10. Thermal Reaction of Azulene and Some of Its Symmetrically Substituted Methyl Derivatives with Dimethyl Acetylenedicarboxylate

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It is shown that azulene (**1**) and dimethyl acetylenedicarboxylate (ADM) in a fourfold molar excess react at 200° in decalin to yield, beside the known heptalene- (**5**) and azulene-1,2-dicarboxylates (**6**), in an amount of 1.6% tetramethyl (1*RS*,2*RS*,5*SR*,8*RS*)-tetracyclo[6.2.2.2^{2,5}0^{1,5}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate ('*anti*'-**7**) as a result of a SHOMO(azulene)/LUMO(ADM)-controlled addition of ADM to the seven-membered ring of **1** followed by a *Diels-Alder* reaction of the so formed tricyclic intermediate **16** (*cf. Scheme 3*) with a second molecule of ADM. The structure of '*anti*'-**7** was confirmed by an X-ray diffraction analysis. Similarly, the thermal reaction of 5,7-dimethylazulene (**3**) with excess ADM in decalin at 120° led to the formation of *ca.* 1% of '*anti*'-**12**, the 7,12-dimethyl derivative of '*anti*'-**7**, beside of the corresponding heptalene- **10** and azulene-1,2-dicarboxylates **11** (*cf. Scheme 2*). The introduction of Me groups at C(1) and C(3) of azulene (**1**) and its 5,7-dimethyl derivative **3** strongly enhance the thermal formation of the corresponding tetracyclic compound. Thus, 1,3-dimethylazulene (**2**) in the presence of a sevenfold molar excess of ADM at 200° yielded 20% of '*anti*'-**9** beside an equal amount of dimethyl 3-methylazulene-1,2-dicarboxylate (**8**; *cf. Scheme 1*), and 1,3,5,7-tetramethylazulene (**4**) with a fourfold molar excess of ADM at 200° gave a yield of 37% of '*anti*'-**15** beside small amounts of the corresponding heptalene- **13** and azulene-1,2-dicarboxylates **14** (*cf. Scheme 2*).

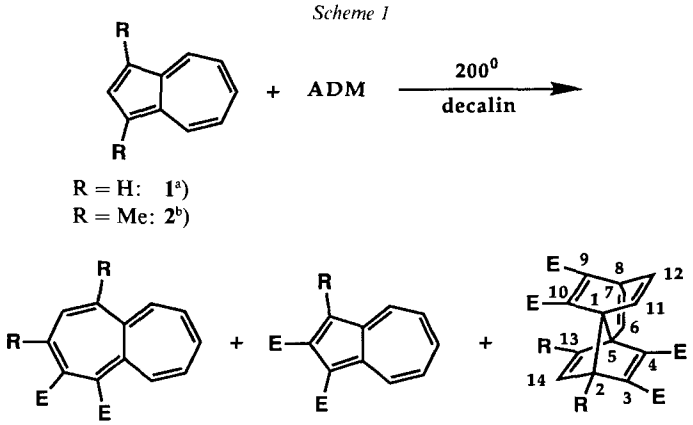
1. Introduction. – In the preceding two communications [1] [2], we exemplified that the thermal reaction of substituted azulenes with dimethyl acetylenedicarboxylate (ADM) in apolar solvents such as decalin follows two primary pathways which are controlled by the corresponding HOMO(azulene)/LUMO(ADM) and SHOMO(azulene)/LUMO(ADM) (SHOMO = subjacent HOMO) interactions in the transition state of the corresponding cycloadditions. The two primary tricyclic compounds which result from the addition of ADM to the five- and seven-membered ring of the substituted azulenes may further react with excess ADM to yield corresponding tetracyclic tetracarboxylates alongside with the expected heptalene- and azulenedicarboxylates which arise from the primary tricyclic adduct of ADM to the five-membered ring of the substituted azulenes [1] [2] (*cf.* also [3] [4]). The two primary pathways are influenced by the nature and number of substituents at the azulene skeleton. Thus, Me substituents in *peri*-positions of the azulenes, in general, favor the formation of products derived from the tricyclic adduct of ADM to the five-membered ring, and bulky alkyl substituents at C(6) of the azulenes suppress the addition of ADM to the seven-membered ring of the azulenes. On the other hand, electron-attracting substituents (*e.g.* MeOCO group) at C(2), which is passed by a nodal plane in the HOMO, seem to favor product formation from the ADM adduct to the five-membered ring. However, MeOCO substituents at C(1) and C(2) of the azulenes seem to suppress completely the ADM addition

