Synthesis of 6-Styrylheptalenes

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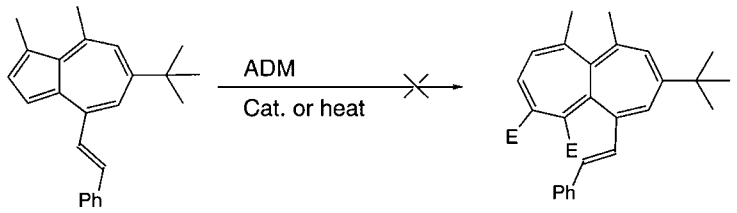
4-Methylazulenes **3**, **15**, and **23** were transformed into 4-[(methylthio)methyl]azulene **4**, and azulene-4-carbaldehyde dimethyl dithioacetals **16** and **24**, respectively. *Vilsmeier* formylation of **4** and **16**, and subsequent reduction led to the 1-methyl derivatives **6** and **18**, respectively. The thermal reaction of azulenes **6**, **18**, and **24** with dimethyl acetylenedicarboxylate (ADM) in toluene afforded heptalenes with a (methylthio)methyl group or a [bis(methylthio)]methyl group at C(6). Chlorination of [(methylthio)methyl]heptalene **7**, followed by treatment with HgO and $BF_3 \cdot OEt_2$ in aqueous tetrahydrofuran (THF), led to 6-formylheptalene-dicarboxylate **12** in excellent yield. Similarly, hydrolysis of **18** and **24** by HgO and $BF_3 \cdot OEt_2$ in aqueous THF afforded the 6-formyl derivatives **21** and **27**, respectively. *Wittig* reaction of the 6-formyl-substituted heptalenes and phosphonium salts **13a**–**e** in the two-phase system CH_2Cl_2/2N aqueous NaOH resulted in the formation of 6-styryl-substituted heptalenes.

Introduction. – Several years ago, we reported on the thermal and Ru-catalyzed reactions of styryl-substituted azulenes with dimethyl acetylenedicarboxylate (ADM), which led to corresponding styryl-substituted heptalenes [1]. 7-Isopropyl-1-methyl-4-[(*E*)-styryl]azulene, as well as its 4-methoxystyryl derivative, were reacted with ADM under catalytic conditions to give the corresponding dimethyl 9-isopropyl-1-methyl-6-styrylheptalene-4,5-dicarboxylate in *ca.* 30% yield, which is still much poorer than that of the reaction between guaiazulene and ADM [2]. However, because of the difficult access of other 4-styryl-substituted azulenes [3][4], the other type of 6-styryl-substituted heptalenes remained inaccessible.

Recently, we found a simple and efficient method to obtain 4-styrylazulenes [5], which opened the way for the synthesis of 6-styryl-substituted heptalenes. Unfortunately, the reaction of 6-(*tert*-butyl)-1,8-dimethyl-4-[(*E*)-2-phenylethenyl]azulene (**1**) with ADM, either under thermal or Ru-catalysis conditions, led only to trace amounts of heptalene-4,5-dicarboxylates, which were evidenced on TLC by their typical R_f value and pale yellow color (*Scheme 1*). This implies that styryl substituents at C(4) of azulenes seriously hinder the formation of heptalenes-4,5-dicarboxylates from azulenes and ADM. Since a Me group at C(6) of heptalene-dicarboxylates is difficult to functionalize, there is no direct way to introduce a π-substituent at a Me–C(6) moiety of heptalenes starting from corresponding 6-Me derivatives. An alternative solution would be to introduce a precursory group at C(4) of the azulenes, which should easily react with ADM to provide, in a reasonable yield, the corresponding heptalenes with a precursory group at C(6). This precursor should be easily transformed in the subsequent step into a π-substituent. In this paper, we report on the synthesis of such 6-styrylheptalenes *via* (methylthio)- or bis(methylthio)methyl groups at C(6) of the heptalenes.

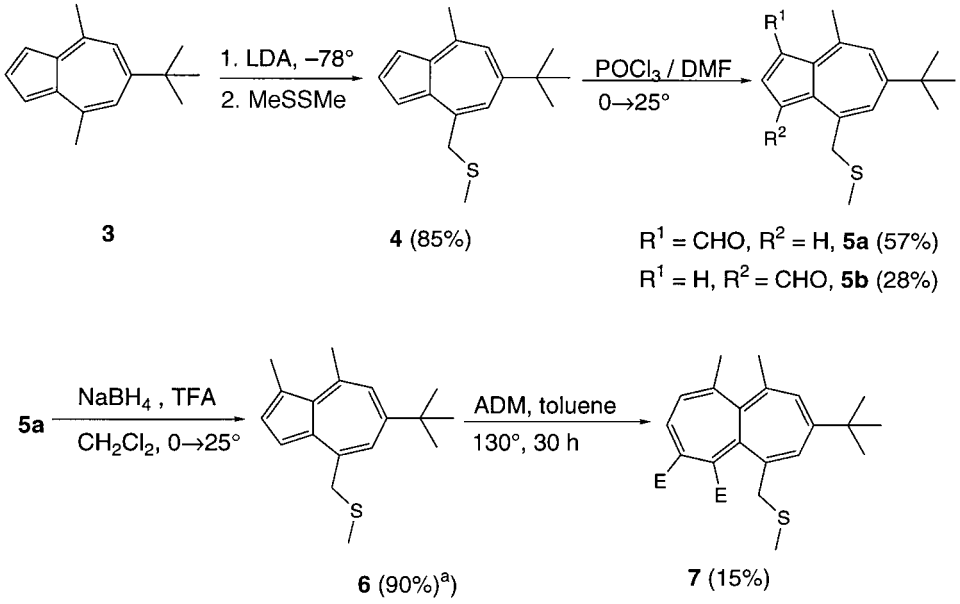
Scheme 1



1 E = MeOCO **2a**

Results and Discussions. – Azulene **3** was deprotonated at one of the Me groups by lithium diisopropylamide (LDA) in THF at −78°. The carbanion formed was reacted with dimethyl disulfide (MeSSMe) to give 8-[(methylthio)methyl]azulene **4** in excellent yield (*Scheme 2*). The *Vilsmeier* formylation of **4** resulted in the two isomers **5a** and **5b**, which were easily separated by column chromatography on silica gel. The distinction between the two isomers was achieved by ^{1}H-NOE measurements. Only **5a** showed strong reciprocal effects on the signal of Me−C(8) and the signal of the H-atom of CHO−C(1). The reduction of **5a** proceeded smoothly by $NaBH_4$ in a mixture of trifluoroacetic acid (TFA) and CH_2Cl_2 to give azulene **6** in almost quantitative yield. The procedure established by *Anderson* and *Breazeale* [6] ($NaBH_4/BF_3 \cdot OEt_2$ in diglyme) led also to the same product **6**, but in a much poorer yield (< 30%). The

Scheme 2



3 **4** (85%) R^1 = CHO, R^2 = H, **5a** (57%)
R^1 = H, R^2 = CHO, **5b** (28%)

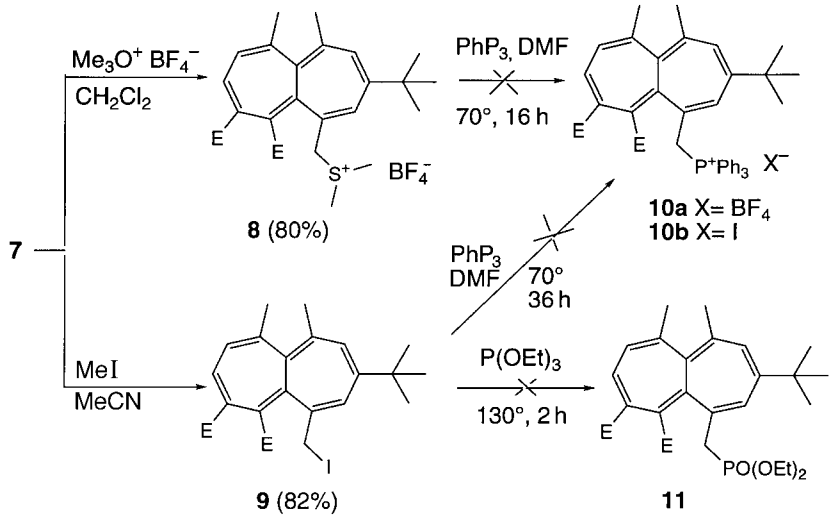
6 (90%)[a] **7** (15%)

[a]) 7% of **5a** was recovered.

thermal reaction of azulene **6** with ADM in toluene afforded 6-[(methylthio)methyl]-heptalene-dicarboxylate **7** in 15% yield, accompanied by azulene-dicarboxylates which were not isolated.

In our first attempt to transform the $MeSCH_2$ group into a styryl substituent, we followed the methods reported by *Hafner*, *Hünig*, and co-workers [3][7]. The methylation of **7** led to dimethylsulfonium tetrafluoroborate **8**, which unfortunately did not react with Ph_3P to give the phosphorus salt **10a** (*Scheme 3*). We assume that the dimethylsulfonium moiety was not a good leaving group. Therefore, the 6-(iodomethyl)heptalene **9** was prepared in 82% yield by heating **7** with MeI in MeCN at 60° for 20 h. Again, heptalene **9** could not be converted either to phosphorous salt **10b** or to phosphonate **11** by reaction with $P(OEt)_3$. Steric hindrance and poor nucleophilicity of Ph_3P and $P(OEt)_3$ may account for the failure of these transformations.

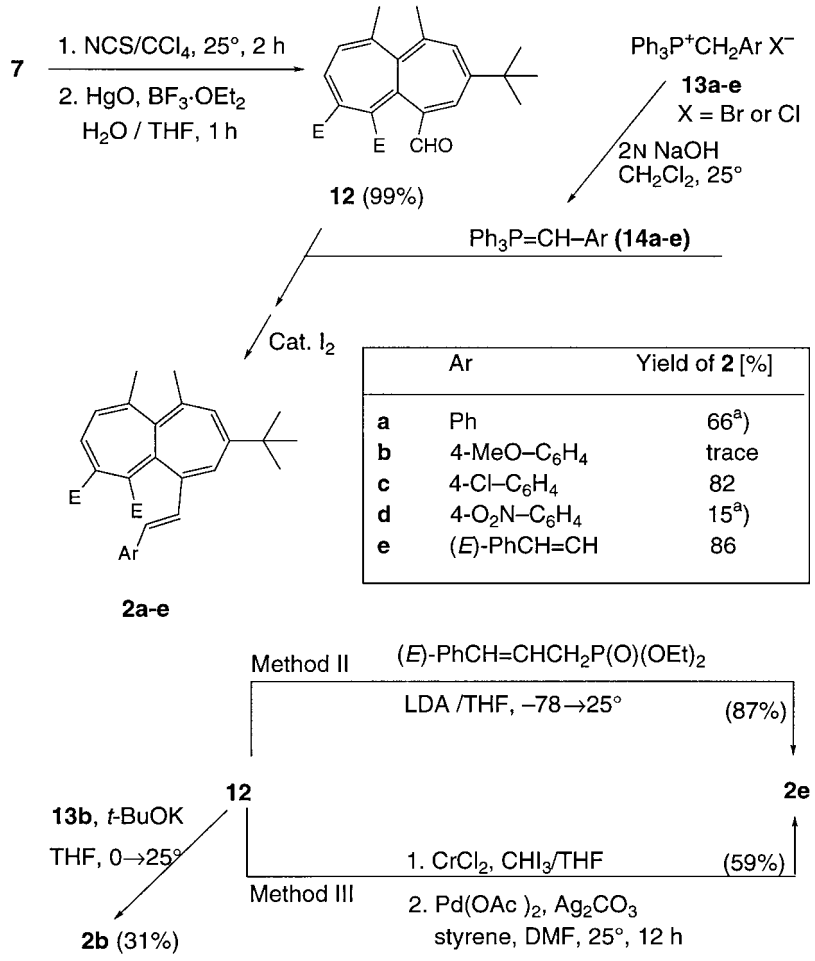
Scheme 3



The other route involved conversion of the $MeSCH_2$ group to a CHO function by the method of *Gassman et al.* [8][9]. For this purpose, heptalene **7** was chlorinated with *N*-chlorosuccinimide (NCS) in CCl_4, followed by hydrolysis with HgO and $BF_3 \cdot OEt_2$ in aqueous THF to give 6-formylheptalene-dicarboxylate **12** in almost quantitative yield (*Scheme 4*).

