18. Synthesis of Benz[*a*]azulenes Substituted at the Benzo Ring

by **Reza-Ali Fallahpour**[1]) and **Hans-Jürgen Hansen***

Organisch-chemisches Institut der Universität, Winterthurerstr. 190, CH–8057 Zürich

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It is shown that the thermal electrocyclic ring-closure reaction of 1,2-di[(*E*)-prop-1-enyl]benzene to yield 2,3-dimethylnaphthalene (*cf. Scheme 1*) [10] can successfully be applied also to the synthesis of benz[*a*]azulenes (*cf. Schemes 2* and *3*). Starting materials are methyl 4,6,8-trimethylazulen-2-yl ketone (**6**) and the corresponding 2-carbaldehyde **5**, which, in a *Horner-Emmons* reaction, are transformed into the (azulen-2-yl)-acrylates (*E*)-**8** and (*E*)-**7**, respectively. *Vilsmeier* formylation of these compounds, followed by the *Horner-Emmons* reaction leads to the formation of the bisacrylates (*E,E*)-**11** and (*E,E*)-**12**, respectively. In an alternative reaction, (*E*)-**8**, on treatment with dimethyl acetylenedicarboxylate (ADM) in the presence of $[RuH_2(PPh_3)_4]$, can be transformed into the methoxycarbonyl-substituted bisacrylates (*E,E*)- and (*E,Z*)-**17**. All three bisacrylates, on heating at 180–190° in *p*-cymene, undergo cyclization to yield the corresponding dihydrobenz[*a*]azulenes **13**, **14**, and **18**, respectively, which could easily be dehydrogenated on heating in the presence of Pd/C. The new benz[*a*]azulenes **15**, **16**, and **19** are fully characterized.

Introduction. – Within the rich ensemble of benz[*a*]azulene syntheses that have been developed over the past 40 years (*cf.* [1]), there are only a few examples dealing with the introduction of substituents at the benzo ring. For instance, *Jutz et al.* have shown that their annelation procedure for aromatic systems (*cf.* [2]), which involves the base-catalyzed reaction of α-CH-acidic compounds with vinamidinium salts, followed by thermal electrocyclic ring closure with elimination of a secondary amine[2]), can successfully be applied also to the synthesis of benz[*a*]azulenes. In this way, starting with (azulen-1-yl)- or (azulen-2-yl)acetonitrile and suitable vinamidinium salts, several benz[*a*]azulenes with substituents at C(1) and C(3), or at C(2) and C(4) have been obtained [2] [4]. Another approach utilizes the [2 + 8] cycloaddition of 8-methoxyheptafulvene with *p*-benzoquinones, followed by dehydrogenation and reductive methylation, for the synthesis of 1,4-dimethoxy-substituted benz[*a*]azulenes [5][3]).

We were interested in a versatile benz[*a*]azulene synthesis that would allow to vary the substituents at C(1)–C(4) as well as at the other positions of the azulene skeleton. On the other hand, the starting azulenes should easily be accessible. The fulfilment of these requirements would open the access to whole variety of benzo[*d*]heptalenes by the transition-metal-catalyzed addition of dimethyl acetylenedicarboxylate (ADM) to the benz[*a*]azulenes (*cf.* [8]; see also [9]).

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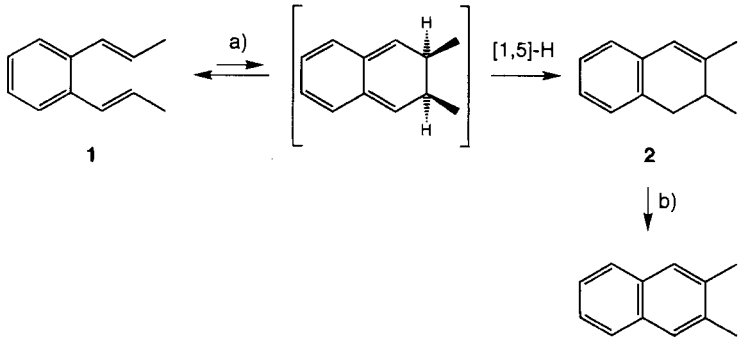
[1]) New address: Institut für Anorganische Chemie der Universität, Spitalgasse 57, CH–4045 Basel.

[2]) The prototype of this reaction sequence has been realized in the *Ziegler-Hafner* synthesis of azulenes [3].

[3]) The recently established synthesis of azuleno[1,2-*a*]acenaphthylene by [2 + 8] cycloaddition of 2*H*-cyclohepta[*b*]furan-2-one and 1-pyrrolidinoacenaphthylene [6] demonstrates the potential of this azulene synthesis (*cf.* [7]) with respect to the possible formation of benz[*a*]azulenes, substituted at C(1)–C(4).

More than 20 years ago, we observed in an investigation of aromatic [1,7]-H shifts the facile thermal cyclization of 1,2-di[(*E*)-prop-1-enyl]benzene (**1**) to yield finally 2,3-dimethyl-1,2-dihydronaphthalene (**2**) which, on treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-carbonitrile) in boiling benzene, gave 2,3-dimethylnaphthalene (**3**; *Scheme 1*) [10]. We report here on first results of the application of this annelation concept to the synthesis of new benz[*a*]azulenes.

Scheme 1



a) 225° in decane, $\tau_{1/2} = 45$ h. b) DDQ in boiling benzene.

Results and Discussions. – Methyl 4,6,8-trimethylazulen-2-yl ketone (**6**) can be prepared in almost quantitative yield by methylenation of methyl 4,6,8-trimethylazulene-2-carboxylate (**4**)[4]) with *Tebbe*'s or *Takai*'s reagent (*cf.* [13]), followed by hydrolysis of the formed enol ether (*cf. Scheme 2*).

