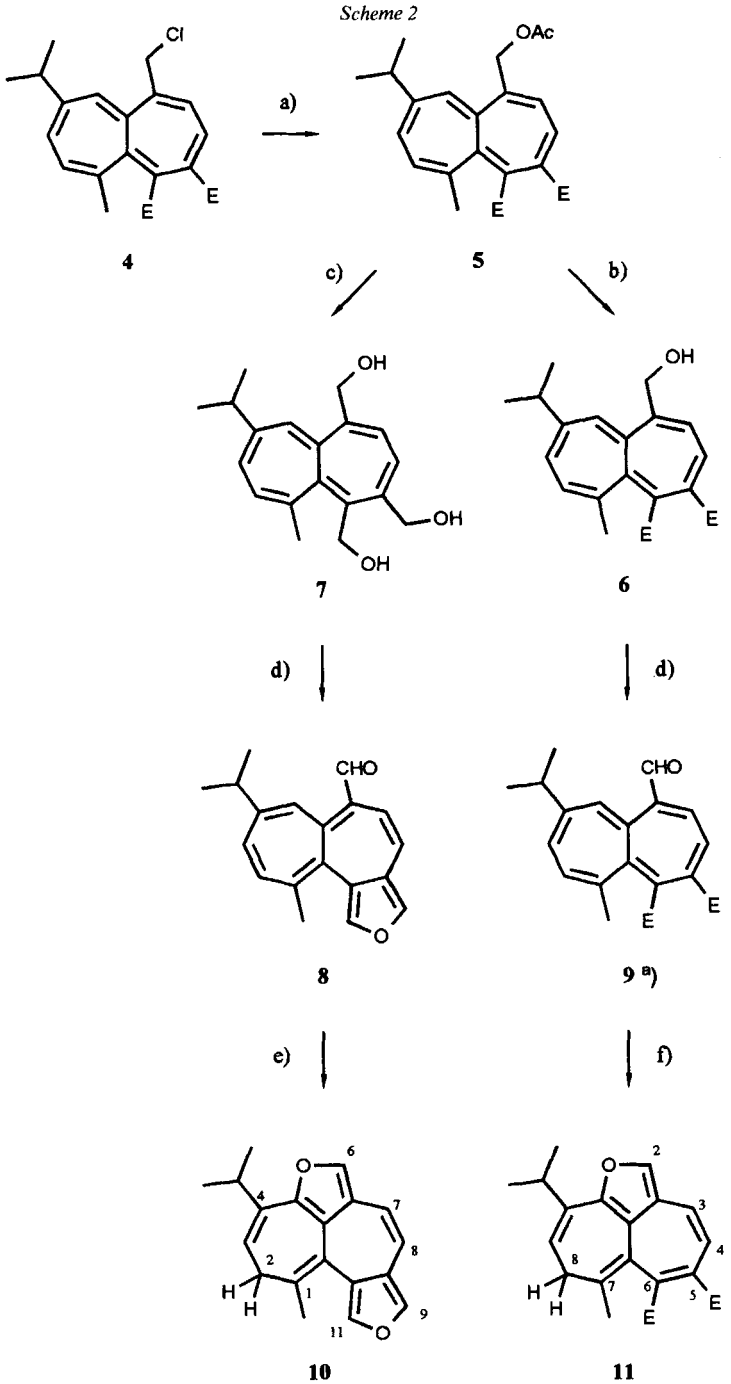
[1]) The reaction of IBX with heptalene-4,5-dimethanols was first studied by *J. Guspanová* in our group who transformed 9-isopropyl-1,6-dimethylheptalene-4,5-dimethanol into the corresponding furan in 70% yield [6]. The dehydrogenation of the same dimethanol with MnO_2 in CH_2Cl_2 gives the furan only in a yield of 28%, since larger amounts of furanones are also formed in this case [1].

Scheme 2



a) AcOK/DMSO, 20°/5 h; 60%. b) Na[B(OMe)$_3$H]/THF, 0°/3 h; 63%. c) DIBAH in hexane/THF, 0°/4 h; 78%. d) 3 (for **7** → **8**) and 1.5 mol-equiv. (for **6** → **9**) of 1-hydroxy-1,2-benziodoxol-3(1*H*)-one 1-oxide (IBX) (*cf.* [3]) in DMSO/acetone, 20°/overnight and 1 h; 79 and 80%, resp. e) Toluene, 130°/3 h; 97%. f) Toluene, 130°/3 d; 74%.

[a]) Compound **9** represents a 9:1 mixture of the two DBS forms (see *Exper. Part*).

cence temperature of *ca.* 320 K for the *AB* system at 2.38 ppm as well as for the signals of the diastereotopic Me groups at 1.08 ppm. At 355 K, a sharp *doublet* was observed for the *AB* system ($^3J = 7.3$ Hz) and for the i-Pr group ($^3J = 7.0$ Hz). The structure of **10** was fully supported by its ^{13}C-NMR spectrum (C_6D_6).

However, the final confirmation of the structure of **10** was provided by the X-ray crystal-structure analysis (*Fig. 1*), showing two independent molecules of **10** in the asymmetric unit (see *Fig. 1,a* and *b*). Both exhibited the largest deviation ($\leq 5°$) in the torsion angles of the i-Pr group in relation to the heptalenofuran core. *Fig. 1* represents both forms as mirror images with respect to the heptalenofuran core that rapidly inverts at temperatures > 320 K as indicated by the exchange dynamics in the ^{1}H-NMR spectrum of **10** in ($^2H_8$) toluene.

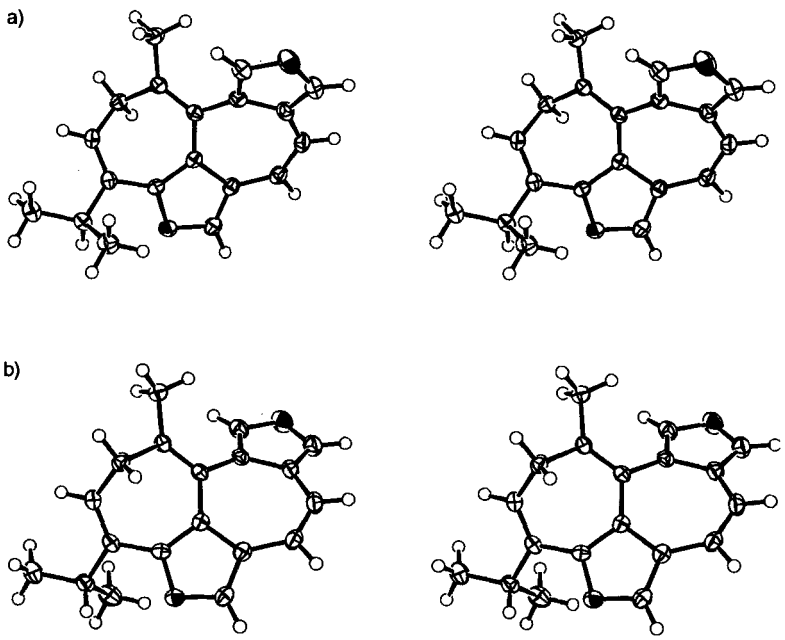
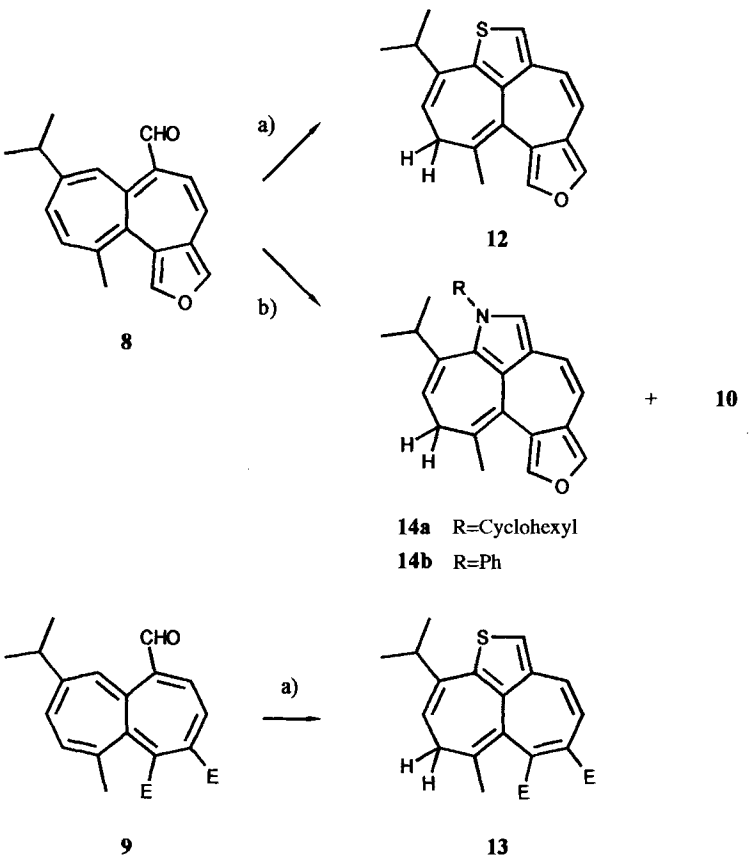