[1]) Part of the planned Ph. D. thesis of *Y. C.*, University of Zurich.

to the five-membered ring, whereas addition to the seven-membered ring still takes place [1] [2][2]). Therefore, we were interested to study the thermal reactivity of azulene (**1**) itself in the presence of excess ADM and compare it with that of some of its symmetrically substituted Me derivatives, especially with 1,3-dimethyl- (**2**), 5,7-dimethyl- (**3**), and 1,3,5,7-tetramethylazulene (**4**), since the nodal plane positions should be the same for all four azulenes, and we had already recognized the tendency that Me groups at C(1) and C(3) diminish the formation of the corresponding heptalene-1,2-dicarboxylates (*cf.* [1] [2]).

2. Results and Discussion. – It has been shown already by *Hafner et al.* [6] (*cf.* [7]) that the thermal reaction of azulene (**1**) with ADM in tetralin at 207° leads mainly to the formation of dimethyl heptalene-1,2-dicarboxylate (**5**) and dimethyl azulene-1,2-dicarboxylate (**6**). We repeated this transformation, reacting **1** with a fourfold molar excess of ADM in decalin at 200°, and found in the reaction mixture, beside **5** and **6**, the tetracyclic compound '*anti*'-**7** in an amount of 1.6% (*Scheme 1*)[3]). The structure of '*anti*'-**7** was assigned on the basis of its ^{1}H-NMR spectrum and confirmed by an X-ray diffraction analysis (*cf. Chapt. 3*).

Scheme 1



R = H: **5** (4.3%)[c])[d]) **6** (7.2%) '*anti*'-**7** (1.6%)
R = Me: –[e]) **8** (19.4%) '*anti*'-**9** (20.1%)

[a]) Azulene (**1**) was reacted with a fourfold molar excess of ADM during 2.5 h. [b]) The azulene **2** was reacted with a sevenfold molar excess of ADM during 4.5 h. [c]) Yields of pure crystallized materials are given; for the definition of '*anti*' *cf.* [1] [2]. [d]) *Hafner et al.* [6] [7] observed the formation of 25% of **5** and 2% of **6** beside 1% of dimethyl 3,4-dihydrocyclopent[*cd*]azulene-1,2-dicarboxylate (tetralin, 207°). [e]) Not observed (*cf.* Footnote 5 in [1]); *Hafner et al.* [7] found 40% of **8** (tetralin, 207°).

When we increased the SHOMO and especially the HOMO energy and, at the same time, the reversibility of the primary addition step of ADM to the five-membered ring of azulene (**1**) by the introduction of Me groups at C(1) and C(3) (*cf.* [1]), we found that this azulene **2** reacted with ADM in decalin at 200° to yield 20% of the tetracyclic compound '*anti*'-**9** beside an equal amount of the corresponding azulene-1,2-dicarboxylate **8**

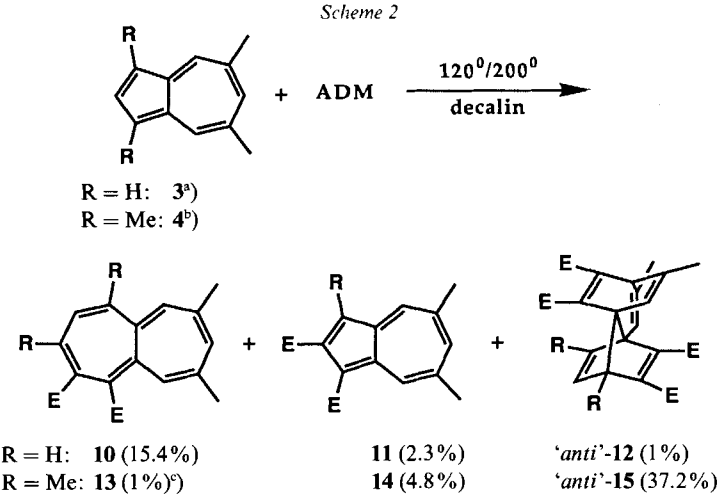
[2]) Indeed, especially electron-withdrawing substituents at C(1) which lower the energy of the HOMO and excert little influence on the energy of the corresponding SHOMO favor pronouncedly the thermal addition of ADM to the seven-membered ring of the azulenes [5].