On the other hand, 4,6,8-trimethylazulene-2-carbaldehyde (**5**) can most conveniently be prepared by reduction of **4** to the corresponding methanol (with DIBAH or $LiAlH_4$) which, in turn, is reacted with MnO_2 in CH_2Cl_2 [12]. Reaction of both carbonyl compounds with diethyl (ethoxycarbonyl)methylphosphonate in THF in the presence of NaH gave the β-substituted acrylates (*E*)-**7** and (*E*)-**8**, respectively. Both azulenes reacted smoothly with the *Vilsmeier* reagent from DMF/$POCl_3$ to yield the azulene-1-carbaldehydes (*E*)-**9** and (*E*)-**10**, respectively. The latter two compounds were again treated with diethyl (ethoxycarbonyl)methylphosphonate/NaH in THF leading to the

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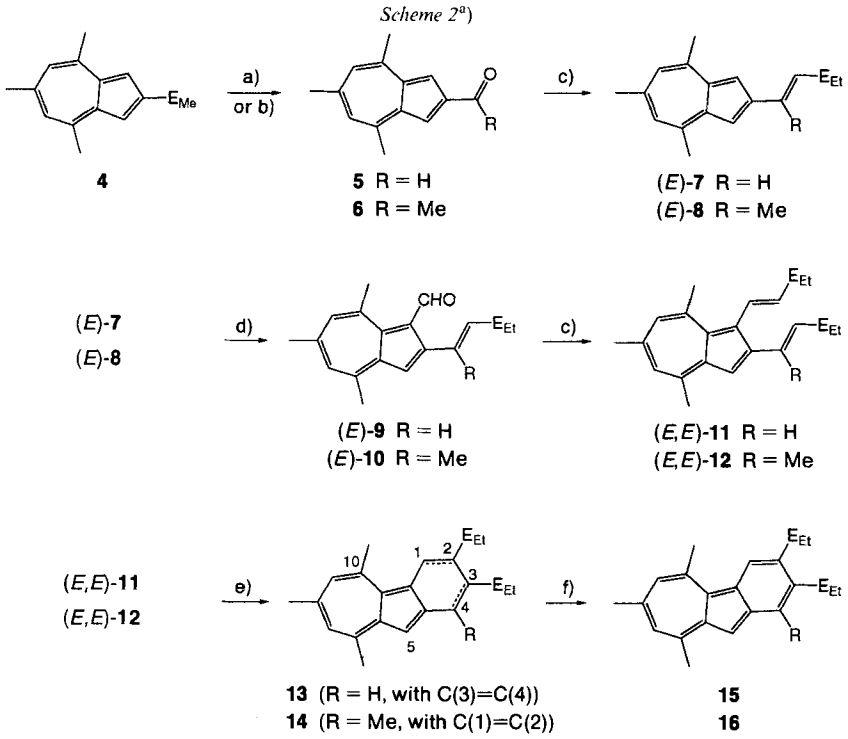
[4]) This and other 4,6,8-trisubstituted methyl azulene-2-carboxylates are easily prepared by the reaction of sodium (methoxycarbonyl)cyclopentadienide [11] with the corresponding pyrylium salts [9] (*cf.* also [12]). 2-Acetylazulenes with other substituent patterns are available from the selective methylenation reaction of azulene-1,2-dicarboxylates with *Tebbe*'s or *Takai*'s reagent, which yields only the enol-ether function at C(2) (*cf.* [13]). Hydrolysis of the enol-ether function, followed by ester cleavage and decarboxylation in H_3PO_4, likewise leads to the formation of 2-acetylazulenes [14]. Similarly, the azulene-1,2-dicarboxylates can selectively be reduced with DIBAH to yield the corresponding 2-(hydroxymethyl)azulene-1-carboxylates (*cf.* [15]) which, in turn, yield the corresponding 2-formylazulene-1-carboxylates on dehydrogenation with MnO_2 in CH_2Cl_2 [14]. Again, ester cleavage with H_3PO_4 leads to the azulene-2-carbaldehydes. In this context, it should be noted that azulene-1,2-dicarboxylates are often the main products in the thermal reaction of azulenes with ADM in apolar solvents (*e.g.* see [15]).

Scheme 2[a])



a) 1. *Tebbe*'s (*Aldrich*®) or *Takai*'s reagent [16] in THF; 2. 2N HCl. b) 1. $LiAlH_4$ in Et_2O; 2. MnO_2 in CH_2Cl_2 (*cf.* [12]). c) $(EtO)_2P(O)CH_2E_{Et}$/NaH in THF, 0–20°. d) DMF/$POCl_3$, 20°. e) In *p*-cymene, 180–190°. f) 10% Pd/C, *p*-cymene, 180–190°.