Fig. 1. *Stereoscopic view of the X-ray crystal structure of 4-isopropyl-1-methyl-2*H*-heptaleno[1,2-c:6,5-b'c']-difuran* (**10**) *showing the two independent molecules* (*a* and *b*) *in the asymmetric unit, drawn as mirror images*

In contrast to **8**, the formyl diester **9**, occurring as a 9:1 mixture of two double-bond-shifted (DBS) forms, was thermally stable at room temperature. Nevertheless, prolonged heating at 130° in toluene transformed **9** also into the corresponding 8*H*-heptaleno[1,10-*bc*]furan **11** (*Scheme 2*). The signals for the *AB* system of CH_2(8) at 2.54 and 2.25 ppm appeared in the ^{1}H-NMR spectrum ($CDCl_3$) of **11** as resolved *doublet* of *doublets* with $J_{AB} = 13.2$ and $J_{vic} = 7.8$ and 6.4 Hz. The value of the observed geminal coupling constant is in agreement with those of other cycloheptatriene systems (*cf.* [7]). The i-Pr group of **11** displayed also two well resolved *doublets* at 1.09 and 1.02 ppm for their diastereotopic Me groups.

Treatment of **8** and **9** with *Lawesson*'s reagent [8] in toluene at 110° led to a rapid formation of the corresponding thieno-anellated compounds **12** and **13**, respectively (*Scheme 3*). It is remarkable that the formation of the corresponding thioaldehydes and their cyclization, followed by [1,5]-H shift, proceeded much easier than the cyclization reaction of the starting materials themselves.

Scheme 3



a) 2 Mol-equiv. *Lawesson*'s reagent in toluene at 100°/30 min; 61% (→ **12**) and 68% (→ **13**). b) In a 1:1 mixture of cyclohexylamine/toluene in the presence of catalytic amounts of TsOH and molecular sieve (4 Å) at 110°/75 min, resp., in aniline at 100°/1 h; 53 and 74%, resp. The difuran **10** is formed as side product both in cases, see *Exper. Part.*

Both thieno compounds offered, as expected, very similar ^{1}H-NMR spectra in comparison to the furo systems. However, the thieno analogues displayed much better resolved signal patterns for CH_2(10) and CH_2(8), as well as for the *doublets* of the diastereotopic Me groups of the i-Pr residue. In accordance with these findings are heating experiments of **12** in ($^2H_8$)toluene since no coalescence of the discussed signals was observed at temperatures up to 373 K.

The synthesis of the furoheptalenopyrroles **14** could also be accomplished (*Scheme 3*). When **8** was heated in a 1:1 mixture cyclohexylamine/toluene at 110° in the presence of catalytic amounts of TsOH and molecular sieve, the corresponding 7-cyclohexyl-substituted pyrrole derivative **14a** could be isolated in 53% yield. The difuran formation could not be suppressed completely in this case (*Scheme 3*). Both compounds could be separated by column chromatography on silica gel (see *Exper. Part*). Compound **14a** crystallized in colorless prisms from AcOEt. We established the structure of **14a** also by an X-ray crystal-structure analysis (*Fig. 2*) which revealed again two independent molecules in the asymmetric unit. In this case, both molecules exhibited strong deviations of up to 50° in the torsion angles of the two prochiral groups (cyclohexyl and i-Pr) with respect to the heptalene core. On the other hand, the heptalene skeleton itself showed deviations of the torsion angles of less than 10°.

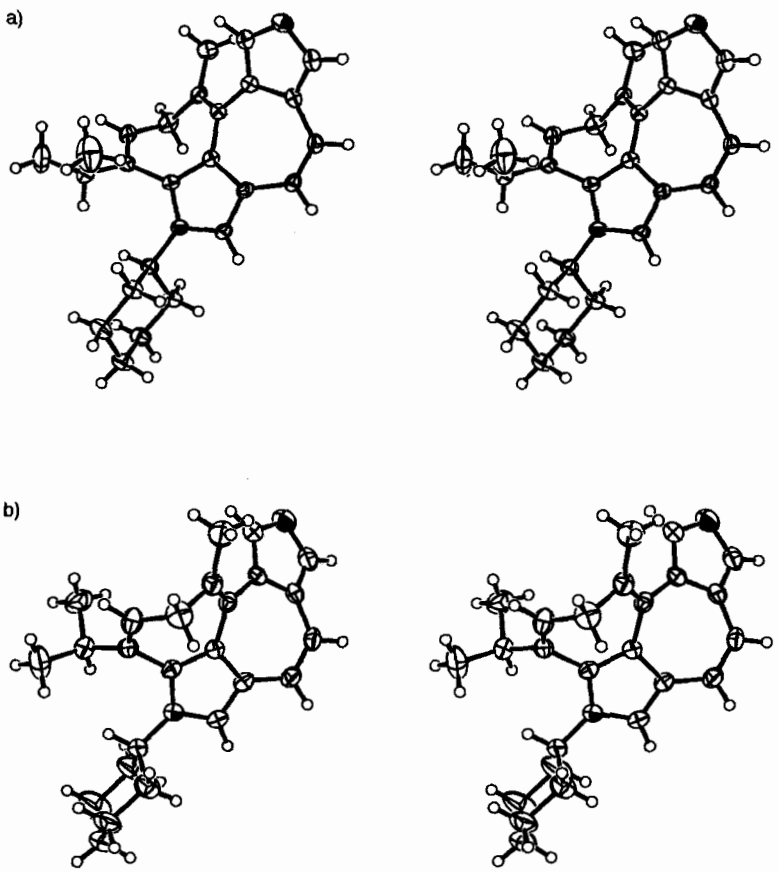


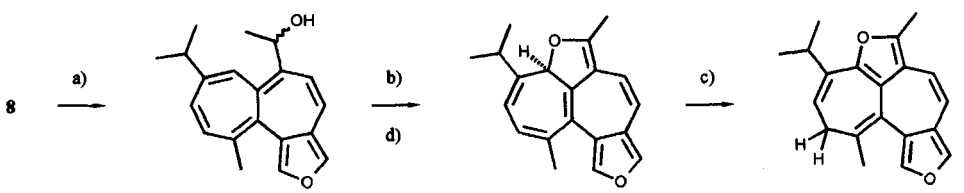
Fig. 2. *Stereoscopic view of the X-ray crystal structure of 5-cyclohexyl-4-isopropyl-1-methyl-2*H,5H*-furo-[3,4:1,2]heptaleno[6,5-*bc*]pyrrole* (**14a**) *showing the two independent molecules* (*a* and *b*) *in the asymmetric unit, drawn as mirror images*

The reaction of **8** with aniline proceeded much more smoothly than with cyclohexylamine. As a result, less difuran formation was observed in this case, and the furopyrrole **14b** was isolated in a yield of 74%.

The ^{1}H-NMR spectrum ($(^2H_8)$toluene) of **14a**, especially with respect to the signals of the *AB* system of CH_2(10) and the signals of the diastereotopic Me groups of the i-Pr residue, showed no coalescence up to temperatures of 373 K.

The cyclization reaction, followed by a [1,5]-H shift is not restricted to molecules of type **8** with a CHO group at C(6) as shown in *Scheme 4*. The reaction of **8** with MeMgI in Et_2O led to a 1:1 mixture of diastereoisomers of the secondary alcohol **15**. According to the rapid double-ring inversion of the heptalene core of **8** at room temperature, one would indeed expect for **15** a thermodynamically controlled mixture of diastereoisomers. Dehydrogenation of **15** with IBX at 0° did not allow isolation of the corresponding 6-acetyl derivative, since it cyclized immediately to the 4a*H*-difuran **16** which was already accompanied by a small amount of the final [1,5]-H-shifted product **17**.

Scheme 4



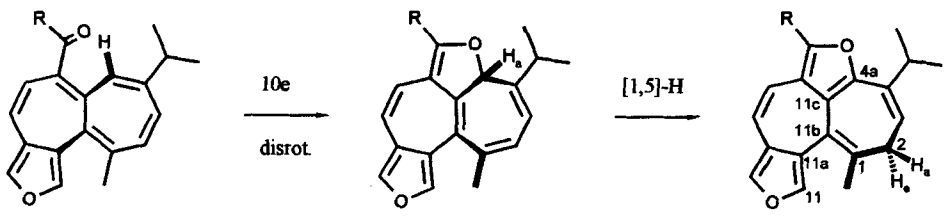
15 **16** **17**

a) 1.5 Mol-equiv. of MeMgI in Et_2O at room temperature/30 min; 71% of a *ca.* 1:1 mixture of diastereoisomers. b) 1.5 Mol-equiv. IBX in DMSO/acetone at 0°/1 h; 33%, plus 7% of **17**. c) Toluene, 20°/4 h; 68%. d) 1.5 Mol-equiv. IBX in DMSO/acetone at 20°/4 h; 43% of **17**.