[3]) Augmentation of the molar ratio of ADM did not increase significantly the amount of '*anti*'-7.

(*Scheme 1*). The formation of a corresponding heptalene-1,2-dicarboxylate was not recognized (*cf.* also [7]).

The introduction of Me groups at C(5) and C(7) of azulene (**1**) should also raise the SHOMO as well as the HOMO energy of 5,7-dimethylazulene (**3**). On the other hand, the Me groups at C(5) and C(7) should sterically not interfere with the thermal addition of ADM neither to the five- nor to the seven-membered ring. Indeed, 5,7-dimethylazulene (**3**) turned out to be one of the most reactive azulenes in the presence of ADM. To avoid overreaction with ADM which led to a whole variety of new products [8], the temperature had to be lowered to 120° (*Scheme 2*). At this temperature the formation of the corresponding heptalene- and azulene-1,2-dicarboxylates, **10** and **11**, respectively, were observed. The tetracyclic compound '*anti*'-**12** was isolated chromatographically in a yield of *ca.* 1%. The introduction of two additional Me groups at C(1) and C(3) of **3**, further elevating the SHOMO and HOMO energy level as well as making the primary addition step of ADM to the five-membered ring more reversible, leads to the symmetrically methylated azulene **4** that gave the highest yield of a tetracyclic compound, namely '*anti*'-**15**, we have observed until now (*Scheme 2*). Correspondingly, the yield of the expected heptalene- and azulene-1,2-dicarboxylates, **13** and **14**, respectively, was very small.