There are several routes to transform a CHO function into a styryl group. It is noteworthy that *Wittig-Horner* reaction with **12** gave 6-styrylheptalene derivatives **2a**–**b** in only poor yields (< 20%). We assume that the neighboring MeOCO–C(5) trapped the formed oxy anion arising from CHO–C(6) during the reaction since MeOCO–C(5) is very close to CHO–C(6) (see *Fig. 1* and the corresponding discussion). By this side reaction, the formation of the styryl C=C is blocked. This effect may also account for the relatively poor yield of heptalene **2b** in an established *Wittig* reaction in the presence of *t*-BuOK in THF. However, in the two-phase system CH_2Cl_2/2N aqueous NaOH, the *Wittig* reaction was completed within 2 h to give a mixture of (1*E*,3*E*)-**2e** and (1*Z*,3*E*)-**2e**, which could be isomerized to pure (1*E*,3*E*)-**2e**

Scheme 4



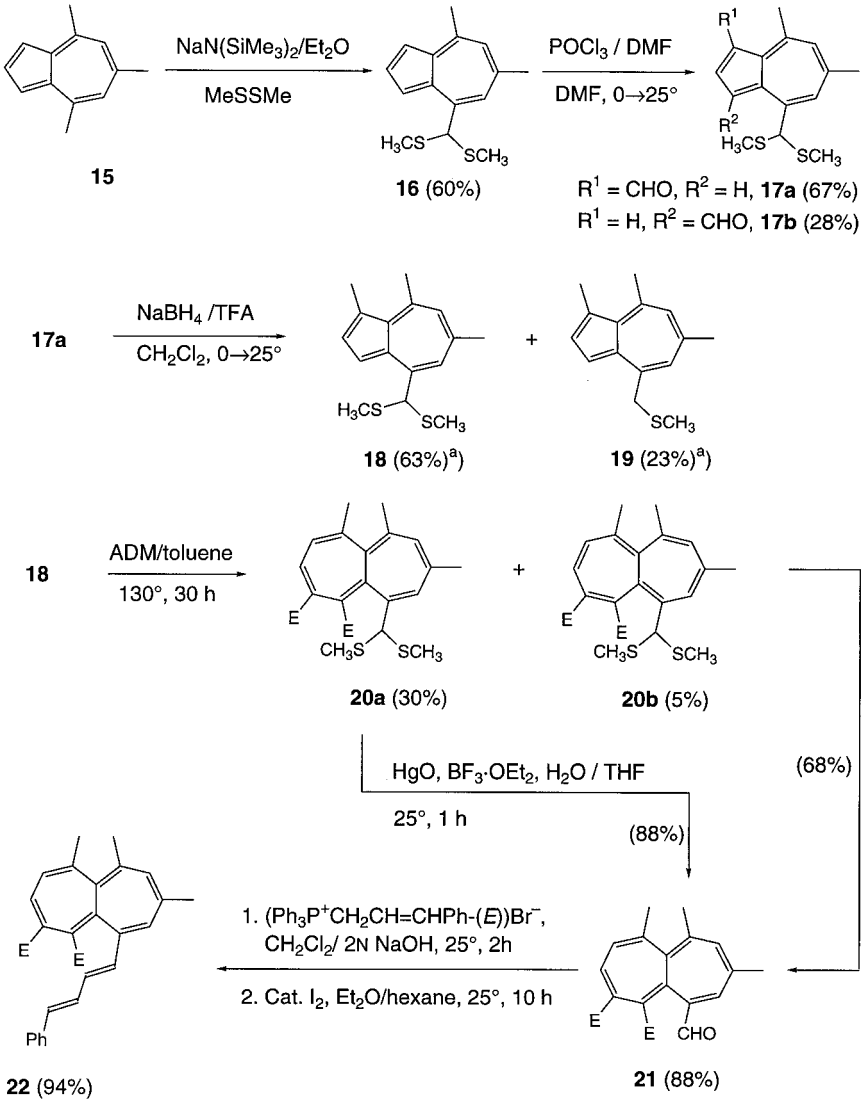
[a]) 26% of **12** was recovered.

by treatment with a catalytic amount of I_2 at room temperature. The reaction between **12** and **13a** was relatively slow and incomplete, and 26% of **12** was recovered, although 66% of styryl derivative **2a** was obtained. On the other hand, the reaction of (4-methoxybenzyl)triphenylphosphonium chloride (**13b**) and **12** gave only trace amounts of **2b**. When the ylide of **13b** was prepared in *t*-BuOK/THF at 0°, and added to the two-phase system, the typical red color of the ylide disappeared immediately, but no heptalene **2b** could be detected. This experiment demonstrated that the ylide of **13b** is not stable in the two-phase system. The reaction between **13c** and **12** proceeded smoothly to give, in 82% yield, the mixture *cis*-**2c**/*trans*-**2c**. This mixture gave, in the presence of catalytic amounts of I_2, only in boiling toluene quantitatively the pure *trans*-form, in contrast to the *cis*/*trans*-mixture of **2a** and **2e**, which isomerized to the

pure *trans*-form already at room temperature. The reaction of the very stable ylide from **13d** with **12**, even after the addition of more equivalents of **13d** and prolongation of the reaction time, yielded only 15% of **2d**, and 26% of starting material **12** could be recovered. This indicates that the two-phase *Wittig* reaction worked well for the preparation of **2a**, **2c**, and **2e**. However, it was very sensitive to the strong electron-donor or -acceptor functional groups on the aromatic ring of triphenylphosphonium salt **13**. Fortunately, we found that 6-[(*E*,*E*)-4-phenylbuta-1,3-dienyl]heptalene-dicarboxylate **2e** could also be prepared in 87% yield by a *Wittig-Horner* reaction; however, it should be considered an exceptional case. As a more general method to prepare the (buta-1,3-dienyl)-substituted heptalenes, iodomethylenation [10] of **12** with $CHI_3/CrCl_2$ followed by *Heck* reaction [11] in the presence of styrene led to **2e** in 56% yield. Replacement of styrene by any substituted styrene in the *Heck* reaction should lead to the corresponding [4-(X-phenyl)buta-1,3-dienyl]heptalene derivatives, since the *Heck* reaction is not affected by the electronic properties of the substituents at the styrene [12].

For 4,6,8-trimethylazulene (**15**) with Me groups at both reactive positions, we had to solve the problem of regioselectivity. When the reaction is carried out in THF [13] or DMF [4], the formation of azulenes modified at C(6) rather than at C(4) has been reported. *Hafner*, *Hünig*, and co-workers [7] found that **15** is deprononated exclusively at Me–C(4/8) with sodium *N*-methyl-*N*-phenylamide in Et_2O at $-20°$. The formed sodium azulenide was isolated and then reacted with MeSSMe in Et_2O at 25° to give selectively the C(4)-modified product. The preparation of sodium *N*-methyl-*N*-phenylamide in Et_2O is laborious, and, last but not least, the whole procedure is very complicated. When we used LDA to deprotonate 4,6,8-trimethylazulene (**15**) in Et_2O/hexane at $-15°$, followed directly by addition of MeSSMe, the mixture of 4- and 6-modified azulenes was obtained in a ratio of 85:15 according to ^{1}H-NMR analysis. When 1 equiv. of sodium bis(trimethylsilyl)amide was employed in the deprotonation reaction in Et_2O/toluene, without isolation of the formed sodium salt, the addition of MeSSMe at 25° gave preferentially the 4-modified azulene (ratio according to ^{1}H-NMR anaylsis: 95:5). Finally, we found that treatment of **15** with 2 equiv. of sodium bis(trimethylsilyl)amide and 2 equiv. of MeSSMe led in one step to dimethyl dithioacetal **16** in 60% yield (*Scheme 5*). The *Vilsmeier* formylation of **16** again resulted in the formation of two isomeric carbaldehydes **17a** and **17b**, which were separated by column chromatography on silica gel. The structure assignment of **17a** and **17b** is based on ^{1}H-NOE measurement. Only **17a** showed strong reciprocal effects on the signal of the Me group at C(8) and the signal of the H-atom of the CHO group at C(1). The reduction of **17a** by $NaBH_4$ in TFA/CH_2Cl_2 led to a mixture of the desired product **18** and the partially dethiolated product **19**. Although **18** and **19** can be recognized on TLC, any attempt to separate the mixture either by column chromatography on silica gel or by preparative TLC failed. Since all other reduction methods either under basic [14] or acidic conditions [15] affected the thioacetal group, we were not able to obtain **18** without formation of **19**. Finally, **18** was found to crystallize much easier than **19** from hexane, and the fractional crystallization afforded pure **18** in 52% yield. The thermal reaction of azulene **18** and ADM in toluene gave heptalene-dicarboxylate **20a** in 30% yield as a yellow crystals and its DBS (double-bond shifted) isomer **20b** in 5% yield as a yellow oil. Both compounds were separated by column chromatography. It is easy to distinguish **20a** from **20b** by the difference of their

Scheme 5



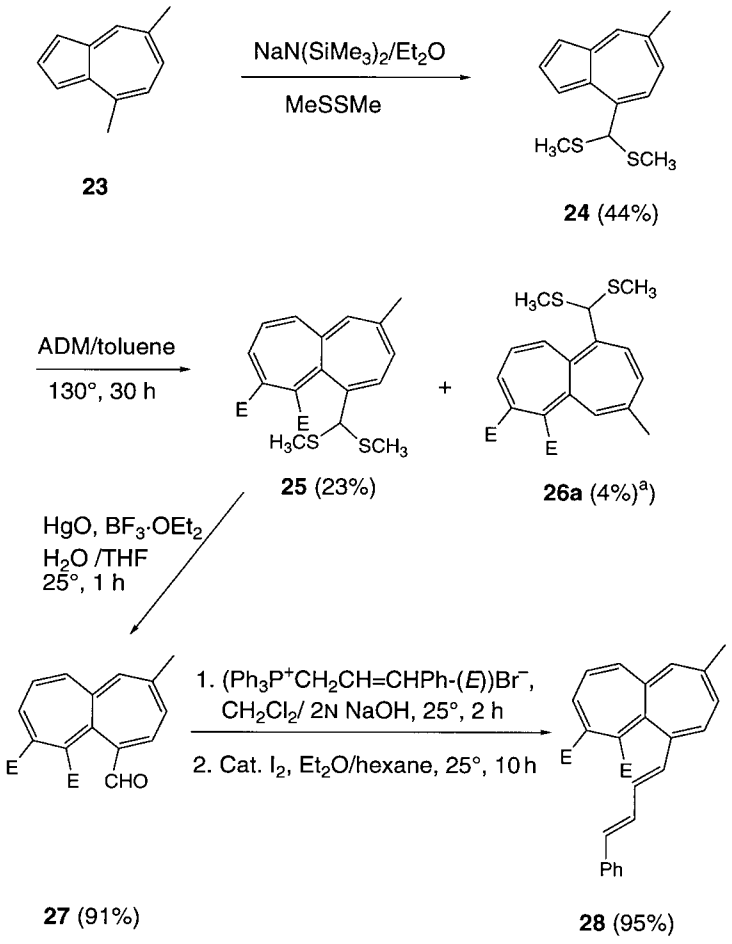
[a]) The yield was determined by ^{1}H-NMR spectroscopy of the mixture of **18** and **19**, from which pure **18** (52%) was isolated by recrystallization.

chemical shifts and coupling constants, *e.g.*, **20a** showed H–C(2) and H–C(3) as an *AB* system with fine structure at 6.34 and 7.57 ppm with $J(2,3) = 5.9$ Hz, whereas **20b** exhibited the signals of H–C(3) and H–C(4) as an *AB* system at 6.86 and 6.81 ppm with $J(3,4) = 11.8$ Hz. The hydrolysis of **20a** with 2 equiv. of HgO and $BF_3 \cdot OEt_2$ in aqueous THF [9] led to formylheptalene-dicarboxylate **21** in 88% yield. It is interesting

to note that hydrolysis of **20b** as well afforded **21** in 68% yield, indicating that the thermal equilibrium of **21** with its DBS isomer is at ambient temperature to >99% on the side of **21**. In the two-phase system CH_2Cl_2/2N NaOH, the *Wittig* reaction was complete within 2 h to give the mixture (1*E*,3*E*)-**22**/(1*Z*,3*E*)-**22**. The latter was transformed to pure (1*E*,3*E*)-**22** by treatment with a catalytic amount of I_2 in hexane/Et_2O at room temperature overnight.

Under the same conditions as described above, 4,7-dimethylazulene (**23**) was converted to bis(methylthio)methyl-substituted azulene **24** in 44% yield (*Scheme 6*). Heating **24** with ADM in toluene gave the heptalene **25** in 23% yield together with its structural isomers **26a**/**26b** (3.6%). Hydrolysis of **25** readily provided formylheptalene-

Scheme 6



a) At room temperature, **26a** is in thermal equilibrium with 35% of its DBS isomer **26b** ($CDCl_3$).