The structure of the intermediate compound **16** could be deduced unequivocally from its ^{1}H-NMR spectrum (300 MHz, $CDCl_3$). The signals of H–C(2) and H–C(3) of the heptalene core appeared as an *AB* system with J_{AB} = 5.1 Hz, indicating that both H-atoms are separated by a C–C bond. On the other hand, H–C(7) and H–C(8) displayed an *AB* system with J_{AB} = 11.3 Hz as in the starting alcohol **15** (J_{AB} = 11.7 Hz in both diastereoisomers). Of high interest was the fact that the signal of H–C(4a) appeared as a slightly broadened *singlet* at 4.99 ppm. The signal for H–C(4a) of a second diastereoisomer could not be detected. The fact that **16** represented a single diastereoisomer was supported by all the other H-signals of **16** which altogether showed no indication for the presence of a second diastereoisomer. *Dreiding* models of **8** and of its acetyl analogue **18** show that there is indeed only one possible mode of ring closure whereby C(7) of **8** or **18** in the (*M*)-configuration is attacked by the C=O group at C(6) from the backside, in agreement with a disrotatory ring closure of the involved 8-acyl-substituted heptafulvene substructure of **8** and **18** (see *Scheme 5*). The restricted disrotatory ring closure pushes H–C(4a) of the intermediate **16** or **19** in the pseudoaxial position of the formed rigid cycloheptatriene substructure in the boat conformation. The H-atom at C(4a) is, therefore, in an optimal position for the subsequent suprafacial

[1,5]-H shift leading to the observed products **10** and **17**. The defined structure of **16** explains why the [1,5]-H shift already takes place at room temperature, on standing of **16** in toluene solution.

Scheme 5



R = Me: **18**
R = H: **8**

16
19

17
10

The ^{1}H-NMR spectrum of **17** is very similar to that of its 6-demethyl derivative **10**. It showed, however, a distinctly better resolution for the signals of the *AB* system of CH_2(2) at 2.65 and 2.25 ppm, whereby the *B* part was partly covered by the sharp *singlet* of Me–C(6). J_{AB} amounted to 12.9 Hz.

3. Concluding Remarks. – The observed transformations, described above, can be characterized as 10e electrocyclization reactions which should take place thermally in a disrotatory mode as has been found explicitely for the formation of **17**. The fundamental substructures that undergo these reactions are the corresponding 8-acyl-, 8-(thioformyl)-, and (formimino)heptafulvene systems. They all can be regarded as hetero analogues of the 8-vinylheptafulvene system. Except for the thia forms which, as we have shown, are easily available by thiation reactions of the corresponding formyl derivatives with *Lawesson*'s reagent, there are precedents for the electrocyclization reactions.

Thermal cyclizations of the 8-vinylheptafulvene structures which may be regarded as inverse *Hafner-Ziegler* systems [9], important for the synthesis of azulenes (*cf.* [10] and systems discussed there), have been frequently observed. First examples have been investigated by *Prinzbach* and *Herr* [11], as well as by *Mukai* and coworkers [12]. The latter authors also discussed the possibility that [1,5]-H shifts may conclude the thermal cyclization process. A thermal vinylheptafulvene cyclization is also involved as crucial step in the benz[*a*]azulene synthesis of *Wege* and coworkers [13]. Most intensive studies on the chemical behavior of 1,8a-dihydroazulenes have been performed by *Daub et al.* [14] who showed that 2-aryl- or 2-furyl-substituted 1,8a-dihydroazulene-1,1-dicarbonitriles are ideally suited for a set-up of chromogenic systems, since they photochemically undergo ring opening to the corresponding deep-red-colored 8-(1-aryl or 1-furyl-2,2-dicyanoethen-1-yl)heptafulvenes which, on standing in the dark at room temperature, slowly undergo ring closure to the starting compounds.

The recognition of thermal 10e electrocyclization reactions of 8-acylheptafulvene structures to corresponding 8a*H*-cyclohepta[*b*]furans is, in principle, as established as that of the discussed 'all-carba' systems if we take into account the early work of *Proctor* and coworkers [15], and *Nozoe* and *Takahashi* [16] on the base-induced cyclization of

(2-hydroxyphenyl)-substituted tropylium ions. Similar results have been reported later by *Saito* and coworkers [17] on the cyclization of the (diacetyl)methyl-tropylium ion on treatment with base. In line with this work are more detailed studies of *Reichardt et al.* [18] on the thermal behavior of heptafulvene-8,8-dicarbaldehyde which exhibits in solution a solvent-dependent equilibrium with its cyclized form, 8a*H*-cyclohepta[*b*]furan-3-carbaldehyde. In context with our work is the fact of special interest that the equilibrium can be interrupted by admixture of aniline or 4-nitroaniline, since the formed intermediate imino cores irreversibly cyclize at room temperature to give the corresponding 8a*H*-cyclohepta[*b*]pyrrole-3-carbaldehydes which easily undergo follow-up [1,5]-H shifts to their 6*H*-isomers [17]. In full agreement with these results are observations of *Houk* and *Liu* [19] who found that the intramolecular [8 + 2]-cycloaddition reaction of ethyl 6-(heptafulven-8-yl)-6-oxohex-2-enoate in toluene at 170° is heavily competed by the 10e electrocyclization reaction of the 8-acylheptafulvene substructure, followed by a [1,5]-H shift to give finally a corresponding 6*H*-cyclohepta[*b*]furan derivative.

In all the cited cases, there are no direct indications of the stereochemical nature of the 10e electrocyclization step. The configuration of our heptaleno[1,2-*c*]furans (*cf.* also [1]) allows on steric grounds, only a disrotatory ring-closure of their 6-acyl, 6-(thioformyl), or 6-(iminomethyl) substituent, since a conrotatory mode would lead to a highly strained intermediate with H–C(4a) in an equatorial position and, hence, C(11b) of the ring system in the axial position. The ease with which the cyclization reactions take place, especially that of the not isolable 6-acetyl derivative (see *Schemes 4* and *5*), speaks clearly for the disrotatory mode.

We thank Dr. *A. Linden* for the X-ray crystal-structure analyses, Prof. *M. Hesse* and his coworkers for mass spectra, Prof. *W. von Philipsborn* and his coworkers for NMR support and several COSY and NOESY as well as temperature-dependent measurements, and *J. Kessler* for elemental analyses. The financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. TLC: Precoated silica gel TLC sheets $60F_{254}$ from *Merck*. Prep. column flash chromatography (FC): silica gel *C-Gel C-560* (*CU Chemie Uetikon AG*); 0.2 bar. M.p.: *Mettler FP5* (heating rate 2°/min); values uncorrected. UV/VIS: *Perkin-Elmer Lambda 9*; λ in nm (log ε). IR: *Perkin-Elmer FT-IR 1600*. ^{1}H- and ^{13}C-NMR: *Bruker AC 300*, *ARX 300*, and *AMX 600*, δ in ppm rel. to TMS (= 0); J in Hz. MS: *Finnigan MAT SSQ 700* (EI at 70 eV).

1. 4-Isopropyl-1-methyl-2*H*-heptaleno[1,2-*c*:6,5-*b'c'*]difuran (10). – 1.1. *Dimethyl 1-(Acetoxymethyl)-9-isopropyl-6-methylheptalene-4,5-dicarboxylate* (**5**). A soln. of *dimethyl 1-(chloromethyl)-9-isopropyl-6-methylheptalene-4,5-dicarboxylate* (**4**) [2] (0.46 g, 1.22 mmol), AcOK (0.26 g, 2.65 mmol), and abs. DMSO (20 ml) was stirred at r.t. for 5 h under N_2, then diluted with Et_2O (50 ml), and washed with sat. NaCl soln. (3 × 50 ml). The aq. phases were re-extracted with Et_2O (2 × 50 ml), the combined org. layers dried (Na_2SO_4), and evaporated. FC (15 g of silica gel, 2 × 11 cm; hexane/AcOEt 5:1 (100 ml), 4:1 (100 ml)) gave 0.29 g (0.73 mmol, 60%) of **5**, which crystallized from Et_2O. Orange needles. M.p. 104°. R_f (hexane/AcOEt 3:1): 0.25, R_f (hexane/AcOEt 1:1): 0.70. UV (EtOH): λ_{max} 326 (sh with tailing, 3.50), 278 (4.12), 251 (4.21), 208 (4.43); λ_{min} 274 (4.12) 241 (4.20). IR (KBr): 2955*m*, 1732*s*, 1684*w*, 1577*w*, 1457*w*, 1435*m*, 1385*w*, 1362*w*, 1250*s*, 1228*s*, 1194*m*, 1160*m*, 1088*m*, 1037*m*, 986*w*, 792*w*, 751*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.54 (br. *d*, $^3J(2,3)$ = 6.1, H–C(3)); 6.37 (*dt*-like, $^3J(2,3)$ = 6.1, ^4J(H–C(2),CH_2–C(1)) = 1.3, H–C(2)); 6.30 (*d*, $^3J(7,8)$ = 6.6, H–C(8)); 6.15 (*dd*-like, $^3J(7,8)$ = 6.6, ^4J(H–C(7), Me–C(6)) = 1.2, H–C(7)); 5.84 (*s*, H–C(10)); 4.71 (*dt*-like, *A* of *ABXY*, $^2J_{AB}$ = 14.6, $^4J_{AX}$ = $^5J_{AY}$ = 1.3, 1 H, CH_2); 4.62 (*dt*-like, *B* of *ABXY*, $^2J_{AB}$ = 14.6, $^4J_{AX}$ = $^5J_{AY}$ = 1.3, 1 H, CH_2); 3.72, 3.71 (2*s*, 2MeOCO); 2.49 (*sept.*, Me_2CH); 2.08 (*s*, $MeCOOCH_2$); 2.01 (*d*-like, ^4J(H–C(7),Me–C(6)) = 1.2, Me–C(6)), 1.09, 1.05 (2*d*, J = 6.9, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.20 ($MeCOOCH_2$); 167.66, 167.16 (2 MeOCO); 148.23 (C(9)); 145.02