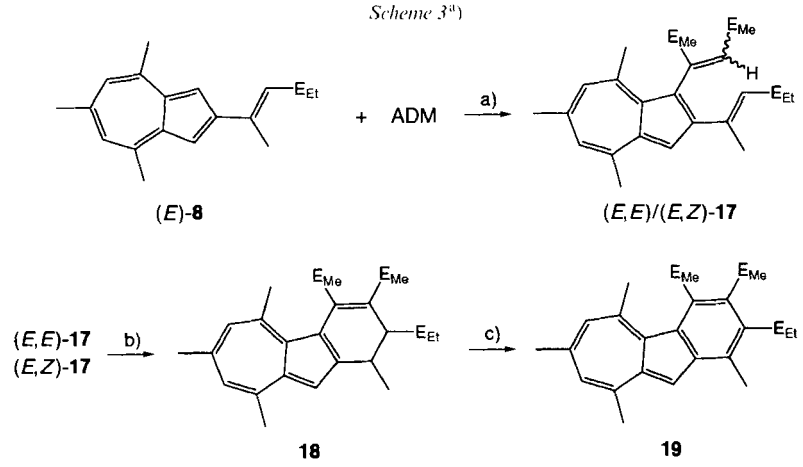
[a]) E_{Me} = COOMe; E_{Et} = COOEt.

bisacrylates (*E,E*)-**11** and (*E,E*)-**12**. Heating of these bisacrylates in *p*-cymene at 180–190° induced the electrocyclic ring closure with subsequent [1,5]-H shift and yielded the dihydrobenz[*a*]azulenes **13** and **14**, respectively. The position of the C=C bond in **14** was easily assigned, since we observed a *d* for the Me group at C(4) in the ^{1}H-NMR spectrum. The position of the C=C bond in **13** was derived from a comparison of the UV spectra (hexane) of **13** and a similar compound with COOMe groups at C(3) and C(4), the structure of which had been determined by an X-ray crystal-structure analysis [17]. Both compounds showed a typical twin absorption at 425 nm ($\log \varepsilon = 3.95$) and 409 nm ($\log \varepsilon = 3.96$) for **13** and at 414 nm ($\log \varepsilon = 3.76$) and 395 nm ($\log \varepsilon = 3.80$) for the reference compound. The dehydrogenation of **13** and **14** was accomplished on heating in *p*-cymene in the presence of Pd/C. However, there was a clear difference in the rate of dehydrogenation. Whereas the dehydrogenation of **14** was completed after 12 h and occurred, to a certain extend, already on standing in the air at room temperature without the dehydrogenation catalyst, the dehydrogenation of **13** took place only reluctantly and after 20 h of boiling in *p*-cymene, starting material was still present beside product **15**. The best yield of dehydrogenation of **13** was obtained with $PtO_2 \cdot H_2O$. The last two steps could be

combined, *i.e.*, heating of (*E,E*)-**11** and (*E,E*)-**12** in *p*-cymene in the presence of Pd/C yielded directly the benz[*a*]azulenes **15** and **16**, respectively. As a model reaction, **16** was reduced with DIBAH in hexane to the corresponding 2,3-dimethanol (see *Exper. Part*).

A further benz[*a*]azulene (*cf.* **19**; *Scheme 3*) was derived from (*E*)-**8**. Reaction of this compound with ADM in the presence of catalytic amounts of $[RuH_2(PPh_3)_4]$ in MeCN/H_2O (*cf.* [8] [9]) led to the formation of an (*E*)/(*Z*)-mixture of the ethene-1,2-dicarboxylates **17**.

Scheme 3[a])



a) $[RuH_2(PPh_3)_4]$, MeCN/H_2O, 20°. b) In *p*-cymene, 180–190°. c) 10% Pd/C, *p*-cymene, 180–190°.

[a]) E_{Me} = COOMe; E_{Et} = COOEt.

The mixture could be separated by chromatography on silica gel (hexane/Et_2O 1:1). However, both isomers, *i.e.*, (*E,E*)-**17** and (*E,Z*)-**17**, behaved identically on heating in *p*-cymene and yielded the ring-closed product **18**. This compound was easily transformed into the mixed tricarboxylate **19** on heating in the presence of Pd/C in *p*-cymene. The ring closure and dehydrogenation of (*E,E*)-**17** and (*E,Z*)-**17** could also be achieved directly to yield **19**.

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Experimental Part

General. See [13].

1. *Diethyl 4,6,8,10-Tetramethylbenz[a]azulene-2,3-dicarboxylate* (**16**). 1.1. *Methyl 4,6,8-Trimethylazulen-2-yl Ketone* (**6**). *Method A* (*cf.* [16]). In a typical reaction, THF (25 ml) was cooled to 0° under N_2 and $TiCl_4$ (8.8 mmol as a 1.0 M soln. in CH_2Cl_2) added from a syringe. The yellow soln. was allowed to warm up to r.t. within 15 min. *N,N,N',N'*-Tetramethylethane-1,2-diamine (TMEDA; 2.6 ml, 17.5 mmol) was added and the brown soln. stirred for 10 min. Zn dust (1.29 g, 19.7 mmol) was introduced and the resulting suspension stirred for 30 min during which time the soln. turned blue. A soln. of the *methyl 4,6,8-trimethylazulene-2-carboxylate* (**4**) [9] (0.5 g, 2.19 mmol) and

CH_2Br_2 (0.84 g, 4.8 mmol) in THF (10 ml) was added from a syringe. Stirring was continued for 3 h at r.t. During this time the color of the mixture had changed to black. It was stirred for additional 3 h at 25° and then poured on ice in 2N NaOH. The resulting mixture was filtered over *Celite* and the filter cake thoroughly washed with CH_2Cl_2. The CH_2Cl_2 phases were separated and dried ($MgSO_4$). The solvent was distilled off (RE) and the residue subjected to CC (silica gel; hexane/Et_2O 1:1; for the separation of ethenyl methyl ethers, the silica gel was pre-treated with Et_3N) to yield 0.450 g (96%) of pure **6**.

Method B (*cf.* [18]). To a soln. of **4** (0.5 g; 2.19 mmol) in THF (10 ml), cooled to 0°, *Tebbe*'s reagent in toluene (*Aldrich*; 4.4 ml, 2.20 mmol) was added. After 30 min, the mixture was poured on ice 2N NaOH. The resulting mixture was filtered over *Celite* and the filter cake thoroughly washed with CH_2Cl_2. The workup described above yielded 0.460 g (99%) of pure **6**.