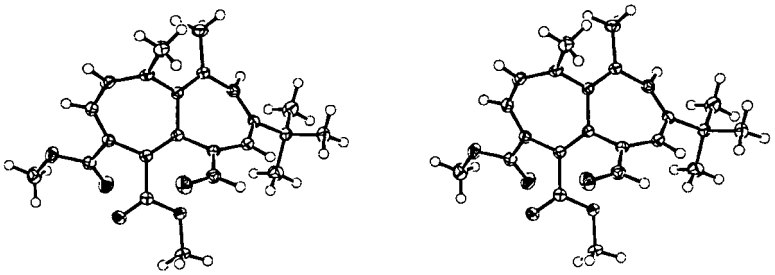


Fig. 1. *Stereoscopic view of the X-ray crystal structure of heptalene* **12**

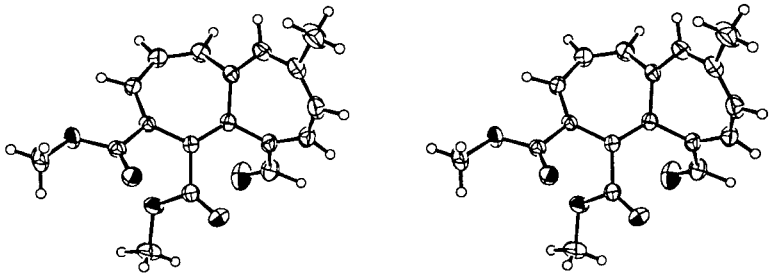


Fig. 2. *Stereoscopic view of the X-ray crystal structure of heptalene* **27**

dicarboxylate **27** in excellent yield. Compounds **27** and **12** resemble each other in that the CHO–C(6) and MeOCO–C(5) moieties are close together in both compounds (see *Figs. 1* and *2*). Indeed, the distance between the O-atom of the CHO–C(6) moiety and the carbonyl C-atom of the MeOCO–C(5) moiety is in both heptalenes 3.00 Å. In turn, the distance of the carbonyl C-atom of the CHO–C(6) moiety and the O-atom of the MeO group of the MeOCO–C(5) moiety (see *Fig. 1*), or the O-atom of the carbonyl C-atom of the MeOCO–C(5) (see *Fig. 2*), respectively, is also 3.00 Å in both heptalenes. In other words, the trajectory for a nucleophilic attack at CHO is strongly impeded on one of the diastereotopic sites, and the carbonyl C-atom of the MeOCO–C(5) moiety is in a optimal position to intermolecularly trap the evolving oxy anion at CHO–C(6) in the course of a nucleophilic attack. Nevertheless, applying *Wittig-Horner* reaction to **27** resulted in only trace amounts of heptalene-dicarboxylate **28**. Whereas, under the same conditions, styryl derivative **2e** was obtained in 86% in the case of formylheptalene-dicarboxylate **12** (*Scheme 4*). On the other hand, in the two-phase system CH_2Cl_2/2N NaOH, the *Wittig* reaction with (cinnamyl)triphenylphosphonium salt and isomerization transformed **27** into **28** in 95% yield (*Scheme 6*). Iodomethylenation of **27**, followed by the *Heck* reaction with styrene, resulted only in a yield of 38% of **28**.

The (1*E*,3*E*)-configuration of the 4-phenylbuta-1,3-dienyl chain of **28** could not be deduced from its ^{1}H-NMR spectrum, since the signals of H–C(1) and H–C(2) were too close together at 6.45 ppm. Finally, the (1*E*,3*E*)-configuration was confirmed by an X-ray crystal-structure analysis of **28** (*Fig. 3*).

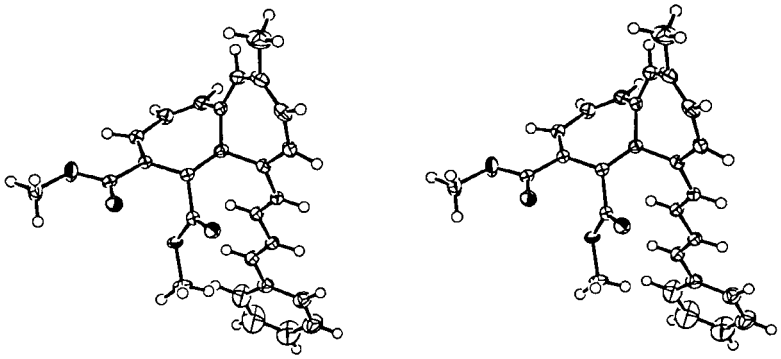


Fig. 3. *Stereoscopic view of the X-ray crystal structure of heptalene* **28**

The successful syntheses of 6-styrylheptalenes offered important intermediates to introduce a second π-substituent in the heptalene ring to form various bis-π-substituted heptalenes for the investigations of their DBS behavior [16].

We thank Dr. *A. Linden* for the X-ray crystal-structure analyses, Prof. *M. Hesse* and his co-workers for mass spectra, our NMR department for NMR support and 2D-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. See [5].

1. Syntheses of Azulenes and Heptalenes. – 1.1. *6-(*tert*-Butyl)-8-methyl-4-[(methylthio)methyl]azulene* (**4**). At $-78°$, to a stirred soln. of LDA (32.5 mmol; prepared from BuLi soln. (20.3 ml, 32.5 mmol) and (i-Pr)$_2$NH (6.8 ml, 48 mmol) in THF (110 ml), azulene **3** (5.31 g, 25 mmol) was added slowly. After the temp. was raised to $-20°$ and kept there for 10 min, the mixture was cooled again to $-78°$, followed by addition of MeSSMe (2.44 ml, 27.5 mmol). The reaction was quenched by H_2O after the mixture was warmed to 25° in 4 h. Extraction by hexane and CC (silica gel; hexane) yielded **4** (5.43 g, 85%). Blue crystals. M.p. 78.0–78.6° (hexane). R_f (hexane/Et$_2$O 95 : 5) 0.42. UV/VIS (hexane): λ_{max} 550 (3.23), 350 (3.79), 289 (4.68), 247 (4.46); λ_{min} 447 (3.15), 325 (3.67), 260 (4.01), 225 (4.21). IR (KBr): 2963*s*, 1576*s*, 1490*s*, 1458*w*, 1433*m*, 1360*m*, 1336*m*, 1241*m*, 1218*m*, 1174*w*, 1158*w*, 1094*w*, 1070*w*, 1014*w*, 960*w*, 906*w*, 870*m*, 762*s*, 736*w*, 716*w*. ^{1}H-NMR (300 MHz, CDCl$_3$): 7.71 (*t*, $J(1,2) \approx J(2,3) = 3.9$, H–C(2)); 7.45 (*d*, $J = 1.6$, H–C(5)); 7.41 (*dd*, $J(1,3) = 1.4$, $J(1,2) = 3.9$, H–C(1)); 7.37 (*d*, $J(1,3) = 1.4$, $J(2,3) = 3.9$, H–C(3)); 7.33 (*s*, H–C(7)); 4.27 (*s*, MeSCH_2); 2.93 (*s*, Me–C(8)); 2.07 (*s*, *Me*SCH$_2$); 1.48 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, CDCl$_3$): 158.15 (*s*); 145.22 (*s*); 144.39 (*s*); 136.71 (*s*); 135.95 (*s*); 133.59 (*d*); 124.23 (*d*); 122.87 (*d*); 116.12 (*d*); 115.07 (*d*); 40.90 (*t*, MeSCH$_2$); 38.68 (*s*, Me$_3$*C*); 31.99 (*q*, *Me*$_3$C); 25.76 (*q*, Me–C(8)); 16.04 (*q*, *Me*SCH$_2$). CI-MS: 259 (100, $[M+1]^+$), 213 (32). Anal. calc. for $C_{17}H_{22}S$ (258.43): C 79.00, H 8.58; found: C 78.93, H 8.42.

1.2. *6-(*tert*-Butyl)-8-methyl-4-[(methylthio)methyl]azulene-1-carbaldehyde* (**5a**) *and 6-(*tert*-Butyl)-8-methyl-4-[(methylthio)methyl]azulene-3-carbaldehyde* (**5b**). The *Vilsmeier* formylation of **4** (11.63 g, 45 mmol) was performed as described in [5] to yield, after CC (silica gel; hexane/Et$_2$O/CH$_2$Cl$_2$ 80 : 5 : 15), **5b** (3.6 g, 28%) as a first fraction and **5a** (7.6 g, 59%) as a second fraction.

Data of **5a**: Violet crystals. M.p. 111.6–112.4° (Et$_2$O). R_f (hexane/Et$_2$O 1 : 1) 0.38. UV/VIS (hexane): λ_{max} 525 (3.21), 387 (4.00), 316 (4.60), 249 (4.38); λ_{min} 430 (3.08), 349 (3.08), 272 (3.96). IR (KBr): 2954*w*, 1625*s*, 1576*w*, 1544*w*, 1497*w*, 1429*w*, 1353*m*, 1336*m*, 1245*w*, 1217*w*, 1065*w*, 800*w*, 771*w*, 729*w*. ^{1}H-NMR (600 MHz, CDCl$_3$): 10.60 (*s*, CHO); 8.32 (*d*, $J(2,3) = 4.6$, H–C(2)); 7.73 (*d*, $J = 1.3$, H–C(5)); 7.67 (*s*, H–C(7)); 7.38 (*d*, $J(2,3) = 4.6$, H–C(3)); 4.27 (*s*, MeSCH_2); 3.23 (*s*, Me–C(8)); 2.08 (*s*, *Me*SCH$_2$); 1.50 (*s*, *t*-Bu). ^{1}H-NOE: CHO → H–C(2), Me–C(8); MeSCH_2 → H–C(5), H–C(3); Me–C(8) → CHO, H–C(7). ^{13}C-NMR (75 MHz, CDCl$_3$): 186.74 (*d*, CHO); 159.96 (*s*); 148.07 (*s*); 146.82 (*s*); 142.28 (*s*); 138.74 (*d*); 137.74 (*s*);

130.64 (*d*); 130.20 (*s*); 128.23 (*d*); 116.43 (*d*); 41.63 (*t*, MeS*C*H$_2$); 38.81 (*s*, Me$_3$*C*); 31.79 (*q*, *Me*$_3$C); 31.60 (*q*, Me–C(8)); 16.07 (*q*, *Me*SCH$_2$). EI-MS: 287 (21), 286 (100, $M^{+\cdot}$), 271 (16, $[M-Me]^+$), 240 (49), 212 (64). Anal. calc. for $C_{18}H_{22}OS$ (286.44): C 75.48, H 7.74; found: C 75.21, H 7.60.

Data of **5b**: Violet crystals. M.p. 89.6–90.2° (Et_2O). R_f (hexane/Et_2O 1:1) 0.50. UV/VIS (hexane): λ_{max} 518 (3.30), 388 (4.02), 316 (4.59), 249 (4.42), 226 (4.44); λ_{min} 429 (3.05), 351 (3.91), 274 (4.00), 237 (4.34). IR (KBr): 2960*w*, 1631*s*, 1578*w*, 1543*w*, 1498*w*, 1464*w*, 1420*w*, 1335*s*, 1243*m*, 1094*w*, 1050*w*, 883*w*, 796*w*, 770*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 10.40 (*s*, CHO); 8.24 (*d*, *J*(1,2) = 4.4, H–C(2)); 7.80 (*d*, *J* = 2.0, H–C(5)); 7.64 (*s*, *J* = 1.3, H–C(7)); 7.31 (*d*, *J*(1,2) = 4.4, H–C(1)); 4.68 (*s*, MeSC*H*$_2$); 2.96 (*s*, Me–C(8)); 2.03 (*s*, *Me*SCH$_2$); 1.50 (*s*, *t*-Bu). ^{1}H-NOE: CHO → H–C(2), MeSC*H*$_2$; MeSC*H*$_2$ → CHO, H–C(5); Me–C(8) → H–C(7), H–C(1). ^{13}C-NMR (75 MHz, $CDCl_3$): 186.74 (*d*, CHO); 160.27 (*s*); 148.46 (*s*); 147.75 (*s*); 144.04 (*s*); 141.95 (*d*); 135.71 (*s*); 129.53 (2*d*); 128.32 (*s*); 116.93 (*d*); 44.61 (*t*, MeS*C*H$_2$); 38.85 (*s*, Me$_3$*C*); 31.78 (*q*, *Me*$_3$C); 26.89 (*q*, Me–C(8)); 15.80 (*q*, *Me*SCH$_2$). EI-MS: 287 (17), 286 (100, $M^{+\cdot}$), 271 (20, $[M-Me]^+$), 238 (78). Anal. calc. for $C_{18}H_{22}OS$ (286.44): C 75.48, H 7.74; found: C 75.32, H 7.57.

1.3. *6-(*tert*-Butyl)-1,8-dimethyl-4-[(methylthio)methyl]azulene* (**6**). Carbaldehyde **5a** (2.58 g, 9.0 mmol) was reduced by $NaBH_4$ according to the procedure described in [5] to yield 0.19 g (7.4%) of the starting material **5a** and 2.20 g (90%) of **6** as blue crystals. R_f (hexane/Et_2O 95:5) 0.43. UV/VIS (hexane): λ_{max} 581 (2.68), 355 (3.68), 290 (4.68), 249 (4.41); λ_{min} 421 (1.63), 265 (3.99), 226 (4.06). IR (KBr): 2963*s*, 1573*s*, 1512*m*, 1441*m*, 1362*w*, 1340*w*, 1243*m*, 1198*w*, 1174*w*, 1042*w*, 948*w*, 860*w*, 784*w*, 719*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.50 (*d*, *J*(2,3) = 4.0, H–C(2)); 7.32 (*d*, *J*(2,3) = 4.0, H–C(3)); 7.23 (*s*, H–C(5)); 7.11 (*s*, H–C(7)); 4.21 (*s*, MeSC*H*$_2$); 3.07 (*s*, Me–C(8)); 2.88 (*s*, Me–C(1)); 2.10 (*s*, *Me*SCH$_2$); 1.46 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): 157.71 (*s*); 146.86 (*s*); 143.82 (*s*); 137.83 (*s*); 136.59 (*s*); 133.59 (*s*); 126.90 (*s*); 124.93 (*d*); 121.60 (*d*); 113.82 (*d*); 41.36 (*t*, MeS*C*H$_2$); 38.35 (*s*, Me$_3$*C*); 31.60 (*q*, *Me*$_3$C); 28.27 (*q*); 19.59 (*q*); 16.14 (*q*). EI-MS: 273 (20), 272 (100, $M^{+\cdot}$), 257 (29, $[M-Me]^+$), 226 (73).