(C(6)); 140.38 (C(1)); 138.81 (C(3)); 133.73 (C(4)); 128.54 (C(5a)); 127.67 (C(7)); 126.93 (C(2)); 126.72 (C(10a)); 126.24, 126.04 (C(8), C(10)); 123.25 (C(5)); 66.24 (CH_2); 52.22, 52.12 (2 *Me*OCO); 35.64 (Me_2CH); 23.05, 22.48 (Me_2CH); 20.80 (*Me*–C(6)). CI-MS (NH_3): 416 (18, $[M + NH_4]^+$), 340 (21, $[(M + 1) - MeOCO$ or $MeCOO]^+$), 339 (100, $[M - MeOCO$ or $MeCOO]^+$). Anal. calc. for $C_{23}H_{26}O_6$ (398.46): C 69.33, H 6.58; found: C 69.28, H 6.53.

1.2. *9-Isopropyl-6-methylheptalene-1,4,5-trimethanol* (**7**). To a 1M DIBAH soln. in hexane (55 ml), **5** (3.43 g, 8.6 mmol) in abs. THF (20 ml) was added at 0° under N_2. The mixture was stirred at 0° for 4 h under N_2, then the reaction was stopped under ice-cooling with 1M HCl soln. (55 ml), diluted with AcOEt (500 ml) and washed with sat. NaCl soln. (3 × 300 ml). The aq. phases were re-extracted with AcOEt (3 × 100 ml), the combined org. layers dried (Na_2SO_4) and evaporated. The resulting oil was crystallized after treatment with CH_2Cl_2 and recrystallized from EtOH (2.00 g, 78%). Yellow crystals. M.p. 162°. R_f (CH_2Cl_2/MeOH 9:1): 0.38. UV (EtOH): λ_{max} 300 (sh with tailing, 3.52), 251 (4.34), 204 (4.39); λ_{min} 227 (4.07). IR (KBr): 3312*s* (OH), 2956*s*, 1648*w*, 1604*w*, 1485*w*, 1444*s*, 1381*m*, 1329*m*, 1240*w*, 1107*m*, 1084*s*, 1058*s*, 1016*s*, 986*s*, 915*s*, 855*s*, 839*m*, 817*m*, 794*w*, 765*w*, 713*s*, 673*m*, 615*m*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 6.46 (*d*, $^3J(2,3) = 6.4$, H–C(3)); 6.19 (*d*, $^3J(2,3) = 6.4$, H–C(2)); 6.07 (*m*, H–C(7), H–C(8)); 5.63 (*s*, H–C(10)); 5.19, 4.93, 4.62 (3*t*, 3 OH); 4.35–3.85 (*m*, 3 CH_2OH); 2.36 (*sept.*, Me_2CH); 2.06 (*s*, Me–C(6)); 1.00, 0.96 (2*d*, $J = 6.8$, Me_2CH). ^{13}C-NMR (75 MHz, (D_6)DMSO): 147.72 (C(9)); 143.21 (C(6)); 139.90, 134.54, 133.07 (C(1), C(4), C(5)); 131.74, 129.23 (C(5a), C(10a)); 127.65, 126.67, 123.66, 123.59, 122.97 (C(2), C(3), C(7), C(8), C(10)); 63.86, 63.72, 57.16 (3 CH_2OH); 38.60 (Me_2CH); 24.15 (*Me*–C(6)); 22.82, 22.55 (Me_2CH). CI-MS (NH_3): 318 (3, $[M + NH_4]^+$), 301 (3, $[M + 1]^+$), 283 (100, $[M - OH]^+$). Anal. calc. for $C_{19}H_{24}O_3$ (300.40): C 75.97, H 8.05; found: C 75.71, H 7.98.

1.3. *8-Isopropyl-11-methylheptaleno[1,2-c]furan-6-carbaldehyde* (**8**). After stirring a soln. of 1-hydroxy-1,2-benziodoxol-3(1*H*)-one (IBX [3]; 0.700 g, 2.5 mmol) in DMSO (10 ml)/acetone (5 ml) for 1 h at r.t., **7** (0.250 g, 0.83 mmol) was added, whereby the color of the soln. changed from yellow to red. The mixture was stirred overnight leading to a yellow suspension. The reaction was stopped with H_2O (5 ml), the suspension filtered, the filtrate diluted with Et_2O (50 ml) and washed with sat. NaCl soln. (2 × 200 ml). The aq. phases were re-extracted with Et_2O (2 × 50 ml), the combined org. layers dried (Na_2SO_4) and evaporated. Purification by FC (15 g of silica gel, 2 × 11 cm; hexane (100 ml), hexane/AcOEt 95:5 (100 ml), 9:1 (100 ml)) led to 0.183 g (0.66 mmol, 79%) of **8**. Orange oil. R_f (hexane/AcOEt 5:1): 0.58. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.03 (br. *s*, CHO); 7.46 (*d*, $^4J(1,3) = 1.5$, H–C(3)); 7.19 (*dd*, $^4J(1,3) = 1.5$, $^5J(1,4) = 0.6$, H–C(1)); 6.73 (*d*, $^3J(4,5) = 11.7$, H–C(4)); 6.54 (*AB*, $^3J_{AB} = 11$, H–C(9), H–C(10)); 6.46 (*d*, $^3J(4,5) = 11.7$, H–C(5)); 5.31 (*s*, H–C(7)); 2.65 (*sept.*, Me_2CH); 2.00 (*s*, Me–C(11)); 1.19, 1.17 (2*d*, $J = 4.7$, Me_2CH). ^{1}H-NMR (300 MHz, (D_6)DMSO): 9.89 (br. *s*, CHO); 7.79 (*d*, $^4J(1,3) = 1.5$, H–C(3)); 7.62 (br. *d*, $^4J(1,3) = 1.5$, H–C(1)); 6.74 (*d*, $^3J(4,5) = 11.7$, H–C(4)); 6.58 (*AB*, $^3J_{AB} = 10$, H–C(9), H–C(10)); 6.54 (*s*, H–C(7)); 6.28 (*d*, $^3J(4,5) = 11.7$, H–C(5)); 2.64 (*sept.*, Me_2CH); 1.81 (*s*, Me–C(11)); 1.11, 1.08 (2*d*, $J = 7.3$, Me_2CH).

1.4. *Thermal Rearrangement of* **8** *into* **10**. In a closed vessel, **8** (0.555 g, 2.0 mmol) was stirred in dry toluene (3 ml) under N_2 at 130° for 3 h. The solvent was evaporated and the residue submitted to FC (10 g of silica gel, 2 × 8 cm; hexane (50 ml), hexane/AcOEt 30:1 (50 ml)) yielding 0.538 g (1.9 mmol, 97%) of **10**. Yellow irregular prisms from Et_2O. M.p. 87°. R_f (hexane/AcOEt 9:1): 0.77. UV (EtOH): λ_{max} 374 (sh, 4.13), 237 (4.35); λ_{min} 215 (4.22). IR (KBr): 3135*w*, 2958*m*, 2868*w*, 1582*w*, 1533*w*, 1450*w*, 1406*w*, 1308*m*, 1141*s*, 1059*m*, 1010*m*, 863*m*, 863*m*, 852*s*, 810*m*, 792*s*, 766*m*, 595*m*. ^{1}H-NMR (600 MHz, (D_6)benzene): 7.07 (*d*, $^4J(9,11) = 1.6$, H–C(9)); 7.02 (*s*, H–C(6)); 7.01 (*d*, $^4J(9,11) = 1.6$, H–C(11)); 6.17 (*AB*, $^3J_{AB} = 11.5$, H–C(7), H–C(8)); 5.37 (*t*, $^3J(2_{ax}, 3) \approx {}^3J(2_{eq}, 3) \approx 6.9$, H–C(3)); 2.90 (*sept.*, $J = 6.8$, Me_2CH); 2.48, 2.31 (2*m*, 2 H–C(2)); 1.92 (*s*, Me–C(1)); 1.14, 1.05 (2 br. *d*, $J = 6.0$, Me_2CH). ^{13}C-NMR (150 MHz, (D_6)benzene): 154.49 (C(4a)); 142.15 (C(11)); 140.94 (C(9)); 138.60 (C(4)); 138.21 (C(6)); 132.00 (C(1)); 127.26 (C(11c)); 124.43 (C(8a)); 123.93 (C(6a)); 123.29 (C(11b)); 120.15 (C(11a)); 119.33 (C(7)); 119.28 (C(8)); 118.04 (C(3)); 36.34 (C(2)); 30.98 (Me_2CH); 23.62 (*Me*–C(1)); 23.10, 21.58 (Me_2CH). CI-MS (NH_3): 279 (100, $[M + 1]^+$). Anal. calc. for $C_{19}H_{18}O_2$ (278.35): C 81.99, H 6.52; found: C 81.66, H 6.69.