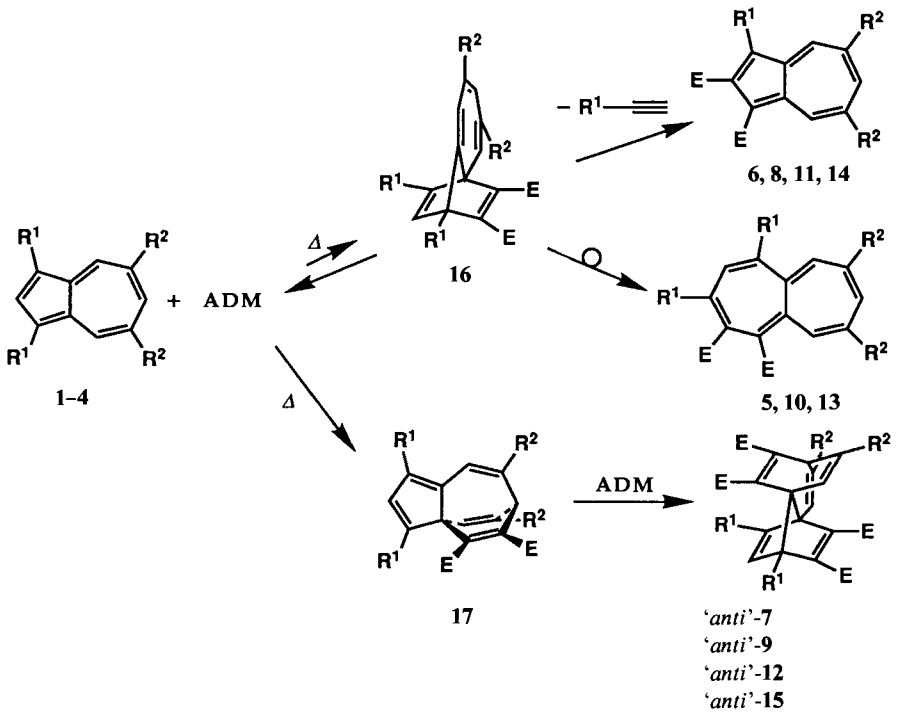
Scheme 2



a) The azulene **3** was reacted with a fourfold molar excess of ADM at 120°. At 200°, **10** (10.7%) and **11** (4.2%) were accompanied by a whole variety of (1 + 2)-, (1 + 3)-, and (1 + 4)-addition products of **3** and ADM [8]. The tetracyclic compound '*anti*'-**12** was not detected. b) The azulene **4** was reacted with a fourfold molar excess of ADM at 200°. c) When **13** was dissolved in $CDCl_3$ at r.t., the thermal equilibrium between **13** (87%) and its DBS isomer (13%) was readily established (^{1}H-NMR evidence).

No doubt, the two primary pathways of the thermal addition of ADM to azulenes (*cf.* [1] [2]) play also the decisive role in the cases studied here (*cf. Scheme 3*). Me groups at C(8) and C(11) in the primary intermediates **16** favor the formation of the corresponding azulene-1,2-dicarboxylates **8** and **14** at the expense of heptalene formation, since the *retro-Diels-Alder* reactions of **16**, leading back to the starting materials or to the azulene-

Scheme 3



1,2-dicarboxylates, will follow transition states of little or no polarity which are fostered by Me groups placed at termini where bonds are cleaved (*cf.* [1]). On the other hand, the heterolytic cleavage of the C(1)–C(10) bond, which is crucial for the formation of the heptalene-1,2-dicarboxylates *via* zwitterionic intermediates (*cf.* [3]), will be hindered by a Me group at C(1) on steric grounds and by the lack of electron-donating Me groups at the seven-membered ring of intermediates of type **16** (*cf.* [1] [3] [4]). Thus, the heptalene formation is completely suppressed in the case of azulene **2**, and azulene **4** yields only 1% of the corresponding heptalene-1,2-dicarboxylate **13**. The high degree of reversibility of the formation of intermediates of type **16** in the cases of R^1 = Me favors the pathway for the – under reaction conditions – irreversible formation of the intermediates **17** which are effectively trapped by a consecutive *Diels-Alder* reaction with ADM not sterically hindered by the Me substituents of **17** (*cf.* [1] [2]). Therefore, azulenes **2** and **4** show the maximum yield of the tetracyclic compounds arising from **17**. The '*anti*'-structure of all four (1 + 2) adducts is in agreement with the approach of ADM at the sterically less hindered side of **17**, *i.e.* H–C(11) as compared to MeOCO–C(10).

3. Structure Assignments of the Tetracyclic Compounds. – The structure of the tetracyclic compound '*anti*'-**7** is shown in *Fig. 1*. It can be described as composed of a homobarrelene part, the homo-C-atom of which is spiro-linked to a 1,4-cyclohexadiene which in turn is attached (with C(4)) to the adjacent bridgehead C-atom of the homobarrelene part, thus forming a norbornadiene substructure. Therefore, '*anti*'-**7** and the other tetracyclic compounds of this type can also be regarded as norbornadienes which are

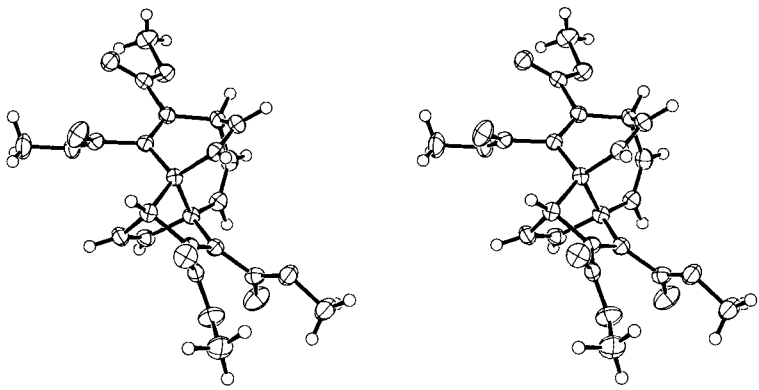


Fig. 1. *Stereoscopic projection of the X-ray structure of tetramethyl (1*RS,*2*RS,*5*SR,*8*RS*)-tetracyclo[6.2.2.2^{2,5}.0^{1,5}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate ('*anti*'-**7**)

spiro-linked at C(7) with a 1,4-cyclohexadiene part whose C(4) is linked *via* an ethene-1,2-diyl bridge with one of the bridgehead C-atoms of the norbornadiene partial structure. Both descriptions show that the tetracyclic compounds of type '*anti*'-**7** comprise two ^{1}H-spin systems, namely that of the norbornadiene part and that of the homobarrelene part, which are nearly not interfering through bonds, however, which are related spatially.