1.4. *Dimethyl 8-(*tert*-Butyl)-1,10-dimethyl-6-[(methylthio)methyl]heptalene-4,5-dicarboxylate* (**7**). Azulene **6** (2.20 g, 8.1 mmol) and ADM (3.64 g, 25.6 mmol) in toluene (85 ml) were heated at 130° for 30 h. After removal of toluene under reduced pressure, CC (silica gel; hexane/Et_2O/CH_2Cl_2 80:5:15), followed by recrystallization from CH_2Cl_2/hexane gave **7** (0.517 g, 15.4%). Yellow crystals. M.p. 154.1–155.4° (hexane). R_f (hexane/Et_2O 1:1) 0.47. UV/VIS (hexane): λ_{max} 314 (sh, 3.68), 264 (4.22); λ_{min} 250 (4.21). IR (KBr): 2947*w*, 1718*s*, 1573*w*, 1435*w*, 1304*w*, 1272*m*, 1254*m*, 1198*w*, 1152*w*, 1098*w*, 1082*w*, 1050*w*, 783*w*, 768*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.51 (*dd*, *J*(2,3) = 6.1, ^{5}*J*(3, Me–C(1)) = 0.8, H–C(3)); 6.29 (*s*, H–C(7)); 6.27 (*dd*, *J*(2,3) = 6.1, ^{4}*J*(2 Me–C(1)) = 1.2, H–C(2)); 6.22 (*s*, H–C(9)); 3.71, 3.66 (2*s*, 2 MeOCO); 3.39, 3.17 (*AB*, J_{AB} = 13.7, MeSC*H*$_2$); 2.12 (*t*-like, *J* = 1.0, Me–C(1)); 2.00 (*s*, *Me*SCH$_2$); 1.76 (*s*, Me–C(10)); 1.19 (*s*, *t*-Bu). ^{13}C-NMR (300 MHz, $CDCl_3$): 167.78, 167.44 (*s*, 2 MeOCO); 151.60 (*s*); 143.73 (*s*); 143.28 (*s*); 139.30 (*d*); 132.27 (*s*); 130.94 (*s*); 130.64 (*s*); 129.10 (*s*); 127.78 (*d*); 126.50 (*d*); 125.85 (*d*); 123.33 (*s*); 51.92, 51.73 (*q*, 2 *Me*OCO); 40.11 (*t*, MeS*C*H$_2$); 36.26 (*s*, Me$_3$*C*); 30.04 (*q*, *Me*$_3$C); 24.21 (*q*, Me–C(1)); 18.77 (*q*, Me–C(10)); 15.60 (*q*, *Me*SCH$_2$). EI-MS: 415 (22), 414 (100, $M^{+\cdot}$), 367 (58, $[M-MeS]^+$), 353 (73), 335 (73). Anal. calc. for $C_{24}H_{30}O_4S$ (414.57): C 69.53, H 7.29; found: C 69.96, H 7.22.

1.5. *{[8-(*tert*-Butyl)-4,5-bis(methoxycarbonyl)-1,10-dimethylheptalen-6-yl]methyl}dimethylsulfonium Tetrafluoroborate* (**8**). To the stirred soln. of **7** (32 mg, 0.077 mmol) in CH_2Cl_2 (2 ml), trimethyloxonium tetrafluoroborate (17 mg, 0.116 mmol) was added at 25°. After stirring overnight, the suspension was removed by filtration. Recrystallization from CH_2Cl_2/Et_2O gave pure **6** (32 mg, 80%). Yellow solid. M.p. 183.2–184.1° (CH_2Cl_2/Et_2O). UV/VIS (CH_2Cl_2/hexane): λ_{max} 328 (sh, 3.4), 270 (4.08); λ_{min} 257 (4.05). IR (KBr): 2953*m*, 1719*s*, 1642*w*, 1435*m*, 1392*w*, 1374*w*, 1259*s*, 1199*m*, 1155*w*, 1083*s*, 780*w*, 770*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.50 (*d*, *J*(2,3) = 6.1, H–C(3)); 6.82 (*s*, H–C(7)); 6.35 (*s*, H–C(9)); 6.32 (*dd*, *J*(2,3) = 6.3, ^{4}*J*(2, Me–C(1)) = 1.2, H–C(2)); 4.33, 4.01 (*AB*, J_{AB} = 12.7, Me$_2$S$^+$C*H*$_2$); 3.69, 3.68 (2*s*, 2 MeOCO); 2.99, 2.87 (2*s*, *Me*$_2$S$^+$CH$_2$); 2.08 (*s*, Me–C(1)); 1.78 (*s*, Me–C(10)); 1.18 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.40, 167.99 (*s*, 2 MeOCO); 152.22 (*s*); 142.88 (*s*); 139.81 (*d*); 139.37 (*s*); 136.73 (*d*); 132.74 (*s*); 131.07 (*s*); 129.24 (*d*); 128.90 (*s*); 127.05 (*d*); 125.49 (*s*); 120.18 (*s*); 52.33, 52.12 (*q*, 2 MeOCO); 50.41 (*t*, Me$_2$S$^+$*C*H$_2$); 36.37 (*s*, Me$_3$*C*); 29.83 (*q*, *Me*$_3$C); 25.20 (*q*); 24.24 (*q*); 23.92 (*q*); 18.91 (*q*). FAB-MS: 429 (18, M^+, cation), 392 (24), 368 (99), 367 (100, $[M-Me_2S]^+$), 307 (50).

1.6. *Dimethyl 8-(*tert*-Butyl)-6-(iodomethyl)-1,10-dimethylheptalene-4,5-dicarboxylate* (**9**). Heptalene **7** (17 mg, 0.04 mmol) and MeI (80 mg, 0.56 mmol) in MeCN (0.36 ml) were heated at 60° for 24 h [17]. After removal of the solvent, CC (silica gel; hexane/Et_2O 1:) yielded **9** (16 mg, 82%). Yellow crystals. M.p. 151.0–151.8° (hexane). R_f (hexane/Et_2O 1:1) 0.40. UV/VIS (hexane): λ_{max} 320 (sh, 3.60), 276 (sh, 4.15), 249 (4.29); λ_{min} 236 (4.28). IR (KBr): 2951*m*, 1712*s*, 1434*m*, 1303*m*, 1285*m*, 1261*s*, 1218*w*, 1197*w*, 1156*m*, 1010*w*, 1053*m*, 778*w*, 767*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.57 (*d*, *J*(2,3) = 6.2, H–C(3)); 6.58 (*s*, H–C(7)); 6.33 (*dd*, *J*(2,3) = 6.2, ^{4}*J*

(2, Me–C(1)) = 1.3, H–C(2)); 6.28 (*s*, H–C(9)); 4.31, 3.92 (*AB*, J_{AB} = 12.7, CH_2I); 3.71, 3.68 (2*s*, 2 MeOCO); 2.28 (*s*, Me–C(1)); 1.78 (*s*, Me–C(10)); 1.19 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.70, 167.30 (*s*, 2 MeOCO); 151.29 (*s*); 144.11 (*s*); 141.24 (*s*); 139.84 (*d*); 134.25 (*s*); 131.11 (*s*); 131.06 (*d*); 131.01 (*s*); 129.60 (*s*); 128.09 (*d*); 126.88 (*d*); 124.50 (*s*); 51.97, 51.88 (*q*, 2 *Me*OCO); 36.30 (*s*, Me_3C); 29.96 (*q*, Me_3C); 24.39 (*q*, Me–C(1)); 19.16 (*q*, Me–C(10)); 7.76 (*t*, CH_2I). CI-MS: 512 (35, $[M+NH_4]^+$), 495 (22, $[M+1]^+$), 463 (100).

1.7. *Dimethyl 8-(*tert*-Butyl)-6-formyl-1,10-dimethylheptalene-4,5-dicarboxylate* (**12**). To compound **7** (83 mg, 0.2 mmol) in CCl_4 (10 ml) at 25°, *N*-chlorosuccinimide (30 mg, 0.22 mmol) was added in portions. After the suspension had been stirred at 25° for 2 h, the resulting succinimide was removed by filtration. The filtrate was concentrated under reduced pressure and then dissolved in THF (1 ml). This yellow soln. was added to the suspension of HgO (44 mg, 0.2 mmol) and $BF_3 \cdot OEt_2$ (28 mg, 0.2 mmol) in H_2O/THF 4:1 (4 ml). The mixture was stirred for 1 h at 25°. Et_2O and aq. Na_2CO_3 were added subsequently. After filtration and extraction with Et_2O, the solvent was removed under reduced pressure to give a yellow residue, which was recrystallized from CH_2Cl_2/hexane to yield **12** in nearly quantitative yield (76 mg, 99%). Yellow crystals. M.p. 208.9–209.7° (CH_2Cl_2/hexane). R_f (hexane/Et_2O 1:1) 0.25. UV/VIS (hexane): λ_{max} 310 (sh, 3.75), 266 (4.33); λ_{min} 256 (4.32). IR (KBr): 2949*w*, 1724*s*, 1702*s*, 1675*m*, 1640*w*, 1437*w*, 1375*w*, 1299*w*, 1273*m*, 1255*s*, 1190*w*, 1156*w*, 1089*w*, 1055*w*, 782*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.53 (*s*, CHO); 7.56 (*dd*, *J*(2,3) = 5.9, ^{5}*J*(3, Me–C(1)) = 0.9, H–C(3)); 7.23 (*d*, *J* = 1.0, H–C(7)); 6.56 (*s*, H–C(9)); 6.33 (*dd*, *J*(2,3) = 5.9, ^{4}*J*(2, Me–C(1)) = 1.4, H–C(2)); 3.71, 3.51 (2*s*, 2 MeOCO); 1.95 (*d*, ^{4}*J*(2, Me–C(1)) = 1.1, Me–C(1)); 1.81 (*s*, Me–C(10)); 1.28 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz): 189.92 (*d*, CHO); 167.24, 166.94 (2*s*, MeOCO); 151.11 (*s*); 144.69 (*d*); 141.72 (*s*); 139.39 (*d*); 135.13 (*s*); 133.97 (*s*); 132.13 (*d*); 131.94 (*s*); 131.80 (*s*); 131.15 (*s*); 126.63 (*d*); 125.29 (*s*); 51.97, 51.77 (2*q*, *Me*OCO); 36.40 (*s*, Me_3C); 30.09 (*q*, Me_3C); 23.68 (*q*); 19.00 (*q*). CI-MS: 400 (36, $[M+NH_4]^+$), 368 (62), 351 (100). Anal. calc. for $C_{23}H_{26}O_5$ (382.46): C 72.23, H 6.85; found: C 72.58, H 7.17. The structure of **12** was confirmed by an X-ray crystals-structure analysis (*cf. Fig. 1*).