The structure of **10** was confirmed by an X-ray crystal-structure analysis (*cf. Fig. 1* and *Sect. 7*).

2. 4-Isopropyl-1,6-dimethyl-2*H*-heptaleno[1,2-*c*:6,5-*b'c'*]difuran (17). – 2.1. *1:1 Mixture of the 1'-Epimers of* (MP)*-6-(1-Hydroxyethyl)-8-isopropyl-11-methylheptaleno[1,2-c]furan* (**15a**/**15b**). From Mg (for *Grignard* reaction; 0.105 g, 4.32 mmol) and MeI (0.27 ml, 4.32 mmol) in abs. Et_2O (1 ml), a soln. of MeMgI was prepared. Aldehyde **8** (0.800 g, 2.87 mmol) in abs. Et_2O (1 ml) was added within 30 min. A white precipitate was formed. After stirring for 30 min, the reaction was stopped with sat. NH_4Cl soln. and diluted with Et_2O (50 ml). The org. layer was washed with sat. NaCl soln. (2 × 50 ml), and the aq. phases were re-extracted with Et_2O (2 × 50 ml). The combined org. layers were dried ($MgSO_4$) and evaporated. After purification by FC (20 g of silica gel, 3 × 6 cm; hexane/AcOEt 8:1 (100 ml), 7:1 (100 ml)) and co-evaporation with CH_2Cl_2, 0.600 g (2.03 mmol, 71%) of **15a**/**15b**

were obtained. Yellow foam. R_f (toluene/AcOEt 9:1): 0.24. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.43 (br. *s*, H–C(3)); 7.16 (*2d*, $^4J(1,3) = 1.5$, H–C(1) of **15a/15b**); 6.73 (*2d*, $^3J(4,5) = 11.7$, H–C(4) of **15a/15b**); 6.44 (*m*, H–C(9), H–C(10)); 6.21 (*d*, $^3J(4,5) = 11.7$, H–C(5)); 5.62, 5.89 (*2s*, H–C(7) of **15a/15b**); 4.97, 4.85 (*2q*, $J = 6.5$, MeCH(O*H*) of **15a/15b**); 2.53 (*sept.*, Me_2CH); 1.90, 1.86 (*2s*, Me–C(11) of **15a/15b**); 1.22–1.11 (*m*, Me_2CH, *Me*CH(OH)); the ratio of integration of the signals of **15a** and **15b** amounted in all cases to 1:1. CI-MS (NH_3): 295 (15, $M^{+\cdot}$), 277 (100, $[M - OH]^+$).

2.2. *4-Isopropyl-1,6-dimethyl-4a*H*-heptaleno[1,2-c:6,5-b'c']difuran* (**16**). After stirring a mixture of IBX (0.503 g, 1.8 mmol), DMSO (5 ml), and acetone (5 ml) for 30 min at r.t., the soln. was cooled to 0° and the mixture of **15a/15b** (0.348 g, 1.18 mmol) added. The mixture was stirred for 1 h at 0°. Then, the reaction was stopped with H_2O (5 ml), the suspension filtered, the filtrate diluted with Et_2O (50 ml) and washed with sat. NaCl soln. (3 × 50 ml). The aq. phases were re-extracted with Et_2O (2 × 50 ml), the combined org. layers were dried ($MgSO_4$) and evaporated. The residue was submitted to FC (10 g of silica gel, 2 × 7 cm; hexane (25 ml), hexane/AcOEt 99:1 (25 ml), 98:2 (25 ml), 97:3 (25 ml), 96:4 (25 ml), 9:1 (25 ml)). With hexane/AcOEt 97:3, 0.025 g (0.086 mmol, 7%) of **17** were obtained. Hexane/AcOEt 96:4 and 9:1 eluted 0.114 g (0.34 mmol, 33%) of **16**. Yellow oil. R_f (toluene/AcOEt 9:1): 0.58. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.02 (*dd*, $^4J(9,11) = 1.6$, $^5J(8,11) = 0.7$, H–C(11)); 7.00 (*d* $^4J(9,11) = 1.6$, H–C(9)); 6.21 (*dq*, $^3J(2,3) = 5.1$, ^4J(H–C(2),Me–C(1)) = 1.2, H–C(2)); 5.73 (*AB*, $^3J_{AB}$ = 11.3, H–C(7), H–C(8)); 5.55 (*dsext.*-like, $^3J(2,3) = 5.1$, ^4J(H–C(4a), H–C(3)) ≈ $^4J(Me_2CH$–C(4), H–C(3)) ≈ ^5J(Me–C(1), H–C(9)) ≈ 1.1, H–C(3)); 4.99 (br. *s*, H–C(4a)); 2.45 (*sept.*, $J = 6.8$, Me_2CH); 2.16 (*t*-like, Me–C(1)); 2.01 (*s*, Me–C(6)); 1.11, 0.99 (*2d*, $J = 6.8$, Me_2CH).

2.3. *Thermal Rearrangement of* **16** *into* **17**. The 4a*H*-isomer **16** (0.100 g, 0.34 mmol) was stirred at r.t. in dry toluene (1 ml) under N_2 for 4 h. The solvent was evaporated and the residue submitted to FC (10 g of silica gel, 2 × 8 cm; hexane (25 ml), hexane/AcOEt 99:1 (25 ml), 98:2 (25 ml), 97:3 (25 ml), 96:4 (25 ml)) to give 0.068 g (0.23 mmol, 68%) of **17**. R_f (toluene/AcOEt 9:1): 0.80, (hexane): 0.29. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.28 (*d*, $^4J(9,11) = 1.5$, H–C(9)); 7.16 (*d*, $^4J(9,11) = 1.5$, H–C(11)); 6.32 (*d*, $^3J(7,8) = 11.3$, H–C(8)); 6.27 (*d*, $^3J(7,8) = 11.3$, H–C(7)); 5.33 (*t*, $^3J(2_{ax}, 3) \approx {}^3J(2_{aq}, 3) \approx 7.2$, H–C(3)); 2.77 (*sept.*, $J = 6.8$, Me_2CH); 2.65 (*dd*, $^2J(2_{ax}, 2_{eq}) = 12.9$, $^3J(2_{eq}, 3) = 7.9$, H_{eq}–C(2)); 2.26 (*s*, Me–C(6)); *ca.* 2.25 (*dd*, partially covered, H_{ax}–C(2)); 2.10 (*s*, Me–C(1)); 1.10, 0.97 (*2d*, $J = 6.8$, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 151.45 (C(4a)); 146.63 (C(6)); 141.67 (C(11)); 140.38 (C(9)); 138.14 (C(4)); 131.05 (C(1)); 127.47 (C(11c)); 123.90 (C(8a)); 122.93 (C(11b)); 119.91 (C(7)); 119.41 (C(11a)); 117.64 (C(6a)); 117.30 (C(3)); 116.44 (C(8)); 36.22 (C(2)); 30.44 (Me_2CH); 23.62 (*Me*–C(1)); 22.98, 21.51 (Me_2CH); 11.70 (*Me*–C(6)). EI-MS: 292 (50, $M^{+\cdot}$), 277 (29, $[M - Me]^+$), 249 (100, $[M - i\text{-}Pr]^+$).

2.4. *Formation of* **17** *Directly from* **15a/15b**. After stirring a soln. of IBX (0.030 g, 0.11 mmol), DMSO (1 ml), and acetone (1 ml) for 30 min at r.t, the mixture of **15a/15b** (0.020 g, 0.068 mmol) was added. The mixture was stirred for 4 h at r.t. The reaction was then stopped with H_2O (1 ml), the suspension filtered, the filtrate diluted with Et_2O (20 ml) and washed with sat. NaCl soln. (3 × 20 ml). The aq. phases were re-extracted with Et_2O (2 × 20 ml). The combined org. layers were dried ($MgSO_4$) and evaporated. Purification by FC (3 g of silica gel, 1 × 9 cm; hexane (10 ml), hexane/AcOEt 99:1 (10 ml), 98:2 (10 ml)) led to 0.008 g (0.029 mmol, 43%) **17** as a pale-yellow oil.