Data of **6**: blue crystals from hexane/Et_2O. M.p. 156°. R_f 0.59. IR (KBr): 2923*w*, 1659*s*, 1578*m*, 1537*m*, 1475*m*, 1375*m*, 1318*s*, 1211*s*, 1112*m*, 977*m*, 852*m*, 816*m*, 654*w*, 614*w*, 535*w*. ^{1}H-NMR: 7.72 (*s*, H–C(1,3); 7.09 (*s*, H–C(5,9)); 2.89 (*s*, Me–C(4,8)); 2.73 (*s*, COOMe); 2.64 (*s*, Me–C(6)).

1.2. *Ethyl (*E*)-3-(4,6,8-Trimethylazulen-2-yl)but-2-enoate* ((*E*)-**8**). NaH (0.120 g, 3.0 mmol) was suspended in THF (20 ml) and cooled to 0°. Diethyl (ethoxycarbonyl)methylphosphonate (0.80 g, 3.6 mmol) was added, and the mixture stirred for 1 h at r.t. Then, **6** (0.200 g, 0.94 mmol) in THF (10 ml) was slowly added, and the mixture stirred for 20 h. The solvent was distilled off (RE) and the residue subjected to CC (silica gel; hexane/Et_2O 1:1) to yield 0.244 g (92%) of pure (*E*)-**8**. Blue crystals from hexane/Et_2O. M.p. 139–140°. R_f 0.31. ^{1}H-NMR[5]: 7.49 (*s*, H–C(1′,3′)); 7.05 (*s*, H–C(5′,7′)); 6.61 (*s*, H–C(2)); 4.25 (*q*, J = 7.1, COOCH_2Me); 2.85 (*s*, Me–C(4′,8′)); 2.75 (*s*, Me–C(3)); 2.61 (*s*, Me–C(6′)); 1.35 (*t*, J = 7.1, COOCH$_2$*Me*).

1.3. *Ethyl (*E*)-3-(1-Formyl-4,6,8-trimethylazulen-2-yl)but-2-enoate* ((*E*)-**10**). Compound (*E*)-**8** (0.244 g, 0.86 mmol) was formylated with DMF/$POCl_3$ in the usual way (cf. [19]) to yield 0.244 g (91%) of pure (*E*)-**10**. Red crystals from hexane/Et_2O. M.p. 116–117°. R_f 0.14. ^{1}H-NMR: 10.58 (*s*, CHO); 7.43 (*s*, H–C(3′)); 7.38 (*s*, H–C(5′)); 7.10 (*s*, H–C(7′)); 5.98 (*q*, J = 1.3, H–C(2)); 4.24 (*q*, J = 7.1, COOCH_2Me); 3.11 (*s*, Me–C((8′)); 2.89 (*s*, Me–C(4′)); 2.68 (*s*, Me–C(6′)); 2.60 (*d*, J = 1.3, Me–C(3)); 1.32 (*t*, J = 7.1, COOCH$_2$*Me*).

1.4. *Ethyl (*E*)-3-{1-[(*E*)-2-(Ethoxycarbonyl)ethen-1-yl]-4,6,8-trimethylazulen-2-yl}but-2-enoate* (**12**). NaH (0.122 g, 18.3 mmol) was suspended in THF (20 ml) and cooled to 0°. Diethyl (ethoxycarbonyl)methylphosphonate (0.82 g, 21.96 mmol) was added and the mixture was stirred for 1 h at r.t. Then a soln. of **10** (0.244 g) in THF (10 ml) was slowly added and the mixture stirred for 20 h at r.t. The solvent was distilled off (RE) and the residue subjected to CC (silica gel; hexane/Et_2O 1:1) to yield 0.268 g (90%) of pure (*E,E*)-**12**. Blue crystals from hexane/Et_2O. M.p. 111–112°. R_f 0.42. ^{1}H-NMR: 8.56 (*d*, J(1″,2″) = 15.7, H–C(1″)); 7.16 (*s*, H–C(3′)); 7.10 (*s*, H–C(5′,7′)); 6.11 (*q*-like, H–C(2)); 5.90 (*d*, J(2″,1″) = 15.7, H–C(2″)); 4.25 (*q*, J = 7.1, 2 COOCH_2Me); 3.01 (*s*, Me–C(8′)); 2.79 (*s*, Me–C(4′)); 2.58 (*s*, Me–C(6′)); 2.52 (*d*-like, Me–C(3)); 1.34 (*t*, J = 7.1, 2 COOCH$_2$*Me*).

1.5. *Diethyl 3,4-Dihydro-4,6,8,10-tetramethylbenz[*a*]azulene-2,3-dicarboxylate* (**14**). Compound (*E,E*)-**12** (0.268 g, 0.705 mmol) was heated in *p*-cymene (20 ml) at 180° during 12 h. The solvent was distilled off in a *Kugelrohr* apparatus at 50°/12 mm. The residue was subjected to CC (silica gel; hexane/Et_2O 1:1) to yield 0.201 g, (75%) of pure **14**. Blue crystals from hexane/Et_2O. M.p. 124–125. R_f 0.18. ^{1}H-NMR: 8.60 (*s*, H–C(1)); 7.14 (*s*, H–C(5)); 7.06 (*s*, H–C(9)); 7.05 (*s*, H–C(7)); 4.28 (*q*, J = 7.1, MeCH_2OCO–C(2)); 4.02 (*q*, J = 7.1, MeCH_2OCO–C(3)); 3.84 (*d*, J(3,4) = 7.2, H–C(3)); 3.54 (*q*-like, J(4,3) = 7.2, J(4,Me–C(4)) = 7.1, H–C(4)); 3.07 (*s*, Me–C(10)); 2.81 (*s*, Me–C(6)); 2.57 (*s*, Me–C(8)); 1.60 (*d*, J(Me–C(4),4) = 7.1, Me–C(4)); 1.34 (*t*, J = 7.1, *Me*CH$_2$OCO–C(2)); 1.14 (*t*, J = 7.1, *Me*CH$_2$OCO–C(3)).