1.8. *Dimethyl 8-(*tert*-Butyl)-1,10-dimethyl-6-[(*E*)-2-phenylethenyl]heptalene-4,5-dicarboxylate* (**2a**). To **12** (7.7 mg, 0.02 mmol) in the two-phase system CH_2Cl_2/2N NaOH (1:1; 2 ml), a soln. of (benzyl)triphenylphosphonium chloride (**13a**; 46.7 mg, 0.12 mmol) in CH_2Cl_2 (1 ml) was added at 25°. After 2 h, the org. phase was separated, and the solvent was removed. CC (silica gel; hexane/Et_2O 1:1) yielded starting material **12** (2 mg, 26%) and a mixture of (*E*)-**2a** and (*Z*)-**2a**, which was isomerized with a catalytic amount of I_2 in hexane/Et_2O soln. at 25° overnight to afford pure (*E*)-**2a** (6 mg, 66%). Yellow crystals. M.p. 174.1–175.0°. R_f (hexane/Et_2O 1:1) 0.50. UV/VIS (hexane): λ_{max} 334 (sh, 4.20), 295 (4.38), 260 (4.43); λ_{min} 279 (4.34). IR (KBr): 2950*m*, 1721*s*, 1598*w*, 1559*w*, 1435*m*, 1390*w*, 1256*s*, 1196*w*, 1167*w*, 1088*w*, 1056*w*, 961*w*, 770*w*, 751*w*, 692*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.68 (*dd*, *J* = 0.9, *J*(2,3) = 6.1, H–C(3)); 7.40 (*m*, 2 arom. H); 7.32 (*m*, 2 arom. H); 7.26 (*m*, 1 arom. H); 6.92 (*d*, *J* = 15.8, CH=C*H*–C(6)); 6.59 (*s*, H–C(7)); 6.47 (*d*, *J* = 15.8, C*H*=CH–C(6)); 6.46 (*dd*, *J*(2,3) = 6.1, ^{4}*J*(2, Me–C(1)) = 1.4, H–C(2)); 6.33 (*s*, H–C(9)); 3.78, 3.55 (*s*, 2 MeOCO); 2.04 (*s*, Me–C(1)); 1.84 (*s*, Me–C(10)); 1.28 (*s*, *t*-Bu). ^{13}C-NMR (150 MHz, $CDCl_3$): 167.92, 167.64 (*s*, 2 MeO*C*O); 153.00 (*s*); 143.06 (*s*); 139.52 (*d*, C(3)); 138.49 (*s*); 137.52 (*s*); 133.51 (*s*); 131.26 (*s*); 131.11 (*s*); 129.48 (*d*, C(7)); 129.31 (*s*); 128.72 (*d*, 2 arom. C); 128.72 (*d*, CH=CH–C(6)); 128.44 (*d*, CH=CH–C(6)); 127.67 (*d*, 1 arom. C); 127.15 (*d*, C(9)); 126.76 (*d*, 2 arom. C); 126.36 (*d*, C(2)); 125.06 (*s*); 52.28, 52.00 (*q*, 2 *Me*OCO); 36.76 (*s*, Me_3C); 30.59 (*q*, Me_3C); 23.35 (*q*, Me–C(1)); 18.94 (*q*, Me–C(10)). EI-MS: 457 (14), 456 (47, $M^{+\bullet}$), 441 (9, $[M-Me]^+$), 424 (14), 397 (100, $[M-MeOCO]^+$), 365 (43).

1.9. *Dimethyl 8-(*tert*-Butyl)-1,10-dimethyl-6-[(*E*)-2-(4-methoxyphenyl)ethenyl]heptalene-4,5-dicarboxylate* (**2b**). At 0°, a 1M *t*-BuOK soln. (0.03 ml, 0.03 mmol) was added to the suspension of *(4-methoxyphenyl)-triphenylphosponium chloride* (**13b**; 16.8 mg, 0.04 mmol) in THF (0.5 ml). After the temp. had been raised to 25°, **12** (7.7 mg, 0.02 mmol) was added to this soln. The reaction was stopped by addition of H_2O after 30 min. Extraction with Et_2O and CC (silica gel; hexane/Et_2O 1:1) provided pure (*E*)-**2b** (3 mg, 31%). Yellow crystals. M.p. 182.0–182.8°. R_f (hexane/Et_2O 1:1) 0.37. UV/VIS (hexane): λ_{max} 334 (sh, 4.25), 302 (4.36), 262 (4.39); λ_{min} 282 (4.31). IR (KBr): 2961*m*, 1723*s*, 1605*w*, 1510*m*, 1435*w*, 1389*w*, 1254*s*, 1197*w*, 1173*m*, 1087*w*, 1032*w*, 954*w*, 843*w*, 769*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.66 (*dd*, *J*(2,3) = 6.1, ^{5}*J*(3, Me–C(1)) = 0.9, H–C(3)); 7.31 (*d*, *J* = 8.8, 2 arom. H); 6.85 (*d*, *J* = 8.8, 2 arom. H); 6.78 (*d*, *J* = 16.0, CH=C*H*–C(6)); 6.53 (*s*, H–C(7)); 6.45 (*dd*, *J*(2,3) = 6.1, ^{4}*J*(2, Me–C(1)) = 1.4, H–C(2)); 6.40 (*d*, *J* = 16.0, C*H*=CH–C(6)); 6.29 (*s*, H–C(9)); 3.83, 3.76 (*s*, 2 MeOCO); 3.53 (*s*, *Me*OC_6H_4); 2.01 (*s*, Me–C(1)); 1.82 (*s*, Me–C(10)); 1.28 (*s*, *t*-Bu). EI-MS: 487 (12), 486 (38, $M^{+\bullet}$), 428 (32), 427 (100).

1.10. *Dimethyl 8-(*tert*-Butyl)-6-[(*E*)-2-(4-chlorophenyl)ethenyl]-1,10-dimethylheptalene-4,5-dicarboxylate* (**2c**). The *Wittig* reaction of **12** (19.1 mg, 0.05 mmol) and *(4-chlorophenyl)triphenylphosphonium chloride* (**13c**; 127 mg, 0.3 mmol) in the two-phase system CH_2Cl_2/2N NaOH (1:1, 5 ml) was carried out as described for **2a** to give the mixture of (*E*)-**2c** and (*Z*)-**2c**, which was isomerized in the presence of a catalytic amount of I_2 in boiling

toluene overnight to pure (*E*)-**2c** (20 mg, 82%). Yellow crystals. M.p. 178.0–179.0° (hexane). R_f (hexane/Et_2O 1:1) 0.52. UV/VIS (hexane): λ_{max} 332 (sh, 4.20), 296 (4.39), 262 (4.39); λ_{min} 279 (4.34). IR (KBr): 2951*m*, 1728*s*, 1559*w*, 1490*w*, 1435*m*, 1391*w*, 1255*s*, 1196*w*, 1168*w*, 1090*m*, 1056*w*, 1011*w*, 964*w*, 846*w*, 812*w*, 780*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.67 (*dd*, *J*(2,3) = 6.0, ^{5}*J*(3, Me–C(1) = 1.0, H–C(3)); 7.30 (*d*-like, *J* = 9.1, 2 arom. H); 7.29 (*d*-like, *J* = 9.1, 2 arom. H); 6.87 (*dd*, *J* = 16.0, CH=C*H*–C(6)); 6.58 (*s*, H–C(7)); 6.45 (*dd*, *J*(2,3) = 6.1, ^{4}*J*(2, Me–C(1)) = 1.4, H–C(2)); 6.40 (*d*, *J* = 16.0, C*H*=CH–C(6)); 6.33 (*s*, H–C(9)); 3.76, 3.53 (*s*, 2 MeO-CO); 2.02 (*t*, *J* = 1.1, Me–C(1)); 1.83 (*s*, Me–C(10)); 1.28 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.62, 167.25 (*s*, 2 MeO*C*O); 152.66 (*s*); 142.73 (*s*); 139.28 (*d*); 137.93 (*s*); 135.71 (*s*); 132.98 (*s*); 132.92 (*s*); 130.95 (*s*); 129.73 (*d*); 129.00 (*s*); 128.76 (*d*); 128.61 (*d*, 2 arom. C); 127.57 (*d*, 2 arom. C); 127.11 (*d*); 127.01 (*d*); 126.13 (*d*); 124.88 (*s*); 51.97, 51.67 (*q*, 2 *Me*OCO); 36.42 (*s*, Me_3C); 30.23 (*q*, Me_3C); 23.01 (*q*, Me–C(1)); 18.61 (*q*, Me–C(10))[1]). CI-MS: 510, 508 (8/22, $[M+NH_4]^+$), 493, 491 (12/29, $[M+1]^+$), 461 (37), 459 (100).

1.11. *Dimethyl 8-(*tert*-Butyl)-1,10-dimethyl-6-[(*E*)-2-(4-nitrophenyl)ethenyl]heptalene-4,5-dicarboxylate* (**2d**). To **12** (7.7 mg, 0.02 mmol) in the two-phase system CH_2Cl_2/2N NaOH (1:1; 2 ml), a soln. of *(4-nitrobenzyl)triphenylphosphonium bromide* (**13d**; 57.4 mg, 0.12 mmol) in CH_2Cl_2 (1 ml) was added at 25° under stirring. After 4 h, additional **13d** (57.4 mg, 0.12 mmol) was introduced. After another 4 h, the org. phase was separated. CC (silica gel, hexane/Et_2O 1:1) afforded starting material **12** (2 mg, 26%) and the mixture of (*E*)-**2d** and (*Z*)-**2d**. The isomerization in the presence of a catalytic amount of I_2 in boiling toluene overnight afforded pure (*E*)-**2d** (1.5 mg, 15%). Yellow crystals. M.p. 184.1–185.4° (hexane). R_f (hexane/Et_2O 1:1) 0.43. UV/VIS (hexane): λ_{max} 358 (4.30), 260 (sh, 4.25), 242 (4.48); λ_{min} 313 (4.22). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.13 (*d*, *J* = 8.8, 2 arom. H); 7.65 (*d*, *J*(2,3) = 5.9, H–C(3)); 7.45 (*d*, *J* = 8.8, 2 arom. H); 7.02 (*d*, *J* = 15.8, CH=C*H*–C(6)); 6.65 (*s*, H–C(7)); 6.44 (*d*, *J*(2,3) = 5.9, H–C(2)); 6.43 (*d*, *J* = 15.8, C*H*=CH–C(6)); 6.34 (*s*, H–C(9)); 3.73, 3.49 (*s*, 2 MeOCO); 2.00 (*s*, Me–C(1)); 1.80 (*s*, Me–C(10)); 1.25 (*s*, *t*-Bu). CI-MS: 520 (16), 519 (58, $[M+NH_4]^+$), 502 (16), 501 (7, $M^{+\bullet}$), 487 (10), 471 (31), 470 (100).

1.12. *Dimethyl 8-(*tert*-Butyl)-1,10-dimethyl-6-[(*E*)-4-phenylbuta-1,3-dienyl]heptalene-4,5-dicarboxylate* (**2e**). *Method I:* The *Wittig* reaction of **12** (7.7 mg, 0.02 mmol) and *[(*E*)-3-phenylprop-2-enyl]triphenylphosphonium bromide* (**13e**; 55 mg, 0.12 mmol) in the two phase system CH_2Cl_2/2N NaOH (1:1, 2 ml) was performed as described for **2a** to yield pure **2e** (8.3 mg, 86%).

Method II: At −78°, to a stirred soln. of LDA (0.15 mmol; prepared from BuLi soln. (0.1 mmol, 0.15 mmol) and (i-Pr)$_2$NH (0.03 ml, 0.2 mmol)) in THF (1 ml), diethyl [(*E*)-3-phenylprop-2-enyl] phosphonate (0.046 ml, 0.2 mmol) was added. After stirring for 20 min at −78°, the color of the mixture became pale yellow, and **12** (38.2 mg, 0.1 mmol) was added. The temp. was raised to 25° in 4 h, and the reaction was quenched by addition of H_2O. Extraction by Et_2O, followed by CC (silica gel; hexane/Et_2O 1:1) yielded **2e** (42 mg, 87%).

Method III: At 0°, to the suspension of $CrCl_2$ (344 mg, 2.8 mmol) in THF (4 ml), a soln. of CHI_3 (315 mg, 0.8 mmol) in THF (1 ml) and **12** (76 mg, 0.2 mmol) in THF (3 ml) was added. The mixture was warmed to 25°, and stirring continued for 1 h before the reaction was quenched by addition of H_2O. After extraction with Et_2O, the org. phase was washed with H_2O and dried (anh. Na_2SO_4). Removal of Et_2O left a yellow residue, which was dissolved in DMF (0.5 ml). To this soln., $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), Ag_2CO_3 (55.2 mg, 0.2 mmol), and styrene (62.5 mg, 0.6 mmol) were added at 25°. After stirring overnight, H_2O was added to stop the reaction. Extraction by Et_2O and chromatography on silica gel (hexane/CH_2Cl_2/Et_2O 8:1:1) gave heptalene **2e** (56 mg, 59%).

Data of **2e**: Yellow crystals. M.p. 181.2–183.1° (hexane). R_f (hexane/Et_2O 1:1) 0.43. UV/VIS (hexane): λ_{max} 380 (sh, 4.15), 346 (4.49), 322 (84.50), 262 (4.39), 242 (4.42); λ_{min} 334 (4.48), 279 (4.33), 257 (4.38), 228 (4.40). IR (KBr): 3019*w*, 2954*m*, 1726*s*, 1560*w*, 1437*m*, 1388*w*, 1256*s*, 1194*w*, 1168*w*, 1093*m*, 1056*w*, 986*m*, 831*w*, 783*w*, 768*w*, 756*w*, 690*w*. ^{1}H-NMR (300 MHz, $CDCl_3$)[2]): 7.62 (*d*, *J*(2,3) = 6.1, H–C(3)); 7.35 (*m*, 2 arom. H); 7.27 (*m*, 2 arom. H); 7.19 (*m*, 1 arom. H); 6.76 (*dd*, *J*(3′,4′) = 15.5, *J*(2′,3′) = 10.6, H–C(3′)); 6.49 (*d*, *J*(3′,4′) = 15.6, H–C(4′)); 6.46 (*s*, H–C(7)); 6.43 (*d*, *J*(1′,2′) = 15.6, H–C(1′); 6.41 (*d*, *J*(2,3) = 6.2, H–C(2)); 6.25 (*s*, H–C(9)); 6.24 (*dd*, *J*(2′,3′) = 10.6, *J*(1′,2′) = 15.5, H–C(2′)); 3.65, 3.94 (2*s*, 2 MeOCO); 1.92 (*s*, Me–C(1)); 1.71 (*s*, Me–C(10)); 1.16 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.62, 167.32 (2*s*, MeOCO); 152.72 (*s*); 142.74 (*s*); 139.21 (*d*); 138.24 (*s*); 137.26 (*s*); 133.41 (*s*); 133.06 (*d*); 132.05 (*d*); 130.94 (*s*); 130.84 (*s*); 129.26 (*d*); 129.06 (*d*); 128.93 (*s*); 128.83 (*d*); 128.52 (*d*, 2 arom. C); 127.40 (*d*); 126.90 (*d*); 126.18 (*d*, 2 arom. C); 126.05 (*d*); 124.66 (*s*); 51.95, 51.70 (2*q*, *Me*OCO); 36.42 (*s*, Me_3C); 30.26 (*q*, Me_3C); 23.09 (*q*); 18.59 (*q*). CI-MS: 500 (41,

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[1]) The signals for two quaternary C-atoms coincided.