3. 4-Isopropyl-1-methyl-2*H*-thieno[4,2:5,6]heptaleno[1,2-*c*]furan (12). – In a closed vessel, **8** (0.100 g, 0.36 mmol) and *Lawesson*'s reagent (0.290 g, 0.72 mmol) were stirred in dry toluene (6 ml) under N_2 at 110° for 30 min. The solvent was evaporated and the residue submitted to FC (10 g of silica gel, 2 × 8 cm; hexane (25 ml), hexane/AcOEt 99:1 (25 ml), 98:2 (25 ml), 97:3 (25 ml)) and gave 0.065 g (0.22 mmol, 61%) of **12**. Pale-yellow oil. R_f (hexane): 0.74. UV (EtOH): λ_{max} 350 (very br. sh, 3.25), 275 (4.34), 241 (4.42), 224 (4.42), 208 (4.53); λ_{min} 257 (4.31), 226 (4.41). IR (KBr): 2957*s*, 1643*w*, 1537*m*, 1444*m*, 1363*w*, 1303*w*, 1219*w*, 1135*m*, 1052*s*, 989*m*, 881*s*, 797*s*, 650*w*, 595*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.36 (*d*, $^4J(9,11) = 1.7$, H–C(9)); 7.14 (*d*, $^4J(9,11) = 1.7$, H–C(11)); 6.94 (*s*, H–C(6)); 6.51 (*d*, $^3J(7,8) = 11.4$, H–C(7)); 6.40 (*d*, $^3J(7,8) = 11.4$, H–C(8)); 5.69 (*t*, $^3J(2_{ax}, 3) \approx {}^3J(2_{eq}, 3) \approx 7.1$, H–C(3)); 2.69 (*sept.*, $J = 6.8$, Me_2CH); 2.62 (*dd*, $^2J(2_{ax}, 2_{eq}) = 12.7$, $^3J(2_{eq}, 3) = 7.7$, H_{eq}–C(2)); 2.24 (*dd*, $^2J(2_{ax}, 2_{eq}) = 12.7$, $^3J(2_{ax}, 3) = 6.5$, H_{ax}–C(2)); 2.15 (*s*, Me–C(1)); 1.22, 0.99 (*2d*, $J = 6.8$, Me_2CH). ^{13}C-NMR (150 MHz, $CDCl_3$): 142.11 (C(4a)); 141.59 (C(4)); 141.04 (C(11)); 140.93 (C(11c)); 139.70 (C(9)); 138.47 (C(6a)); 137.03 (C(1)); 124.78 (C(7)); 123.67 (C(11b)); 123.56 (C(8a)); 120.90 (C(3)); 120.82 (C(11a)); 120.34 (C(6)); 117.70 (C(8)); 34.96 (C(2)); 34.41 (Me_2CH); 23.33, 21.37 (Me_2CH); 22.68 (*Me*–C(1)). CI-MS (NH_3): 295 (100, $[M + 1]^+$), 294 (12, $M^{+\cdot}$), 279 (8, $[M - Me]^+$), 251 (7, $[M - i\text{-}Pr]^+$). Anal. calc. for $C_{19}H_{18}OS$ (294.42): C 77.51, H 6.16; found: C 77.50, H 5.99.

4. 2*H*,5*H*-Furo[1,2:3,4]heptaleno[6,5-*bc*]pyrroles 14. – 4.1. *5-Cyclohexyl-4-isopropyl-1-methyl-2*H,5H*-furo[3,4:1,2]heptaleno[6,5-*bc*]pyrrole* (**14a**). In a closed vessel, **8** (0.090 g, 0.32 mmol), a catal. amount of TsOH, some molecular sieve, and cyclohexylamine (1 ml, 8.7 mmol) were stirred in dry toluene (1 ml) under N_2 at 110°

for 75 min. The solvent was evaporated and the residue submitted to FC (10 g of silica gel, 2 × 8 cm; hexane (25 ml), hexane/toluene 9:1 (25 ml), 7:1 (40 ml), 5:1 (60 ml), 3:1 (40 ml)). With hexane/toluene 7:1, **10** was eluted (0.026 g, 0.093 mmol, 29%), with hexane/toluene 5:1 and 3:1 followed **14a** (0.061 g, 0.17 mmol; 53%) as colorless solid, which was recrystallized from AcOEt. Colorless prisms. M.p. 156°. R_f (hexane/toluene 4:1): 0.21. UV (CH_2Cl_2): λ_{max} 320 (sh, 3.83), 306 (4.05), 264 (4.27), 240 (4.30); λ_{min} 253 (4.25). IR (KBr): 2942*s*, 1645*w*, 1618*w*, 1575*w*, 1541*m*, 1490*w*, 1419*m*, 1345*m*, 1168*m*, 1059*s*, 985*m*, 892*w*, 874*m*, 791*s*, 596*m*. ^{1}H-NMR (600 MHz, ($^2H_8$)toluene/300 MHz, $CDCl_3$): 7.11/7.32[2]) (*d*, ^4J(9,11) = 1.6, H–C(9)); 7.07/7.15 (*dd*, ^4J(9,11) = 1.6, ^5J(8,11) = 0.5, H–C(11)); 6.50/6.42 (*d*, ^3J(7,8) = 11.1, H–C(7)); 6.42/6.64 (*s*, H–C(6)); 6.21/6.21 (*d*, ^3J(7,8) = 11.1, H–C(8)); 5.55/5.62 (*t*, $^3(2_{ax}, 3) \approx {}^3J(2_{eq}, 3) \approx 7.5$, H–C(3)); 3.76/3.83 (*t*-like, CH of cyclohexyl); 2.61/2.62–2.56 (*sept.*, J = 6.8, Me_2CH); 2.47/2.62–2.56 (*dd*, $^2J(2_{ax}, 2_{eq}) = 12.5$, $^3J(2_{ax}, 3) \approx 7.3$, H_{ax}–C(2)); 2.32/2.20–2.16 (*dd*, $^2J(2_{ax}, 2_{eq}) = 12.5$, $^3J(2_{eq}, 3) = 7.7$, H_{eq}–C(8)); 2.04/2.16 (*s*, Me–C(1)); 1.89, 1.67, 1.45–1.35, 1.14–0.90/1.96–1.68, 1.18–1.45 (*m*, 5 CH_2 of cyclohexyl); 1.22, 0.79/1.27, 0.78 (2*d*, J = 6.8, Me_2CH). ^{13}C-NMR (150 MHz, ($^2H_8$)toluene): 141.13 (C(11)); 139.86 (C(9)); 137.69 (C(4)); 134.05 (C(4a)); 131.75 (C(1)); 126.25 (C(11c)); 125.66 (C(8a)); 125.22 (C(11b)); 123.75 (C(7)); 122.38 (C(11a)); 120.82 (C(6a)); 119.83 (C(3)); 117.44 (C(6)); 115.11 (C(8)); 57.27 (CH of cyclohexyl); 36.30 (C(2)); 35.23, 33.47, 26.45, 26.30, 25.71 (5 CH_2 of cyclohexyl); 31.98 (Me_2CH); 24.84, 21.85 (Me_2CH); 22.96 (*Me*–C(1)). EI-MS: 359 (100, $M^{+\cdot}$), 316 (75, [M – i-Pr]$^+$), 276 (29, [M – cyclohexyl]$^+$). Anal. calc. for $C_{25}H_{29}NO$ (359.51): C 83.52, H 8.13, N 3.90; found: C 83.13, H 7.53, N 3.87.

The structure of **14a** was confirmed by an X-ray crystal-structure analysis (*cf. Fig. 2* and *Sect. 7*).