1.6. *Dehydrogenation of* **14**. Compound **14** (0.20 g, 0.53 mmol) was heated in *p*-cymene (20 ml) at 180° during 12 h in the presence of Pd/C (10%, 0.20 g). After filtration of Pd/C, the solvent was distilled off in a *Kugelrohr* apparatus at 50°/12 mm. The residue was subjected to CC (silica gel; hexane/Et_2O 1:1) to yield 0.150 g (75%) of pure **16**. Blue crystals from hexane/Et_2O. M.p. 140°. R_f 0.30. UV (hexane): λ_{max} 427 (3.93), 406 (3.94), 339 (4.24), 312 (4.08, sh), 239 (4.00); λ_{min} 411 (3.92), 373 (3.63), 277 (3.74). IR (KBr): 2924*m*, 1724*s*, 1672*s*, 1578*s*, 1522*s*, 1458*m*, 1368*m*, 1328*m*, 1307*m*, 1236*s*, 1181*s*, 1107*s*, 1028*m*. ^{1}H-NMR: 8.66 (*s*, H–C(1)); 7.35 (*s*, H–C(5)); 7.12 (*s*, H–C(7)); 7.11 (*s*, H–C(9)); 4.28 (*q*, J = 7.1, MeCH_2OCO–C(3)); 4.08 (*q*, J = 7.1, MeCH_2OCO–C(2)); 3.12 (*s*, Me–C(10)); 2.84 (*s*, Me–C(6)); 2.59 (*s*, Me–C(8)); 1.86 (*s*, Me–C(4)); 1.34 (*t*, J = 7.1, *Me*CH$_2$OCO–C(3)); 1.19 (*t*, J = 7.1, *Me*CH$_2$OCO–C(2)). ^{1}H-NOE ($CDCl_3$): 3.12 (Me–C(10))→8.66 (*s*, H–C(1)), 7.11 (*s*, H–C(9)); 2.84 (Me–C(6))→7.35 (*s*, H–C(5)), 7.12 (*s*, H–C(7)); 2.59 (Me–C(8))→7.12 (*s*, H–C(7)), 7.11 (*s*, H–C(9)); 1.86 (Me–C(4))→7.35 (*s*, H–C(5)), 4.28 (*s*, MeCH_2OCO–C(3)). EI-MS: 379 (24, $[M + 1]^+$), 378 (100, $M^{+\cdot}$), 333 (7, $[M - EtO]^+$), 304 (15, $[(M + 1) - COOEt]^+$), 303 (15, $[M - COOEt]^+$), 202 (11), 191 (11), 189 (24), 178 (12), 165

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[5]) The locants of the substituent are primed.

(19), 152 (33), 114 (13), 91 (14), 83 (11), 82 (14), 81 (13), 77 (14), 73 (17), 71 (18), 69 (17), 68 (11), 59 (9), 57 (35), 56 (47), 55 (41), 54 (11), 51 (17).

1.7. *Reduction of* **16**. Compound **16** (0.070 g, 0.19 mmol) was dissolved in Et_2O (10 ml) and cooled to 0°. At this temp., a soln. of DIBAH in hexane (10 ml, 10 mmol) was slowly added. The mixture was stirred for an additional h at 0°, and then AcOEt (5 ml) and 2N aq. NaOH (20 ml) were added. The aq. phase was extracted 3× with Et_2O (20 ml). The org. phase was dried ($MgSO_4$) and distilled off. This highly water-soluble diol of **16** was isolated in 45% yield (0.030 g) after purifying by CC (silica gel, Et_2O).

Data of 4,6,8,10-Tetramethylbenz[a]azulene-2,3-dimethanol: blue crystals. M.p. 196–197°. R_f 0.07. ^{1}H-NMR: 8.31 (*s*, H–C(1)); 7.39 (*s*, H–C(5)); 6.90 (*s*, H–C(7)); 6.87 (*s*, H–C(9)); 5.05, 5.03 (2*s*, 2 CH_2OH); 3.12 (*s*, Me–C(10)); 2.83 (*s*, Me–C(6)); 2.75 (*s*, Me–C(8)); 2.51 (*s*, Me–C(4)); signals of OH not recognizable.

2. *Diethyl 6,8,10-Trimethylbenz[a]azulene-2,3-dicarboxylate* (**15**). 2.1. *4,6,8-Trimethylazulene-2-carbaldehyde* (**5**). *Cf.* [12]. 2.2. *Ethyl (E)-3-(4,6,8-Trimethylazulen-2-yl)prop-2-enoate* ((*E*)-**7**). NaH (0.100 g, 4.17 mmol), diethyl (ethoxycarbonyl)methylphosphonate (1.10 g, 4.91 mmol), and **5** (0.440 g, 1.42 mmol) were reacted as described under *1.2*. After purifying by CC, pure (*E*)-**7** (0.570 g, 95%) was obtained. Blue crystals from hexane/Et_2O. M.p. 141–142°. R_f 0.39. ^{1}H-NMR: 7.98 (*d*, *J*(3,2) = 15.9, H–C(3)); 7.44 (*s*, H–C(1′,3′)); 7.05 (*s*, H–C(5′,7′)); 6.63 (*d*, *J*(2,3) = 15.9, H–C(2)); 4.29 (*q*, *J* = 7.1, COOCH_2Me); 2.84 (*s*, Me–C(4′,8′)); 2.61 (*s*, Me–C(6)); 1.35 (*t*, *J* = 7.1, COOCH_2*Me*).