[2]) The C-atoms of the butadienyl side-chain are indicated by primed numbers.

$[M+NH_4]^+$), 483 (100, $[M+1]^+$), 451 (63). Anal. calc. for $C_{32}H_{32}O_4$ (482.62): C 79.64, H 7.10; found: C 79.18, H 7.26.

1.13. *4-[Bis(methylthio)methyl]-6,8-dimethylazulene* (**16**) [7]. To a stirred soln. of **15** (1.7 g, 10 mmol) in Et_2O (70 ml) at −78°, 0.6M of $NaN(SiMe_3)_2$ in toluene (34.2 ml, 20.5 mmol) was added over 10 min. The temp. was raised to 25°, and then MeSSMe (1.88 g, 20 mmol) was added. The reaction was quenched with H_2O after stirring at 25° for 2 h. Extraction with hexane, followed by CC (silica gel; hexane/Et_2O 98:2) afforded disubstituted azulene **16** (1.6 g, 61%). Blue crystals. M.p. 79.2–80.6° (hexane) ([7]: 80–81°). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.88 (*t*, *J*(1,2) ≈ *J*(1,3) ≈ 3.9, H–C(2)); 7.77 (*s*, H–C(5)); 7.65 (*d*, *J*(1,2) = 3.9, H–C(1)); 7.62 (*d*, *J*(2,3) = 3.6, H–C(3)); 7.29 (*s*, H–C(7)); 5.92 (*s*, $(MeS)_2CH$); 3.06 (*s*, Me–C(8)); 2.87 (*s*, Me–C(6)); 2.35 (*s*, $(MeS)_2CH$).

1.14. *4-[Bis(methylthio)methyl]-6,8-dimethylazulene-1-carbaldehyde* (**17a**) *and 4-[Bis(methylthio)methyl]-6,8-dimethylazulene-3-carbaldehyde* (**17b**). The *Vilsmeier* formylation of **16** (1.7 g, 6.48 mmol) was performed according to [5] to yield, after CC (silica gel; hexane/Et_2O/CH_2Cl_2 80:5:15), **17b** (0.52 g, 27.6%) in the first fraction and **17a** (1.26 g, 67%) in the second.

Data of **17a**: Violet crystals. M.p. 129.0–129.5° (Et_2O). R_f (hexane/Et_2O 1:1) 0.23. UV/VIS (hexane): λ_{max} 529 (2.81), 390 (3.92), 316 (4.55), 249 (4.35); λ_{min} 429 (1.75), 351 (3.77), 270 (3.86). IR (KBr): 2981*w*, 2908*w*, 1626*s*, 1581*m*, 1551*w*, 1497*m*, 1430*m*, 1352*s*, 1326*m*, 1304*m*, 1246*w*, 1207*w*, 1076*w*, 962*w*, 907*w*, 854*w*, 721*w*, 694*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 10.68 (*s*, CHO); 8.31 (*d*, *J*(2,3) = 4.7, H–C(2)); 7.89 (*s*, H–C(5)); 7.46 (*s*, H–C(7)); 7.45 (*d*, *J*(2,3) = 4.7, H–C(3)); 5.69 (*s*, $(MeS)_2CH$); 3.19 (*s*, Me–C(8)); 2.74 (*s*, Me–C(6)); 2.18 (*s*, $(MeS)_2CH$). ^{1}H-NOE (600 MHz, $CDCl_3$): CHO → H–C(2), Me–C(8), $(MeS)_2CH$ → H–C(7), H–C(3), $(MeS)_2CH$. ^{13}C-NMR (75 MHz, $CDCl_3$): 186.98 (*d*, CHO); 148.60 (*s*); 148.43 (*s*); 147.90 (*s*); 141.22 (*s*); 138.01 (*s*); 137.95 (*d*); 134.40 (*d*); 131.69 (*s*); 128.73 (*d*); 115.20 (*d*); 56.18 (*d*, $(MeS)_2CH$); 31.09 (*q*, Me–C(8)); 28.46 (*q*, Me–C(6)); 16.15 (*q*, $(MeS)_2CH$). EI-MS: 290 (53, $M^{+\cdot}$), 275 (10), 262 (24), 243 (100). Anal. calc. for $C_{16}H_{18}OS_2$ (290.45): C 66.17, H 6.25, S 22.08; found: C 66.06, H 6.25, S 22.30.

Data of **17b**: Violet crystals. M.p. 93.9–97.7° (Et_2O). R_f (hexane/Et_2O 1:1) 0.43. UV/VIS (hexane): λ_{max} 512 (3.03), 394 (3.03), 316 (4.51), 248 (4.37); λ_{min} 429 (2.34), 354 (3.77), 275 (3.86), 236 (4.26). IR (KBr): 2998*w*, 2918*w*, 1652*s*, 1628*s*, 1588*m*, 1549*w*, 1494*w*, 1434*w*, 1415*m*, 1385*m*, 1358*w*, 1329*s*, 1302*m*, 1211*w*, 1188*w*, 1096*w*, 1057*w*, 794*w*, 781*m*, 725*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 10.20 (*s*, CHO); 8.18 (*d*, *J*(1,2) = 4.4, H–C(2)); 7.98 (*s*, H–C(5)); 7.41 (*s*, H–C(7)); 7.36 (*d*, *J*(1,2) = 4.3, H–C(1)); 7.15 (*s*, $(MeS)_2CH$); 2.90 (*s*, Me–C(8)); 2.73 (*s*, Me–C(6)); 2.17 (*s*, $(MeS)_2CH$). ^{1}H-NOE (600 MHz, $CDCl_3$): CHO → H–C(2), $(MeS)_2CH$; $(MeS)_2CH$ → CHO, H–C(5), $(MeS)_2CH$. ^{13}C-NMR (75 MHz, $CDCl_3$): 186.61 (*d*, CHO); 152.13 (*s*); 149.35 (*s*); 147.68 (*s*); 145.83 (*d*); 145.32 (*s*); 134.59 (*s*); 133.60 (*d*); 129.97 (*d*); 127.67 (*s*); 117.72 (*d*); 57.26 (*d*, $(MeS)_2CH$); 28.33 (*q*, Me–C(8)); 26.27 (*q*, Me–C(6)); 15.77 (*q*, $(MeS)_2CH$). EI-MS: 290 (25, $M^{+\cdot}$), 243 (72), 199 (27), 196 (100). Anal. calc. for $C_{16}H_{18}OS_2$ (290.45): C 66.17, H 6.25, S 22.08; found: C 65.99, H 6.16, S 22.19.

1.15. *4-[Bis(methylthio)methyl]-1,6,8-trimethylazulene* (**18**). The reduction of **17a** (1.21 g, 4.17 mmol) with $NaBH_4$ (4.73 g, 125 mmol) in CF_3COOH/CH_2Cl_2 (1:1, 130 ml) at 25° for 9 h was accomplished as described in [5] to yield the mixture (940 mg) of **18** (723 mg, 63%) and the further reduced product **19** (217 mg, 23%). The fractional crystallization of this mixture from hexane led to pure **18** (600 mg, 52%). Blue crystals. M.p. 80.7–81.9° (hexane). R_f (hexane/Et_2O 95:5) 0.37. UV/VIS (hexane): λ_{max} 585 (2.81), 359 (3.65), 291 (4.63), 246 (4.36); λ_{min} 400 (0.4), 332 (3.42), 264 (3.98), 222 (4.11). IR (KBr): 2974*w*, 2912*m*, 1576*s*, 1516*m*, 1433*s*, 1394*w*, 1378*m*, 1334*w*, 1320*w*, 1297*w*, 1258*w*, 1176*w*, 1148*w*, 1072*m*, 1029*w*, 950*m*, 843*w*, 791*s*, 708*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.44 (*d*, *J*(2,3) = 4.2, H–C(2)); 7.35 (*s*, H–C(5)); 7.34 (*d*, *J*(2,3) = 4.2, H–C(3)); 6.87 (*s*, H–C(7)); 5.66 (*s*, $(MeS)_2CH$); 3.00 (*s*, Me–C(8)); 2.86 (*s*, Me–C(6)); 2.57 (*s*, Me–C(1)); 2.14 (*s*, $(MeS)_2CH$). ^{13}C-NMR (75 MHz, $CDCl_3$): 147.07 (*s*); 146.37 (*s*); 145.54 (*s*); 137.61 (*d*); 136.50 (*s*); 133.66 (*s*); 128.72 (*d*); 128.19 (*s*); 121.97 (*d*); 112.57 (*d*); 55.82 (*d*, Me_2SCH); 28.42 (*q*); 27.83 (*q*); 19.71 (*q*); 16.22 (*q*, Me_2SCH). EI-MS: 277 (14), 276 (89, $M^{+\cdot}$), 229 (100).

Data of 1,6,8-Trimethyl-4-[(methylthio)methyl]azulene (**19**). R_f (hexane/Et_2O 95:5) 0.39. ^{1}H-NMR (300 MHz, $CDCl_3$; taken from the data of the mixture with **18**): 7.51 (*d*, *J*(2,3) = 4.1, H–C(2)); 7.35 (*d*, *J*(2,3) = 4.1, H–C(3)); 7.01 (*s*, H–C(5)); 6.91 (*s*, H–C(7)); 4.20 (*s*, $MeSCH_2$–C(4)); 3.06 (*s*, Me–C(8)); 2.93 (*s*, Me–C(6)); 2.62 (*s*, Me–C(1)); 2.03 (*s*, $MeSCH_2$–C(4)). EI-MS (GC/MS): 231 (26), 230 (100, $M^{+\cdot}$), 215 (58), 200 (64), 184 (92).

1.16. *Dimethyl 1,8,10-Trimethyl-6-[bis(methylthio)methyl]heptalene-4,5-dicarboxylate* (**20a**). The thermal reaction of **18** (329 mg, 1.19 mmol) and ADM (0.44 ml, 3.57 mmol) in toluene (12 ml) was performed as described for **7** to yield **20a** (150 mg, 30%) as yellow crystals and its DBS isomer **20b** (25 mg, 5%) as yellow oil.

Data of **20a**: M.p. 92.1–92.7° (hexane). R_f (hexane/Et_2O 1:1) 0.36. UV/VIS (hexane): λ_{max} 308 (sh, 3.70), 270 (4.14); λ_{min} 252 (4.11). IR (KBr): 2948*w*, 2917*w*, 1722*s*, 1572*w*, 1436*m*, 1298*m*, 1268*s*, 1244*s*, 1195*w*, 1170*w*, 1144*w*, 1099*w*, 1083*m*, 1048*w*, 777*w*, 736*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.54 (*dd*, $J(2,3)=6.1$, $^5J(3, Me-C(1))=0.8$, H–C(3)); 6.27 (*dd*, $J(2,3)=6.1$, $^4J(2, Me-C(1))=1.1$, H–C(2)); 6.25 (*s*, H–C(7)); 6.16 (*s*, H–C(9)); 4.26 (*d*, $J=0.7$, Me_2SCH); 3.71 (*s*, 2 MeOCO); 2.16, 1.90 (2*s*, Me_2SCH); 2.10 (*t*-like, Me–C(1)); 2.09 (*d*, $^4J(9, Me-C(8))=1.1$, Me–C(8)); 1.73 (*s*, Me–C(10)). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.66, 167.35 (2*s*, MeO*C*O); 144.61 (*s*); 142.73 (*s*); 139.90 (*d*); 138.05 (*s*); 131.66 (*d*); 130.96 (*s*); 130.93 (*s*); 130.89 (*s*); 129.39 (*d*); 127.99 (*s*); 126.19 (*d*); 124.55 (*s*); 56.05 (*d*, Me_2SCH); 52.04, 51.96 (2*q*, *Me*OCO); 25.25 (*q*); 24.11 (*q*); 18.61 (*q*); 15.58 (*q*); 11.37 (*q*). EI-MS: 418 (13, $M^{+\cdot}$), 371 (100).