4.2. *4-Isopropyl-1-methyl-5-phenyl-2*H,*5*H-*furo[3,4:1,2]heptaleno[6,5-*bc*]pyrrole* (**14b**). Aldehyde **8** (80 mg, 0.29 mmol) and aniline (1 ml) were stirred under N_2 at 100° for 1 h, then the mixture was diluted with Et_2O (50 ml). It was washed first with 2N HCl soln. (20 ml), then with sat. Na_2CO_3 soln. (2 × 50 ml). The combined org. layers were dried (Na_2SO_4), and evaporated. FC: 5 g of silica gel, 1 × 15 cm; hexane (10 ml), hexane/toluene 9:1 (10 ml), 7:1 (10 ml), 5:1 (10 ml). With hexane/toluene 9:1, **10** was eluted (18 mg, 0.065 mmol, 22%); with 7:1 and 5:1 followed **14b** (0.075 mg, 0.21 mmol; 74%) as pale-yellow solid, which was recrystallized from AcOEt. Pale-yellow needles. M.p. 189°. R_f (hexane/toluene 4:1): 0.50. UV (CH_2Cl_2): λ_{max} 298 (sh, 2.26), 284 (4.32), 272 (4.33); λ_{min} 255 (4.25). IR (KBr): 2952*s*, 1647*w*, 1622*w*, 1596*s*, 1575*m*, 1549*m*, 1498*s*, 1458*m*, 1416*m*, 1357*s*, 1193*m*, 1153*m*, 1136*m*, 1058*s*, 875*s*, 801*s*, 754*m*, 730*m*, 697*m*, 596*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.42–7.25 (*m*, 5 H of phenyl, H–C(9)); 7.20 (*d*, ^4J(9,11) = 1.2, H–C(11)); 6.75 (*s*, H–C(6)); 6.46 (*d*, ^3J(7,8) = 11.1, H–C(8)); 6.31 (*d*, ^3J(7,8) = 11.1, H–C(7)); 5.58 (*td*, $^3(2_{ax}, 3) \approx {}^3J(2_{eq}, 3) \approx 7.4$, ^4J(3, Me_2CH) = 1.0, H–C(3)); 2.73 (*dd*, $^2J(2_{ax}, 2_{eq}) = 12.6$, $^3J(2_{ax}, 3) = 7.4$, H_{ax}–C(2)); 2.46 (*dd*, $^2J(2_{ax}, 2_{eq}) = 12.6$, $^3J(2_{eq}, 3) = 7.3$, H_{eq}–C(2)); 2.22 (*s*, Me–C(1)); 1.96 (*sept.*, J = 6.8, Me_2CH); 0.90, 0.57 (2*d*, J = 6.8, Me_2CH). ^{13}C-NMR (150 MHz, $CDCl_3$): 141.26 (*C*–N of Ph); 141.09 (C(11)); 139.75 (C(9)); 138.28 (C(4)); 133.33 (C(4a)); 132.83 (C(11a)); 129.24 (CH of Ph); 127.49 (C(11c)); 126.54 (CH of Ph); 124.49 (C(8a)); 124.14 (C(11b)); 123.37 (CH of phenyl); 122.51 (C(7)); 121.39 (C(6)); 120.77 (C(6a)); 120.70 (C(1)); 118.88 (C(3)); 116.07 (C(8)); 36.02 (C(2)); 30.09 (Me_2CH); 23.85, 20.40 (Me_2CH); 23.18 (*Me*–C(1)). EI-MS: 353 (98, $M^{+\cdot}$), 338 (20, [M – Me]$^+$), 310 (100, [M – i-Pr]$^+$). Anal. calc. for $C_{25}H_{23}NO$ (353.46): C 84.95, H 6.56, N 3.96; found: C 84.65, H 6.38, N 3.89.

5. Dimethyl 10-Isopropyl-7-methyl-8*H*-heptaleno[1,10-*bc*]furan-5,6-dicarboxylate (11). – 5.1. *Dimethyl 1-(Hydroxymethyl)-9-isopropyl-6-methylheptalene-4,5-dicarboxylate* (**6**). To **5** (1.51 g; 3.79 mmol) and Na[B(OMe)$_3$H] (0.584 g; 4.57 mmol), THF (15 ml) was added at 0° under N_2. After stirring for 3 h at r.t., the mixture was diluted with Et_2O (100 ml) and washed with sat. NaCl soln. (3 × 100 ml). The aq. phases were re-extracted with Et_2O (2 × 50 ml). The combined org. layers were dried (Na_2SO_4), evaporated, and the residue was submitted to FC (15 g of silica gel, 2 × 11 cm; hexane/AcOEt 4:1 (50 ml), 3:1 (40 ml), 2:1 (30 ml)) to give 0.851 g (2.39 mmol; 63%) of **6** which crystallized from Et_2O. Yellow crystals. M.p. 169°. R_f (hexane/AcOEt 1:1): 0.51. UV (EtOH): λ_{max} 330 (sh with tailing, 3.47), 282 (4.03), 252 (4.11), 208 (4.32); λ_{min} 272 (4.01), 243 (4.08). IR (KBr): 3547*m* (OH), 2950*m*, 1711*s*, 1574*w*, 1457*w*, 1440*m*, 1432*w*, 1259*s*, 1197*w*, 1164*w*, 1089*m*, 1046*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): (*d*, ^3J(2,3) = 6.1, H–C(3)); 6.44 (*dt*, ^3J(2,3) = 6.1, ^4J(H–C(2),CH_2) = 1.6, H–C(2)); 6.30 (*d*, ^3J(7,8) = 6.6, H–C(8)); 6.16 (*dd*-like, ^3J(7,8) = 6.6, ^4J(H–C(7), Me–C(6)) = 1.2, H–C(7)); 5.82 (*s*, H–C(10)); 4.35 (*dt*-like, ^2J = 16.0, 1 H, CH_2); 4.14 (br. *d*, ^2J = 16.0, 1 H, CH_2); 3.72, 3.71 (2*s*, 2MeOCO), 2.48 (*sept.*, Me_2CH); 2.00 (br. *s*, Me–C(6)); 1.09, 1.05 (2*d*, J = 6.9, Me_2CH); OH not visible. EI-MS: 356 (100, $M^{+\cdot}$), 325 (42, [M – CH_2OH]$^+$). Anal. calc. for $C_{21}H_{24}O_5$ (356.42): C 70.77, H 6.79; found: C 70.34, H 6.79.

5.2. *Dimethyl 1-Formyl-9-isopropyl-6-methylheptalene-4,5-dicarboxylate* (**9a**) *and Dimethyl 5-Formyl-7-isopropyl-10-methylheptalene-1,2-dicarboxylate* (**9b**). After stirring a soln. of IBX (0.285 g, 1.0 mmol), DMSO (2 ml),

[2]) The second values represent the chemical shifts at 300 MHz in $CDCl_3$.

and acetone (2 ml) for 30 min at r.t., **6** (0.240 g, 0.67 mmol) was added, whereby the color of the soln. changed from yellow to red. The mixture was stirred for 1 h. The reaction was stopped with H_2O (1 ml), the suspension filtered, the filtrate diluted with Et_2O (50 ml), and washed with sat. NaCl soln. (3 × 50 ml). The aq. phases were re-extracted with Et_2O (2 × 50 ml), the combined org. layers dried (Na_2SO_4) and evaporated. Purification by FC (10 g of silica gel, 2 × 8 cm; hexane/AcOEt 4:1 (100 ml), 2:1 (50 ml)) led to 0.190 g (0.54 mmol, 80%) of a thermal equilibrium mixture of 90% **9a** and 10% **9b**, which was recrystallized from AcOEt. Red prisms. M.p. 156°. R_f (hexane/AcOEt 2:1): 0.49. ^{1}H-NMR (300 MHz, $CDCl_3$) of **9a** (90%): 9.51 (*s*, CHO); 7.62 (*d*, ^3J(2,3) = 6.2, H–C(3)); 7.08 (*d*, ^3J(2,3) = 6.2, H–C(2)); 6.30 (*d*, ^3J(7,8) = 6.7, H–C(8)); 6.16 (*dd*, ^3J(7,8) = 6.7, ^4J(H–C(7),Me–C(6)) = 1.2, H–C(7)); 5.67 (*s*, H–C(10)); 3.71, 3.67 (2*s*, 2 MeOCO); 2.46 (*sept.*, *J* = 6.9, Me_2CH); 1.92 (*s*, Me–C(6)); 1.04, 1.01 (2*d*, *J* = 6.9, Me_2CH). ^{1}H-NMR (300 MHz, $CDCl_3$) of **9b** (10%): 9.93 (*s*, CHO); 7.00, 6.57 (2*d*, ^3J(3,4) = 11.6, H–C(3,4)); 6.51 (*s*, H–C(8,9)); 6.36 (*s*, H–C(6)); 3.77, 3.66 (2*s*, MeOCO); 2.60 (*sept.*, Me_2CH); 1.73 (*s*, Me–C(10)); 1.12, 1.11 (2*d*, *J* = 6.7, Me_2CH). CI-MS (NH_3): 372 (18, $[M + NH_4]^+$), 355 (100, $[M + 1]^+$). Anal. calc. for $C_{21}H_{22}O_5$ (354.40): C 71.17, H 6.26; found: C 71.27, H 6.25.