2.3 *Ethyl (E)-3-(1-Formyl-4,6,8-trimethylazulen-2-yl)prop-2-enoate* ((*E*)-**9**). Compound (*E*)-**7** (0.570 g, 1.93 mmol) was formylated with DMF/$POCl_3$ in the usual way (*cf.* [19]) to yield 0.585 g (92%) of pure (*E*)-**9**.

2.4. *Ethyl (E)-3-{1-[(E)-2-(Ethoxycarbonyl)ethen-1-yl]-4,6,8-trimethylazulen-2-yl}prop-2-enoate* ((*E,E*)-**11**). NaH (0.100 g, 4.17 mmol) diethyl (ethoxycarbonyl)methylphosphonate (1.10 g, 4.91 mmol), and (*E*)-**9** (0.585 g, 1.98 mmol) were reacted as described under *1.2*. CC yielded pure (*E,E*)-**11** (0.700 g, 90%). Blue crystals from hexane/Et_2O. M.p. 153–154°. R_f 0.39. ^{1}H-NMR: 8.48 (*d*, *J*(1″,2″) = 15.7, H–C(1″)); 8.02 (*d*, *J*(3,2) = 15.8, H–C(3)); 7.52 (*s*, H–C(3′)); 7.07 (*s*, H–C(5′,7′)); 6.65 (*d*, *J*(2,3) = 15.8, H–C(2)); 5.83 (*d*, *J*(2″,1″) = 15.7, H–C(2″)); 4.30, 4.39 (2*q*, *J* = 7.1, 2 COOCH_2Me); 3.00 (*s*, Me–C(8′)); 2.82 (*s*, Me–C(4′)); 2.59 (*s*, Me–C(6′)); 1.36 (*t*, *J* = 7.1, 2 COOCH_2*Me*).

2.5. *Diethyl 1,2-Dihydro-6,8,10-trimethylbenz[a]azulene-2,3-dicarboxylate* (**13**). Compound (*E,E*)-**11** (0.700 g, 0.705 mmol) was heated in *p*-cymene (20 ml) at 180° during 12 h. The solvent was distilled off in a *Kugelrohr* apparatus at 50°/12 mm. The residue was subjected to CC (silica gel; hexane/Et_2O 1:1) to yield 0.550 g (78%) of pure **13**. Blue crystals from hexane/Et_2O. M.p. 168–169°. R_f 0.28. UV (hexane): λ_{max} 424 (3.95), 409 (3.96), 347 (4.27, sh), 338 (4.31), 314 (4.14, sh), 238 (4.02), 209 (4.10, sh); λ_{min} 418 (3.94), 376 (3.63), 277 (3.65), 220 (3.90). ^{1}H-NMR: 8.60 (*s*, H–C(4)); 7.14 (*s*, H–C(5)); 7.06 (*s*, H–C(9)); 7.05 (*s*, H–C(7)); 4.28 (*m*, *J* = 7.1, Me–CH_2OCO–C(3)); 4.02 (*m*, *J* = 7.1, MeCH_2OCO–C(2)); 3.98 (*X* of *ABX*, J_{AX} = 8.2, J_{BX} = 3.0, H–C(2)); 3.60 (*B* of *ABX*, $^2J_{AB}$ = 17.0, J_{BX} = 3.0, H_B–C(1)); 3.25 (*A* of *ABX*, $^2J_{AB}$ = 17.0, J_{AX} = 8.2, H_A–C(1)); 3.08 (*s*, Me–C(10)); 2.81 (*s*, Me–C(6)); 2.57 (*s*, Me–C(8)); 1.35 (*t*, *J* = 7.1, *Me*CH_2OCO–C(3)); 1.14 (*t*, *J* = 7.1, *Me*CH_2OCO–C(2)). EI-MS: 367 (11, $[M + 1]^+$), 366 (76, M^+), 294 (22, $[(M + 1) - COOEt]^+$), 293 (100, $[M - COOEt]^+$), 263 (17), 221 (23), 220 (79), 206 (23), 205 (23), 204 (14), 203 (23), 202 (21), 190 (19), 189 (29), 179 (11), 178 (17), 165 (28), 152 (11).

2.6. *Compound* **15**. Compound **13** (0.10 g, 0.274 mmol) was heated in toluene (20 ml) at 120° during 1 h in the presence of $PtO_2 \cdot H_2O$ (0.10 g). The solvent was distilled off (RE) and the residue subjected to CC (silica gel; hexane/Et_2O 3:1) to yield 0.050 g (50%) of pure **15** and starting material **13** (0.020 g, 20%).