The spatial relations allow to identify the H or Me substituents at C(2) and C(10) or C(11) as well as at C(6) and C(4) or C(13) by strong reciprocal ^{1}H-NOE of the substituents at these positions. The spatial closeness and nearly parallel orientation of H or Me substituents at C(10) and C(14) as well as at C(3) and C(11) is also expressed in strong ^{1}H-NOE, thus allowing to distinguish easily between '*anti*'- and '*syn*'-orientations of substituents at these positions (*cf.* also [1] [2]).

Fig. 1 clearly shows the perfect zig-zag orientation of H–C(2) and H–C(6) in '*anti*'-**7**. Indeed, in all cases where these two C-atoms carry H-atoms we observed ^5J coupling constants in the order of 0.7–0.9 Hz. This is the only observed ^{1}H coupling between the two described ^{1}H-spin systems in tetracyclic compounds of type '*anti*'-**7**. However, '*anti*'-**7** provides another interesting ^{1}H-coupling situation, since it contains three different ethenylene bridges which show different vicinal ^{1}H-coupling constants, namely 10.68 (J(H–C(6),H–C(7)), 8.11 (J(H–C(11),H–C(12))), and 5.15 Hz (J(H–C(13),H–C(14))). The latter value is quite typical for norbornadienes [9]. As expected, all three ethenylene substructures in '*anti*'-**7** possess torsion angles of 0°, and their C=C bond lengths are very similar (*cf. Exper. Part*). Therefore, the ^3J values should mainly be dependent on the corresponding H–C–C or C–C–C bond angles (*cf.* [9]). *Fig. 2* shows that '*anti*'-**7** exhibits, indeed, a perfect linear relation between the measured ^3J values and the average skeletal C–C–C bond angles, taken from the X-ray structure analysis (*cf. Exper. Part*), at the corresponding C=C bonds. ^3J(H–C(6),H–C(7)) = 10.92 Hz and ^3J(H–C(13),H–C(14)) = 8.26 Hz found for '*anti*'-**9** fit into this linear relation.

Also very typical for tetracyclic structures of type '*anti*'-**7** are the other three observed vicinal ^{1}H-coupling constants, namely ^3J(H–C(7),H–C(8)) = 8.39, ^3J(H–C(8), H–C(12)) = 6.71, and ^3J(H–C(2),H–C(14)) = 3.30 Hz. The latter is again quite charac-

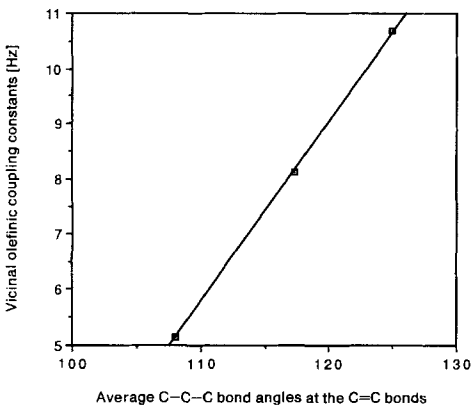


Fig. 2. *Linear relation between the measured olefinic* ^3J *coupling constants and the average skeletal C–C–C bond angle* (Θ_{av}; taken from the X-ray structure axalysis) *of* 'anti'-**7** ($\Theta_{av} = 3.07 \cdot J$ [Hz]+92.3; correlation coefficient $r = 0.9998$)

teristic for norbornadienes [9]. The torsion angle H–C(7)–C(8)–H is nearly 0°, whereas the corresponding torsion angle H–C(8)–C(12)-H amounts to –20°, *i.e.*, in all tetracyclic compounds of type '*anti*'-**7**, we found ^3J(H–C(7),H–C(8)) > ^3J(H–C(8),H–C(12)) and in the range of 8.2 to 8.6 Hz and 6.7 to 7.2 Hz, respectively (*cf.* also [1] [2]).