5.3. *Thermal Rearrangement of* **9a**/**9b** *into* **11**. In a closed vessel, **9a**/**9b** (0.019 g, 0.054 mmol) was stirred in dry toluene (1 ml) under N_2 at 130° for 3 d. The solvent was evaporated and the residue submitted to FC (6 g of silica gel, 1 × 23 cm; hexane/AcOEt 10:1 (25 ml), 7:1 (50 ml)) yielding 0.014 g (40 mmol, 74%) of **11**. Pale-yellow oil. R_f (hexane/AcOEt 2:1): 0.79. UV (EtOH): λ_{max} 351 (3.61), 269 (sh, 3.91), 232 (4.41); λ_{min} 308 (3.27), 209 (4.28). IR (KBr): 2956*m*, 1731*s*, 1629*w*, 1569*w*, 1433*m*, 1251*s*, 1128*m*, 1081*m*, 1041*w*, 943*w*, 850*w*, 820*w*, 772*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.24 (*s*, H–C(2)); 6.66 (*d*, ^3J(3,4) = 11.5, H–C(3)); 6.00 (*d*, ^3J(3,4) = 11.5, H–C(4)); 5.35 (*t*, $^3J(8_{ax}, 9) \approx J(8_{eq}, 9) \approx 7.1$, H–C(9)); 3.69, 3.61 (2*s*, 2 MeOCO); 2.76 (*sept.*, *J* = 6.8, Me_2CH); 2.54 (*dd*, $^2J(8_{ax}, 8_{eq}) = 13.2$, $^3J(8_{eq}, 9) = 7.8$, H_{eq}–C(8)); 2.25 (*dd*, $^2J(8_{ax}, 8_{eq}) = 13.2$, $^3J(8_{ax}, 9) = 6.4$, H_{ax}–C(8)); 1.76 (*s*, Me–C(7)); 1.09, 1.02 (2*d*, *J* = 6.8, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.82 (2MeO*C*O); 153.01 (C(10a)); 137.99 (C(6a)); 137.34 (C(2)); 136.65, 136.16 (C(5), C(10)); 132.31, 130.90 (C(6), C(10b)); 127.28 (C(3)); 122.91 (C(4)); 122.23, 122.09 (C(2a), C(7)); 177.83 (C(9)); 52.42, 52.15 (2 *Me*OCO); 35.41 (C(8)); 30.60 (Me_2CH); 22.86, 21.53, 21.15 (3 Me). CI-MS (NH_3): 372 (63, $[M + NH_4]^+$), 355 (100, $[M + 1]^+$), 323 (46, $[M - MeO]^+$).

6. Dimethyl 10-Isopropyl-7-methyl-8*H*-heptaleno[1,10-*bc*]thiophene-5,6-dicarboxylate (13). – In a closed vessel, **9a**/**9b** (0.106 g, 0.30 mmol) and *Lawesson*'s reagent (0.252 g, 0.62 mmol) were stirred in dry toluene (2 ml) under N_2 at 110° for 30 min. The solvent was evaporated and the residue submitted to FC (10 g of silica gel, 2 × 7 cm; hexane (25 ml), hexane/AcOEt 9:1 (50 ml), 7:1 (60 ml)) affording 0.076 g (0.21 mmol, 68%) of **13**. Yellow oil. R_f (hexane/AcOEt 2:1): 0.79. UV (EtOH): λ_{max} 356 (3.61), 244 (4.47); λ_{min} 311 (3.27), 219 (4.19). IR (KBr): 2954*m*, 1728*s*, 1617*w*, 1576*w*, 1508*w*, 1432*m*, 1248*s*, 1086*m*, 1054*m*, 982*m*, 868*w*, 817*w*, 766*w*, 646*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.03 (*s*, H–C(2)); 6.86 (*d*, ^3J(3,4) = 11.7, H–C(3)); 6.17 (*d*, ^3J(3,4) = 11.7, H–C(4)); 5.62 (*t*, $^3J(8_{ax}, 9) \approx {}^3J(8_{eq}, 9) \approx 6.8$, H–C(9)); 3.77, 3.64 (2*s*, 2 MeOCO); 2.69 (*sept.*, *J* = 6.8, Me_2CH); 2.55 (*dd*, $^2J(8_{ax}, 8_{eq}) = 12.9$, $^3J(8_{eq}, 9) = 7.7$, H_{eq}–C(8)); 2.25 (*dd*, $^2J(8_{ax}, 8_{eq}) = 12.9$, $^3J(8_{ax}, 9) = 6.5$, H_{ax}–C(8)); 1.84 (*s*, Me–C(7)); 1.21, 1.05 (2*d*, *J* = 6.8, Me_2CH). ^{13}C-NMR (150 MHz, $CDCl_3$): 168.47 (MeO*C*O–C(6)); 168.13 (MeOCO–C(5)); 144.87 (C(10b)); 141.08 (C(10)); 140.91 (C(10a)); 140.21 (C(61)); 136.90 (C(2a)); 136.62 (C(5)); 131.95 (C(6)); 131.33 (C(3)); 123.22 (C(7)); 122.14 (C(4)); 120.44 (C(9)); 120.36 (C(2)); 52.49 (*Me*OCO–C(6)); 52.08 (*Me*OCO–C(5)); 34.58 (C(8)); 34.37 (Me_2CH); 23.47, 21.11 (Me_2CH); 20.96 (Me–C(7)). EI-MS: 370 (33, $M^{+\cdot}$), 323 (56, $[M - COOMe]^+$), 43 (100, i-Pr^+). Anal. calc. for $C_{21}H_{22}O_4N$ (370.47): C 68.08, H 5.99; found: C 67.99, H 6.41.

7. Crystal-Structure Determinations of 10 and 14a[3]). – All measurements were conducted on a *Rigaku AFC5R* diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71069 Å) and a 12-kW rotating anode generator. The intensities were collected using ω scans for **10** and $\omega/2\theta$ scans for **14a**. Three standard reflections, which were measured after every 150 reflections, remained stable throughout each data collection. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Each structure was solved by direct methods using SHELXS86 [20] which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. For **10**, the H-atoms were located in difference-electron-density maps, and their positions were refined together with individual isotropic displacement parameters. For **14a**, the H-atoms were fixed in geometrically calculated positions (d(C–H) = 0.95 Å), and they were assigned fixed isotropic displacement parameters with a value equal to 1.2U_{eq} of the parent C-atom. Corrections for secondary extinction were applied. All

[3]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-10/62. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, ambridge CB2 1EZ, UK (fax: + 44-(0)1223-336033 or email: teched@ccdc.cam.ac.uk).

refinements were carried out on F using full-matrix least-squares procedures which minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$. The data collection and refinement parameters for each compound are listed in the *Table*. Neutral atom scattering factors for non-H-atoms were taken from [21a] and the scattering factors for H-atoms from [22]. Anomalous dispersion effects were included in F_c [23]; the values for f' and f'' were taken from [21b]. All calculations were performed using the TEXSAN [24] crystallographic software package and the figures were produced with ORTEPII [25].

Table. *Crystallographic Data of* **10** *and* **14a**

		10	**14a**
Crystallized from		Et_2O	AcOEt
Empirical formula		$C_{19}H_{18}O_2$	$C_{25}H_{29}NO$
Formula weight		278.35	359.51
Crystal color, habit		yellow, irregular prism	colorless, prism
Crystal dimensions [mm]		$0.20 \times 0.28 \times 0.46$	$0.30 \times 0.40 \times 0.50$
Temp. [K]		173 (1)	291 (1)
Crystal system		monoclinic	monoclinic
Space group		$P2_1/n$	$P2_1$
Z		8	4
Reflections for cell determination		25	25
2θ Range for cell determination [°]		37–40	35–39
Unit cell parameters	a [Å]	8.474(3)	9.305(2)
	b [Å]	13.200(2)	9.789(2)
	c [Å]	26.348(2)	22.929(2)
	β [°]	96.14(1)	99.86(1)
	V [Å^3]	2930(1)	2057.6(5)
D_x [g cm^{-3}]		1.262	1.160
$\mu(MoK_\alpha)$ [mm^{-1}]		0.0804	0.0695
Scan type		ω	$\omega/2\theta$
$2\theta_{max}$ [°]		55	55
Total reflections measured		7459	5303
Symmetry independent reflections		6702	5003
Reflections used [$I > 2\sigma(I)$]		4470	3455
Parameters refined		524	487
R		0.0459	0.0477
wR		0.0408	0.0358
Goodness of fit		1.511	1.686
Secondary extinction coefficient		$2.7(4) \times 10^{-7}$	$1.5(1) \times 10^{-6}$
Final Δ_{max}/σ		0.0003	0.0002
$\Delta\rho$ (max; min) [e Å^{-3}]		0.24; −0.19	0.19; −0.19
$\sigma(d(C-C))$ [Å]		0.003	0.004–0.007

Compound **10** crystallizes with two independent molecules in the asymmetric unit, but there are no significant differences in their geometries. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher symmetry space group using the MISSYM routine [26] of the program PLATON [27], but none could be found. Although *Fig. 1* shows the two independent molecules as virtual mirror images of each other, the centrosymmetric space group implies that the molecules are, in fact, virtually identical.

Compound **14a** crystallizes in a polar space group, even though the compound is achiral. The absolute direction of the polar axis has been chosen arbitrarily. This compound also crystallizes with two independent molecules in the asymmetric unit. They are not related by additional symmetry and the main difference in their conformations is that the i-Pr groups differ in their orientations by *ca.* 38°. There are also smaller differences (maximum 18°, most less than 10°) in some of the torsion angles involving the fused rings, which indicates small differences in the puckering of the rings.

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