Data of **15**: blue crystals from hexane/Et_2O. M.p. 144–145°. R_f 0.28. UV (hexane): λ_{max} 424 (3.12), 401 (3.21), 333 (3.88, sh), 318 (3.95), 304 (3.89, sh), 247 (3.67); λ_{min} 412 (3.11), 368 (3.03), 270 (3.48). ^{1}H-NMR: 8.97 (*s*, H–C(1)); 8.12 (*s*, H–C(4)); 7.35 (*s*, H–C(5)); 7.03 (*s*, H–C(9)); 7.00 (*s*, H–C(7)); 4.45, 4.44 (2*q*, *J* = 7.1, 2 COOCH_2Me); 3.19 (*s*, Me–C(10)); 2.75 (*s*, Me–C(6)); 2.56 (*s*, Me–C(8)); 1.35 (*t*, *J* = 7.1, *Me*CH_2OCO–C(3)); 1.24 (*t*, *J* = 7.1, *Me*CH_2OCO–C(2)). EI-MS: 365 (19, $[M + 1]^+$), 364 (78, M^+), 293 (6, $[(M + 1) - COOEt]^+$), 291 (17, $[M - COOEt]^+$), 218 (10), 203 (22), 202 (31), 190 (11), 189 (25), 178 (10), 165 (21), 155 (11), 152 (20), 151 (11), 137 (15), 127 (18), 125 (15), 123 (13), 119 (10), 111 (22), 97 (26), 95 (28), 93 (20), 91 (21), 85 (29), 84 (33), 83 (32), 82 (21), 81 (23), 72 (21), 71 (44), 70 (29), 69 (48), 67 (20), 57 (100), 56 (40), 55 (73). Anal. calc. for $C_{23}H_{24}O_4$ (364.38): C 75.82, H 6.64; found: C 75.65, H 6.58.

3. *3-Ethyl 1,2-Dimethyl 4,6,8,10-Tetramethylbenz[a]azulene-1,2,3-tricarboxylate* (**19**). 3.1. *Dimethyl (E)- and (Z)-2-{2-(E)-[2-(Ethoxycarbonyl)-1-methylethenyl]-4,6,8-trimethylazulen-1-yl}but-2-enedioate* ((*E,E*)- and (*E,Z*)-**17**). Compound (*E*)-**8** (0.10 g, 0.356 mmol), ADM (0.20 g, 1.41 mmol), and $Ru[H_2(PPh_3)_4]$ (0.010 g) were stirred in MeCN (5 ml)/H_2O (0.2 ml) during 48 h at r.t. The solvent was distilled off (RE). The residue subjected to CC (silica gel; hexane/Et_2O 1:1) to yield 0.80 g (53%) of pure (*E,E*)-**17** and 0.064 g (43%) of (*E,Z*)-**17**.

*Data of (E,E)-***17**: blue crystals from hexane/Et_2O. M.p. 113–114°. R_f 0.39. ^{1}H-NMR: 7.26 (*s*, H–C(3)); 7.16 (*s*, H–C(3′)); 7.06 (*s*, H–C(5′)); 7.01 (*s*, H–C(7′)); 5.85 (*q*-like, H–C(2″)); 4.19 (*q*, *J* = 7.1, COOCH_2Me); 3.79,

3.49 (2*s*, 2 COOMe); 2.84 (*s*, Me–C(8′)); 2.71 (*s*, Me–C(4′)); 2.58 (*s*, Me–C(6′)); 2.48 (*d*-like, Me–C(1″); 1.29 (*t*, $J = 7.1$, $COOCH_2Me$).

Data of (E,Z)-**17**: violet oil. R_f 0.29. ^{1}H-NMR: 7.21 (*s*, H–C(3′)); 7.12 (*s*, H–C(5′)); 7.10 (*s*, H–C(7′)); 6.09 (*s*, H–C(3)); 6.01 (*q*-like, H–C(2″)); 4.19 (*q*, $J = 7.1$, $COOCH_2$Me); 3.82, 3.75 (2*s*, 2 COOMe); 2.89 (*s*, Me–C(8′)); 2.85 (*s*, Me–C(4′)); 2.61 (*s*, Me–C(6′)); 2.55 (*d*-like, Me–C(1″)); 1.30 (*t*, $J = 7.1$, $COOCH_2Me$).

3.2. *3-Ethyl 1,2-Dimethyl 3,4-Dihydro-4,6,8,10-tetramethylbenz[a]azulene-1,2,3-tricarboxylate* (**18**). The mixture (0.140 g, 0.33 mmol) of (*E,E*)-**17** and (*E,Z*)-**17** was heated in *p*-cymene (20 ml) at 180° during 12 h. The solvent was distilled off in a *Kugelrohr* apparatus at 50°/12 mm. The residue was subjected to CC (silica gel; hexane/Et_2O 1:1) to yield 0.10 g (71%) of pure **18**. Brown powder. R_f 0.24. ^{1}H-NMR: 7.04 (*s*, H–C(5)); 7.01 (*s* H–C(7), H–C(9)); 4.06 (*q*, $J = 7.1$, $COOCH_2$Me); 3.81 (*s*, 2 COOMe); 3.72 (*d*, $J(3,4) = 7.3$, H–C(3)); 3.46 (*quint.*-like, $J(4,3) \approx J(4,$Me–C(4)$) = 7.3$, H–C(4)); 2.78 (*s*, Me–C(10)); 2.68 (*s*, Me–C(6)); 2.53 (*s*, Me–C(8)); 1.50 (*d*, J(Me–C(4),4) = 7.3, Me–C(4)); 1.11 (*t*, $J = 7.1$, $COOCH_2Me$). EI-MS: 425 (16, $[M + 1]^+$), 424 (57). M^+), 365 (13), 320 (11), 319 (46), 306 (12), 305 (17), 293 (18), 292 (65), 291 (17), 261 (18), 234 (17), 233 (38), 232 (21), 218 (24), 217 (29), 216 (20), 215 (40), 204 (15), 203 (50), 202 (64), 191 (18), 189 (38), 178 (21), 165 (26), 152 (18), 59 (100).