Data of Dimethyl 10-[Bis(methylthio)methyl]-5,6,8-trimethylheptalene-1,2-dicarboxylate (**20b**): R_f (hexane/Et_2O) 0.48. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.86, 6.81 (*AB*, $J_{AB}=11.8$, H–C(3,4)); 6.79 (*s*, H–C(9)); 6.29 (*s*, H–C(7)); 4.87 (*s*, $(MeS)_2CH$); 4.03, 3.96 (*s*, 2 MeOCO); 2.38, 2.04 (2*s*, $(MeS)_2CH$); 2.25 (*m*, Me–C(6,8)); 2.00 (*s*, Me–C(5)). EI-MS: 418 (6, $M^{+\cdot}$), 371 (100, $[M-MeS]^+$).

1.17. *Dimethyl 6-Formyl-1,8,10-trimethylheptalene-4,5-dicarboxylate* (**21**). To a suspension of HgO (76.6 mg, 0.354 mmol) and $BF_3\cdot OEt_2$ (48 mg, 0.354 mmol) in H_2O/THF (4:1; 4 ml), a soln. of **20a** (74 mg, 0.177 mmol) in THF was added at 25°. After stirring for 1 h, Et_2O and aq. Na_2CO_3 soln. was added. Extraction with Et_2O and chromatographic workup (silica gel; hexane/Et_2O 1:1) afforded **21** (53 mg, 88%). Yellow crystals. M.p. 207.5–208.3°. R_f (hexane/Et_2O 1:1) 0.18. UV/VIS (hexane/CH_2Cl_2): λ_{max} 360 (sh, 3.20), 320 (sh, 3.60), 267 (4.25); λ_{min} 255 (4.24). IR (KBr): 2949*w*, 1721*s*, 1678*m*, 1567*w*, 1435*w*, 1298*w*, 1270*s*, 1251*m*, 1199*w*, 1159*w*, 1089*w*, 1055*w*, 836*w*, 771*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.51 (*s*, CHO); 7.57 (*dd*, $J(2,3)=5.9$, $^5J(3, Me-C(1))=1.0$, H–C(3)); 6.93 (*d*, $J=0.7$, H–C(7)); 6.53 (*s*, H–C(9)); 6.34 (*dd*, $J(2,3)=5.9$, $^4J(2\,Me-C(1))=1.4$, H–C(2)); 3.72, 3.60 (*s*, 2 MeOCO); 2.22 (*d*, $^4J(9, Me-C(8))=1.2$, Me–C(8)); 1.97 (*t*, $^4J(2, Me-C(1))\approx{}^5J(3, Me-C(1))\approx1.2$, Me–C(1)); 1.81 (*s*, Me–C(10)). ^{13}C-NMR (75 MHz, $CDCl_3$): 190.13 (*d*, CHO); 167.24, 167.01 (*s*, 2 MeO*C*O); 146.35 (*d*); 142.04 (*s*); 139.73 (*d*); 137.84 (*s*); 137.51 (*d*); 135.47 (*s*); 132.28 (*s*); 132.23 (*s*); 131.26 (*s*); 130.57 (*s*); 126.85 (*d*); 125.37 (*s*); 52.00, 51.85 (*q*, 2 *Me*OCO); 24.31 (*q*); 23.67 (*q*); 18.80 (*q*). CI-MS: 358 (21, $[M+NH_4]^+$), 341 (3, $[M+1]^+$), 326 (50), 310 (21), 309 (100).

1.18. *Dimethyl 1,8,10-Trimethyl-6-[(*E,E*)-4-phenylbuta-1,3-dienyl]heptalene-4,5-dicarboxylate* (**22**). The *Wittig* reaction of **21** (51 mg, 0.15 mmol) and *[(*E*)-3-phenylprop-2-enyl]triphenylphosphonium bromide* (**13e**; 413 mg, 0.90 mmol) in the two-phase system CH_2Cl_2/2N NaOH was carried out as described for **2a** to yield **22** (62 mg, 94%). Yellow crystals. M.p. 218.2–218.8° (hexane). R_f (hexane/Et_2O 1:1): 0.38. UV/VIS (hexane): λ_{max} 347 (4.40), 323 (4.43), 265 (4.29); λ_{min} 337 (4.39), 283 (4.26), 257 (4.28). IR (KBr): 2945*w*, 1722*s*, 1563*w*, 1432*m*, 1254*s*, 1193*w*, 1158*w*, 1090*m*, 1055*w*, 995*w*, 788*w*, 771*w*, 750*w*, 691*w*. ^{1}H-NMR (300 MHz, $CDCl_3$)[2]): 7.63 (*dd*, $J(2,3)=6.0$, $^5J(3, Me-C(1))=1.0$, H–C(3)); 7.35 (*m*, 2 arom. H); 7.27 (*m*, 2 arom. H); 7.20 (*m*, 1 arom. H); 6.78 (*dd*, $J(3',4')=15.5$, $J(2',3')=10.1$, H–C(3′)); 6.49 (*d*, $J(3',4')=15.5$, H–C(4′)); 6.40 (*dd*, $J(2,3)=6.0$, $^4J(2, Me-C(1))=1.4$, H–C(2)); 6.39 (*d*, $J(1',2')=15.2$, H–C(1′)); 6.29 (*dd*, $J(1',2')=15.2$, $J(2',3')=10.1$, H–C(2′)); 6.19 (*s*, H–C(7)); 6.18 (*d*, $^4J(9, Me-C(1))=1.2$, H–C(9)); 3.70, 3.54 (*s*, 2 MeOCO); 2.10 (*d*, $^4J(9, Me-C(1))=1.0$, Me–C(8)); 1.96 (*t*, $^4J(2, Me-C(1))\approx{}^5J(3, Me-C(1))\approx1.1$, Me–C(1)); 1.74 (*s*, Me–C(10)). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.53, 167.32 (*s*, 2 MeOO*C*); 143.10 (*s*); 139.62 (*d*); 139.38 (*s*); 138.46 (*s*); 137.19 (*s*); 133.37 (*d*); 132.05 (*s*); 132.01 (*d*); 131.89 (*d*); 131.45 (*d*); 131.11 (*s*); 131.02 (*s*); 129.62 (*d*); 128.77 (*d*); 128.55 (*d*, 2 arom. C); 127.51 (*d*); 127.07 (*s*); 126.34 (*d*, 2 arom. C); 126.24 (*d*); 124.87 (*s*); 52.00, 51.82 (*q*, 2 *Me*OOC); 25.06 (*q*); 23.09 (*q*); 18.38 (*q*). EI-MS: 441 (29), 440 (100, $M^{+\cdot}$), 408 (10), 381 (72), 349 (51).

1.19. *4-[Bis(methylthio)methyl]-7-methylazulene* (**24**). To a stirred soln. of *4,7-dimethylazulene* (**23**; 2.22 g, 14.22 mmol) in Et_2O (95 ml) at −78°, a 0.6M soln. of $NaN(SiMe_3)_2$ in toluene (47.2 ml, 28.44 mmol) was added over 10 min. The temp. was raised slowly to 25°, and MeSSMe (2.68 g, 28.44 mmol) was added. The reaction was quenched with H_2O after stirring at 25° for 2 h. Extraction with hexane, followed by CC (silica gel; hexane/Et_2O) afforded starting **23** (0.36 g, 16%) and **24** (1.54 g, 44%). Blue crystals. M.p. 69.7–70.5° (hexane). R_f (hexane/Et_2O 95:5) 0.38. UV/VIS (hexane): λ_{max} 591 (2.68), 363 (3.38), 283 (4.54), 242 (4.30); λ_{min} 435 (0.20), 359 (3.20), 260 (4.08). IR (KBr): 2984*w*, 2916*w*, 1552*m*, 1522*w*, 1484*w*, 1458*w*, 1433*m*, 1415*m*, 1365*s*, 1288*w*, 1265*w*, 1191*w*, 1172*w*, 1136*w*, 1014*w*, 964*w*, 948*m*, 910*w*, 832*w*, 798*m*, 774*s*, 728*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.34 (*s*, H–C(8)); 7.89 (*t*, $J(1,2)\approx J(2,3)\approx3.9$, H–C(2)); 7.63 (*m*, H–C(5,6)); 7.48 (*d*, $J(1,2)=3.8$, H–C(1)); 7.37 (*d*, $J(2,3)=3.8$, H–C(3)); 5.74 (*s*, $(MeS)_2CH$); 2.68 (*s*, Me–C(7)); 2.22 (*s*, $(MeS)_2CH$). ^{13}C-NMR (75 MHz, $CDCl_3$): 145.13 (*s*); 140.68 (*s*); 138.64 (*d*); 137.74 (*d*); 136.46 (*s*); 136.26 (*d*); 131.99 (*s*); 122.01 (*d*); 118.68 (*d*); 112.67 (*d*); 55.35 (*d*, $(MeS)_2CH$); 25.99 (*q*, Me–C(7)); 16.08 (*q*, $(MeS)_2CH$). CI-MS: 249 (100, $[M+1]^+$), 248 (24, $M^{+\cdot}$), 201 (53). Anal. calc. for $C_{14}H_{16}S_2$ (248.41): C 67.69, H 6.49; found: C 67.72, H 6.63.

1.20. *Dimethyl 6-[Bis(methylthio)methyl]-9-methylheptalene-4,5-dicarboxylate* (**25**) *and Dimethyl 10-[Bis(methylthio)methyl]-7-methylheptalene-4,5-dicarboxylate* (**26a**). The azulene **24** (1.54 g, 6.2 mmol) and ADM (2.64 g, 18.6 mmol) in toluene (55 ml) were heated at 130° for 30 h. After removal of the solvent, CC (silica gel; hexane/Et_2O/CH_2Cl_2 80:5:15) yielded **25** (0.547 g, 22.6%) and **26a**/**26b** (0.088 g, 3.6%).

Data of **25**: Yellow crystals. M.p. 102.7–103.5° (EtOH). R_f (hexane/Et_2O 1:1) 0.31. UV/VIS (hexane): λ_{max} 318 (sh, 3.70), 262 (4.19); λ_{min} 253 (4.18). IR (KBr): 2917*w*, 1727*s*, 1434*m*, 1258*s*, 1228*m*, 1198*w*, 1132*w*, 1099*w*, 1049*w*, 752*w*, 598*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.59 (*d*, *J*(2,3) = 6.3, H–C(3)); 6.38 (*d*, *J*(7,8) = 6.7, H–C(7)); 6.37 (*dd*, *J*(1,2) = 10.2, *J*(2,3) = 6.4, H–C(2)); 6.33 (*d*, *J*(7,8) = 6.7, H–C(8)); 6.06 (*d*, *J*(1,2) = 10.2, H–C(1)); 5.61 (*s*, H–C(10)); 4.24 (*s*, $(MeS)_2CH$); 3.75, 3.74 (2*s*, MeOCO); 2.17, 1.88 (2*s*, $(MeS)_2CH$); 2.02 (*s*, Me–C(9)). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.65, 167.06 (2*s*, MeO*C*O); 143.08 (*s*); 140.33 (*d*); 139.48 (*s*); 135.67 (*d*); 133.95 (*s*); 130.57 (*d*); 129.71 (*s*); 129.62 (*d*); 128.05 (*s*); 126.78 (*d*, 2 C); 125.30 (*s*); 56.07 (*d*, $(MeS)_2CH$); 52.21, 52.15 (2*q*, *Me*OCO); 24.11 (*q*); 15.57 (*q*); 11.00 (*q*). EI-MS: 390 (6, $M^{+\bullet}$), 343 (7), 283 (100).

Data of **26a**: Orange crystals. In thermal equilibrium in $CDCl_3$ at 25° with 35% of **26b**. M.p. 136.9–137.8° (hexane). R_f (hexane/Et_2O 1:1) 0.29. IR (KBr): 1714*s*, 1438*m*, 1268*s*, 1205*w*, 1135*w*, 1096*w*, 1056*w*, 781*w*, 744*w*. ^{1}H-NMR (600 MHz, $CDCl_3$; taken from the mixture with **26b**): 7.47 (*d*, *J*(2,3) = 5.8, H–C(3)); 6.81 (*d*, *J*(8,9) = 11.9, H–C(9)); 6.55 (*dd*, *J*(8,9) = 11.9, ^{4}*J*(6,8) = 1.0, H–C(8)); 6.38 (*dd*, *J*(1,2) = 10.3, *J*(2,3) = 5.8, H–C(2)); 6.02 (*d*, *J*(1,2) = 10.3, H–C(1)); 5.86 (*s*, H–C(6)); 4.69 (*s*, Me_2SCH); 3.72, 3.67 (*s*, 2 MeOCO); 2.15, 1.92 (*s*, Me_2SCH); 2.02 (*d*, *J* = 1.1, Me–C(7)). EI-MS: 390 (8, $M^{+\bullet}$), 343 (100, $[M - MeS]^+$).