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Experimental Part

General. See [1] [2] [10].

1. Synthesis of Azulenes. – 1.1. *1,3-Dimethylazulene* (**2**; *cf.* [11]). It was synthesized, starting from azulene (**1**), *via* 1-methylazulene [11] following the general formylation/reduction procedure (*cf.* [1] [2] [10]). In the final step, 3-methylazulene-1-carbaldehyde (m.p. 73–74° (hexane); [11]: m.p. 72–73°) gave **2** as blue crystals (m.p. 52–53° (hexane); [11]: m.p. 52°) in a yield of 68%. ^{1}H-NMR (300 MHz): 8.088 (*d*, ^3J(H,H–C(5)) = ^3J(H,H–C(7)) = 9,3, H–C(4), H–C(8)); 7.577 (*s*, H–C(2)); 7.424 (*t*, ^3J(H,H–C(5)) = ^3J(H,H–C(7)) = 9.9, H–C(6)); 6.921 (*t*, ^3J(H,H–C(4)) = ^3J(H,H–C(6)) = ^3J(H,H–C(8)) = 9.7, H–C(5), H–C(7)); 2.629 (*s*, 2 Me).

1.2. *5,7-Dimethylazulene* (**3**; *cf.* [12]). Sodium cyclopentadienide (0.69 mol; prepared from cyclopentadiene and NaH in DMF) and 1-butyl-3,5-dimethylpyridinium bromide (97 g, 0.4 mol; prepared from 3,5-dimethylpyridine and BuBr in boiling toluene as a grey powder which was extremely hygroscopic) were stirred in DMF (200 ml) for 1 h at r.t. and then heated for 3.5 h under reflux. Workup and chromatography (silica gel; hexane) yielded **3** as a blue oil (20 g; 32%) which crystallized in the refrigerator ([12]: m.p. 30°). ^{1}H-NMR (300 MHz): 8.169 (br. *s*, H–C(4),H–C(8)); 7.820 (*t*, ^3J(H,H–C(1)) = ^3J(H,H–C(3)) = 3.7, H–C(2)); 7.453 (br. *s*, H–C(6)); 7.142 (*d*, ^3J(H,H–C(2)) = 3.7, H–C(1) and H–C(3)); 2.613 (*s*, 2 Me). CI-MS: 157 (34, $[M + 1]^+$), 156 (100, M^+), 141 (2).

1.3. *1,3,5,7-Tetramethylazulene* (**4**). 1.3.1. *5,7-Dimethylazulene-1-carbaldehyde* (**18**). Azulene **3** (7.3 g; 0.047 mol) was formylated in the usual manner (*cf.* [13]) to yield, after chromatographic workup (silica gel; pentane/Et_2O 2:1), **18** (3.0 g; 37.7%) and 5,7-dimethylazulene-1,3-dicarbaldehyde (0.73 g; 7.4%) as violet crystals.

Data of **18**: m.p. 96–97° (hexane). R_f (hexane/Et_2O 3:2): 0.39. UV (hexane): λ_{max} 394.4 (4.05), 379.4 (4.07), 310.5 (4.64), 299.2 (4.53), 244.0 (4.25), 222.7 (4.36); λ_{min} 387.4 (4.00), 362.0 (3.52), 303.0 (4.51), 270.0 (3.87), 234.0 (4.32). IR (KBr): 2730, 1634 (CHO), 1499, 1425, 1396, 1294, 1198, 1152, 1046, 961.5, 876, 805, 788, 770, 726, 664, 615.5. ^{1}H-NMR (300 MHz): 10.245 (*s*, CHO); 9.744 (*s*, H–C(8)); 8.300 (*s*, H–C(4)); 8.172 (*d*, ^3J(H,H–C(3)) = 4.2,

H–C(2)); 7.725 (*s*, H–C(6)); 7.088 (*d*, ^3J(H,H–C(2)) = 4.2, H–C(3)); 2.762 (*s*, Me–C(7)); 2.704 (*s*, Me–C(5)). CI-MS: 185.2 (100, $[M + 1]^+$). Anal. calc. for $C_{13}H_{12}O$ (184.24): C 84.75, H 6.57; found: C 84.94, H 6.80.