3.3. *3-Ethyl 1,2-Dimethyl 4,6,8,10-Tetramethylbenz[a]azulene-1,2,3-tricarboxylate* (**19**). Compound **18** (0.10 g, 0.106 mmol) was heated in *p*-cymene (20 ml) at 180° during 12 h in the presence of Pd/C (10%, 0.10 g). After filtration of Pd/C, the solvent was distilled off in a *Kugelrohr* apparatus at 50°/0.01 mm. The residue was subjected to CC (silica gel; hexane/Et_2O 1:1) to yield 0.60 g (60%) of pure **19**. Blue crystals from hexane/Et_2O. M.p. 152–153°. R_f 0.20. UV (hexane): λ_{max} 413 (3.84), 396 (3.88), 321 (4.59), 256 (4.11), 233 (4.10); λ_{min} 406 (3.83), 263 (3.59), 273 (3.78), 242 (4.08) 222 (4.06). ^{1}H-NMR: 7.18 (*s*, H–C(5)); 6.89 (*s*, H–C(9)); 6.83 (*s*, H–C(7)); 4.42 (*q*, $J = 7.1$, $COOCH_2$Me); 3.93, 3.89 (2*s*, 2 COOMe); 2.73 (*s*, Me–C(10)); 2.70 (*s*, Me–C(4)); 2.69 (*s*, Me–C(6)); 2.48 (*s*, Me–C(8)); 1.40 (*t*, $J = 7.1$, $COOCH_2$Me). EI-MS: 423 (17, $[M + 1]^+$), 422 (63, M^+), 361 (11), 331 (31), 330 (20), 329 (28), 202 (22), 189 (34), 165 (32), 152 (27), 135 (100).

REFERENCES

[1] K.-P. Zeller, in 'Houben-Weyl, Methoden der organischen Chemie', 'Carbocyclische π-Elektronen-Systeme', Georg Thieme Verlag, Stuttgart, New York 1985, 4. Aufl., Bd. 5/2c, 127ff.

[2] J. C. Jutz, *Topics Curr. Chem.* **1978,** *73,* 125.

[3] K. Ziegler, K. Hafner, *Angew. Chem.* **1955,** *67,* 301; K. Hafner, *Justus Liebigs Ann. Chem.* **1957,** *606,* 79; K. Hafner, K.-D. Asmus, *ibid.* **1964,** *671,* 31.

[4] C. Jutz, E. Schweiger, *Chem. Ber.* **1974,** *107,* 2383; see also: H. Penker, Ph. D. Thesis, Technische Universität München, 1977.

[5] J. Bindl, J. Daub, A. Hasenhündl, M. Meinert, K. M. Rapp, *Chem. Ber.* **1983,** *116,* 2408; J. Bindl, P. Seitz, U. Seitz, E. Salbeck, J. Salbeck, J. Daub, *ibid.* **1987,** *120,* 1747.

[6] S. Kuroda, M. Mouri, K. Hayashi, M. Ode, M. Yamada, I. Shimao, H. Osaki, M. Yasumani, *Chem. Lett.* **1994,** 85.

[7] P. W. Yang, M. Yasunami, K. Takase, *Tetrahedron Lett.* **1971,** 4275; M. Yasunami, A. Chen, P. W. Yang, K. Takase, *Chem. Lett.* **1980,** 579; see also: T. Nozoe, P. W. Yang, C. P. Wu, T. S. Huang, T. H. Lee, H. Okai, H. Wakabayashi, S. Ishikawa, *Heterocycles* **1989,** *29,* 1225; T. Nozoe, H. Wakabayashi, K. Shindo, S. Ishikawa, *ibid.* **1991,** *32,* 213.

[8] A. J. Rippert, H.-J. Hansen, *Helv. Chim. Acta* **1993,** *76,* 2906.

[9] A. J. Rippert, H.-J. Hansen, *Helv. Chim. Acta* **1995,** *78,* 238; A. J. Rippert, Ph. D. Thesis, University of Zurich, 1994.

[10] H. Heimgartner, H.-J. Hansen, H. Schmid, *Helv. Chim. Acta* **1970,** *53,* 173; *ibid.* **1972,** *55,* 1385.

[11] W. P. Hart, D. Shihua, M. Rausch, *J. Organomet. Chem.* **1985,** *282,* 111.

[12] A. A. S. Briquet, H.-J. Hansen, *Helv. Chim. Acta* **1994,** *77,* 1921.

[13] R.-A. Fallahpour, H.-J. Hansen, *Helv. Chim. Acta* **1994,** *77,* 2297.

[14] R.-A. Fallahpour, H.-J. Hansen, unpublished results.

[15] Y. Chen, R. W. Kunz, P. Uebelhart, R. H. Weber, H.-J. Hansen, *Helv. Chim. Acta* **1992,** *75,* 2447.

[16] T. Okazoe, K. Takai, K. Oshima, K. Utimoto, *J. Org. Chem.* **1987,** *52,* 4412; see also: J. J. Gajewski, K. R. Gee, J. Jurayi, *ibid.* **1990,** *55,* 1813.

[17] A. A. S. Briquet, H.-J. Hansen, *Helv. Chim. Acta* **1994,** *77,* 1940.

[18] S. H. Pine, *Org. React.* **1993,** *43,* 1.

[19] W. Treibs, H.-J. Neupert, J. Hiebsch, *Chem. Ber.* **1959,** *92,* 141; K. Hafner, C. Bernhard, *Justus Liebig's Ann. Chem.* **1959,** *625,* 108.