Data of Dimethyl 6-[Bis(methylthio)methyl]-9-methylheptalene-1,2-dicarboxylate (**26b**; in equilibrium in $CDCl_3$ at 25° with 65% of **26a**): ^{1}H-NMR (600 MHz, $CDCl_3$; taken from the mixture with **26a**): 6.62 (*dd*, *J*(3,4) = 11.6, *J*(4,5) = 6.3, H–C(4)); 6.58 (*d*, *J*(3,4) = 11.6, H–C(3)); 6.41 (*d*, *J*(7,8) = 6.8, H–C(7)); 6.17 (2*d*, superimposed, *J* ≈ 6.4, H–C(5), H–C(8)); 5.68 (*s*, H–C(10)); 4.39 (*s*, Me_2SCH–C(6)); 3.81, 3.73 (*s*, MeOCO); 2.20, 2.05 (*s*, Me_2SCH–C(6)); 2.00 (*s*, Me–C(9)).

1.21. *Dimethyl 6-Formyl-9-methylheptalene-4,5-dicarboxylate* (**27**). The hydrolysis of **25** (567 mg, 1.45 mmol) with HgO (629 mg, 2.90 mmol) and $BF_3 \cdot OEt_2$ (197 mg, 2.90 mmol) in THF/H_2O was performed according to the procedure described for **20a** to yield **27** (411 mg, 91%). Orange crystals. M.p. 201.3–202.1° (Et_2O). R_f (hexane/EtOAc 4:6) 0.49. UV/VIS (hexane): λ_{max} 400 (sh, 3.00), 330 (sh, 3.60), 272 (4.30); λ_{min} 252 (4.24). IR (KBr): 1732*s*, 1712*m*, 1681*s*, 1641*w*, 1604*w*, 1576*w*, 1440*w*, 1276*s*, 1256*m*, 1232*m*, 1195*w*, 1168*w*, 1134*w*, 1108*w*, 1056*m*, 860*w*, 746*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 9.43 (*s*, CHO); 7.52 (*d*, *J*(2,3) = 6.4, H–C(3)); 7.00 (*d*, *J*(7,8) = 6.6, H–C(7)); 6.48 (*d*, *J*(7,8) = 6.6, H–C(8)); 6.36 (*dd*, *J*(1,2) = 10.4, *J*(2,3) = 6.4, H–C(2)); 5.99 (*d*, *J*(1,2) = 10.2, H–C(1)); 5.68 (*s*, H–C(10)); 3.72, 3.58 (2*s*, MeOCO); 2.10 (*s*, Me–C(9)). ^{1}H-NOE (600 MHz, $CDCl_3$): CHO → H–C(7); Me–C(9) → H–C(10), H–C(8); H–C(10) → H–C(1), Me–C(9). ^{13}C-NMR (75 MHz, $CDCl_3$): 190.81 (*d*, CHO); 167.26, 167.00 (2*s*, MeO*O*C); 147.45 (*s*); 146.66 (*d*); 140.44 (*d*); 135.36 (*s*); 134.81 (*d*); 134.76 (*s*); 133.06 (*s*); 132.98 (*d*); 131.46 (*d*); 130.55 (*s*); 127.44 (*s*); 126.92 (*d*); 52.29, 52.12 (2*q*, *Me*OCO); 25.10 (*q*, Me–C(9)). EI-MS: 312 (3, $M^{+\bullet}$), 253 (100, $[M - MeOCO]^+$). The structure of **27** was confirmed by an X-ray crystal-structure analysis (*cf. Fig. 2*).

1.22. *Dimethyl 9-Methyl-6-[(*E,E*)-4-phenylbuta-1,3-dienyl]heptalene-4,5-dicarboxylate* (**28**). To the two-phase system of **27** (62.5 mg, 0.2 mmol) in CH_2Cl_2/2N NaOH (1:1, 20 ml), a soln. of [(*E*)-3-phenylprop-2-enyl]triphenylphosphonium bromide (551 mg, 1.2 mmol) in CH_2Cl_2 (10 ml) was added at 25° under stirring. After 2 h, the org. phase was separated and the solvent evaporated. CC (silica gel; hexane/Et_2O 1:1) yielded a mixture of (1*Z*,3*E*)-**28** and (1*E*,3*E*)-**28**, which was stirred with a catalytic amount of I_2 in hexane/Et_2O at 25° overnight to yield pure (1*E*,3*E*)-**28** (78 mg, 95%). Orange crystals. M.p. 200.1–201.0° (hexane). R_f (hexane/Et_2O 1:1) 0.28. UV/VIS (hexane): λ_{max} 410 (sh, 3.90), 330 (4.51), 246 (4.35); λ_{min} 286 (4.22). IR (KBr): 3021*w*, 2949*w*, 1737*s*, 1714*s*, 1434*m*, 1271*s*, 1234*m*, 1200*w*, 1125*m*, 1097*w*, 1053*w*, 1008*w*, 990*w*, 754*w*, 690*w*. ^{1}H-NMR (600 MHz, $CDCl_3$)[2]): 7.66 (*d*, *J*(2,3) = 6.4, H–C(3)); 7.36 (*m*, 2 arom. H); 7.30 (*m*, 2 arom. H); 7.21 (*m*, 1 arom. H); 6.80 (*dm*-like, *J*(3′,4′) = 15.5, H–C(3′)); 6.54 (*d*, *J*(3′,4′) = 15.5, H–C(4′)); 6.48 (*dd*, *J*(1,2) = 10.2, *J*(2,3) = 6.4, H–C(2)); 6.45 (*m*, H–C(1′,2′)); 6.37 (*d*, *J*(7,8) = 6.9, H–C(8)); 6.29 (*d*, *J*(7,8) = 6.9, H–C(7)); 6.09 (*d*, *J*(1,2) = 10.2, H–C(1)); 5.66 (*s*, H–C(10)); 3.75, 3.56 (2*s*, MeOCO); 2.05 (*s*, Me–C(9)). ^{13}C-NMR (150 MHz, $CDCl_3$): 167.87, 167.29 (2*s*, MeO*C*O); 140.75 (*d*, C(3)); 140.49 (*s*); 139.22 (*s*); 137.57 (*s*); 135.14 (*d*, C(1)); 134.74 (*s*); 133.56 (*d*, C(1′)); 133.44 (*d*, C(4′)); 132.25 (*d*, C(10)); 131.35 (*d*, C(2)); 130.38 (*d*, C(7)); 130.08 (*s*); 129.03 (*d*, C(2′)); 128.99 (*s*); 128.96 (*d*, C(3′)); 128.90 (*d*, C(8)); 128.82 (*d*, 2 arom. C); 127.70 (*d*, 1 arom. C); 126.86 (*s*); 126.50 (*d*, 2 arom. C); 52.52, 52.32 (2*q*, *Me*OCO); 24.76 (*q*, Me–C(9)). EI-MS: 413 (14), 412 (56, $M^{+\bullet}$), 353 (100, $[M - MeOCO]^+$), 321 (58). The structure of (1*E*,3*E*)-**28** was confirmed by an X-ray crystal-structure analysis (*cf. Fig. 3*).

2. X-Ray Crystal-Structure Determinations[3]) **of 12, 27, and 28.** – All measurements were made on a *Rigaku AFC5R* diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å) and a 12-kW rotating anode generator. The $\omega/2\theta$ scan mode was employed and the intensities of three standard reflections were measured after every 150 reflections and remained stable throughout each data collection. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. The data collection and refinement parameters are given in the *Table*.

Table 1. *Crystallographic Data of* **12**, **27**, *and* **28**

Substance	**12**	**27**	**28**
Crystallized from	CH_2Cl_2/Et_2O/hexane	CH_2Cl_2/hexane	CH_2Cl_2/Et_2O/hexane
Empirical formula	$C_{23}H_{26}O_5$	$C_{18}H_{16}O_5$	$C_{27}H_{24}O_4$
Formula weight [g mol^{-1}]	382.45	312.32	412.48
Crystal color, habit	yellow, tablet	red, prism	red, prism
Crystal dimensions [mm]	$0.15 \times 0.40 \times 0.50$	$0.42 \times 0.42 \times 0.48$	$0.42 \times 0.42 \times 0.48$
Temp. [K]	173(1)	296(1)	173(1)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Z	4	4	2
Reflections for cell determination	25	25	25
2θ Range for cell determination [°]	36 – 40	36 – 40	39 – 40
Unit cell parameters a [Å]	9.568(4)	13.261(1)	10.429(2)
b [Å]	20.896(3)	8.570(2)	12.670(3)
c [Å]	10.592(3)	14.110(1)	9.377(1)
α [°]	90	90	93.77(2)
β [°]	107.00(2)	99.010(7)	102.09(2)
γ [°]	90	90	109.83(2)
V [Å^3]	2025.2(8)	1583.8(4)	1110.7(4)
D_x [g cm^{-3}]	1.254	1.310	1.233
μ(MoK_α) [mm^{-3}]	0.0874	0.0957	0.0819
$2\theta_{(max)}$ [°]	55	55	55
Total reflections measured	5069	4040	5374
Symmetry independent reflections	4655	3633	5095
Reflections used [$I > 2\sigma(I)$]	3346	2436	3603
Parameters refined	358	273	377
Final R	0.0442	0.0430	0.0438
wR	0.0402	0.0355	0.0383
Goodness of fit	1.647	1.863	1.887
Secondary extinction coefficient	$1.08(7) \times 10^{-6}$	$2.5(1) \times 10^{-6}$	$1.4(2) \times 10^{-6}$
Final Δ_{max}/σ	0.0002	0.0006	0.0003
$\Delta\rho$ (max; min) [e Å^{-3}]	0.26; −0.20	0.18; −0.13	0.23; −0.25
$\sigma(d(C-C))$ [Å]	0.002 – 0.003	0.002 – 0.003	0.002 – 0.004

Each structure was solved by direct methods with SHELXS86 [18], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were located in difference electron-density maps, and their positions were allowed to refine together with individual isotropic displacement

[3]) Crystallographic data (excluding structure factors) for the structures of compounds **12**, **27**, and **28** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-130627, 130628, and 130629, respectively. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

parameters. Refinement of each structure was carried out on F with full-matrix least-squares procedures, which minimized the function $\Sigma w\,(|F_o|-|F_c|)$, where $w=[\sigma^2(F_o)+(pF_o)^2]^{-1}$. A correction for secondary extinction was applied in each structure.

Neutral atom scattering factors for non-H-atoms were taken from [19], and the scattering factors for H-atoms were taken from [20]. Anomalous dispersion effects were included in F_c [21]; the values for f' and f'' were those of [22]. All calculations for **28** were performed with the TEXSAN crystallographic software package [23], while teXsan was employed for **12** and **27** [24].

REFERENCES

[1] A. A. S. Briquet, H.-J. Hansen, *Helv. Chim. Acta* **1994**, *77*, 1940.
[2] P. Uebelhart, H.-J. Hansen, *Helv. Chim. Acta* **1992**, *75*, 2493.
[3] M. Müller, S. Braun, K. Hafner, *Angew. Chem.* **1980**, *92*, 635.
[4] A. A. S. Briquer, H.-J. Hansen, *Helv. Chim. Acta* **1994**, *77*, 1921.
[5] J. Song, H.-J. Hansen, *Helv. Chim. Acta* **1999**, *82*, 309.
[6] A. G. Anderson, Jr., R. D. Breazeale, *J. Org. Chem.* **1969**, *34*, 2374.
[7] S. Hünig, K. Hafner, B. Ort, M. Müller, *Liebigs Ann. Chem*. **1986**, 1222.
[8] P. G. Gassman, H. R. Grews, *J. Am. Chem. Soc.* **1978**, *100*, 7600.
[9] P. G. Gassman, D. R. Amick, *J. Am. Chem. Soc.* **1978**, *22*, 7611.
[10] K. Takai, K. Nitta, K. Utimoto, *J. Am. Chem. Soc.* **1986**, *108*, 7408.
[11] H. Bienaymé, *Tetrahedron Lett*. **1994**, *35*, 6867.
[12] S. Maillefer-El Hour, Ph. D. Thesis, University of Zürich, 1998.
[13] R. N. McDonald, H. E. Petty, N. L. Wolfe, J. V. Paukstelis, *J. Org. Chem.* **1974**, *39*, 1877.
[14] V. Georgian, R. Harrisson, N. Gubish, *J. Am. Chem. Soc.* **1959**, *81*, 5934.
[15] Y. Kikugawa, *J. Chem. Soc., Perkin Trans. I* **1984**, 609.
[16] J. Song, H.-J. Hansen, *Helv. Chim. Acta* **1999**, *82*, in press.
[17] R. Neidlein, W. Kramer, R. Krotz, *Arch. Pharm. (Weinheim)* **1984**, *317*, 984.
[18] G. M. Sheldrick, SHELX-86, *Acta Crystallogr., Sec. A* **1990**, *46*, 467.
[19] E. N. Maslen, A. G. Fox, M. A. O'Keefe, 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 6.1.1.1, p. 477.
[20] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175.
[21] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964**, *17*, 781.
[22] D. C. Creagh, W. J. McAuley, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.6.8, p. 219.
[23] TEXSAN: Single Crystal Structure Analysis Software, Version 5.0, *Molecular Structure Corporation*, The Woodlands, Texas, 1989.
[24] teXsan: Single Crystal Structure Analysis Software, Version 1.8, *Molecular Structure Corporation*, The Woodlands, Texas, 1997.

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