Data of 5,7-dimethylazulene-1,3-dicarbaldehyde: m.p. 246–247° (MeOH). R_f (hexane/Et_2O 3:2): 0.14. UV (MeOH): λ_{max} 388.2 (4.19), 311.6 (4.57), 293.6 (4.73), 246.6 (4.60); λ_{min} 346.0 (3.64), 306.0 (4.56), 263.0 (3.78), 220.0 (3.98). IR (KBr): 3072, 1646 (CHO), 1509, 1456, 1410, 1366, 1319, 1256.5, 1193, 1150, 1078, 982, 955, 922, 802, 778, 688. ^{1}H-NMR (300 MHz): 10.168 (*s*, 2 CHO); 9.658 (*d*, ^4J(H,H–C(6)) = 1.7, H–C(4), H–C(8)); 8.453 (*s*, H–C(2)); 7.905 (br. *s*, H–C(6)); 2.773 (*s*, 2 Me). CI-MS: 213.2 (100, $[M + 1]^+$), 212.2 (5, $M^{+\cdot}$). Anal. calc. for $C_{14}H_{12}O_2$ (212.25): C 79.22, H 5.70; found: C 78.94, H 5.94.

1.3.2. *1,5,7-Trimethylazulene* (**19**). The formylated azulene **19** (2.68 g, 0.015 mol) was reduced in the usual way with $NaBH_4$ (2.36 g, 0.062 mol)/$BF_3 \cdot Et_2O$ (3.18 ml, 0.025 mol) in diglyme (*cf.* [14]) to yield, after chromatographic workup (silica gel; pentane/Et_2O 3:1), **19** (0.87 g, 35%) as blue crystals.

Data of **19**: m.p. 31–32° (hexane). R_f (hexane): 0.63. UV (hexane): λ_{max} 367.4 (3.92), 349.0 (3.96), 334 (sh, 3.76), 282.0 (4.91), 243.8 (4.46); λ_{min} 358.0 (3.68), 313.0 (3.51), 255.0 (4.38), 227.0 (4.34). IR ($CHCl_3$): 3050, 2920, 2862, 1578, 1415, 1396, 1167, 1038, 971, 930. ^{1}H-NMR (400 MHz): 8.060 (*d*, ^4J(H,H–C(6)) ≈ 1.1, H–C(4)); 8.041 (br. *s*, H–C(8)); 7.662 (*d*, ^3J(H,H–C(3)) = 2.9, H–C(2)); 7.397 (br. *s*, H–C(6)); 7.062 (*d*, ^3J(H,H–C(2)) = 3.2, H–C(3)); 2.630, 2.622 (2*s*, Me–C(5), Me–C(7)); 2.585 (*s*, Me–C(1)). MS: 170.2 (100, $M^{+\cdot}$), 169.2 (33, $[M - 1]^+$), 155.2 (32). Anal. calc. for $C_{13}H_{14}$ (170.26): C 91.71, H 8.29; found: C 91.41, H 8.45.

1.3.3. *3,5,7-Trimethylazulene-1-carbaldehyde* (**20**). Azulene **19** (1.753 g, 1.03 mmol) was formylated as usual (*cf.* [13]), and **20** (1.72 g, 84.3%) isolated by column chromatography (silica gel; hexane/Et_2O 2:1).

Data of **20**: blue crystals. M.p. 138–140° (hexane). R_f (pentane/Et_2O 2:1): 0.50. UV (hexane): λ_{max} 410.0 (4.26), 393.8 (4.30), 314.0 (4.84), 302.9 (4.74), 274 (sh, 4.35), 246.6 (4.56), 219.9 (4.59); λ_{min} 404.0 (4.25), 340.0 (3.65), 307.0 (4.73), 263.0 (4.29), 232.0 (4.47). IR (KBr): 2914, 2712, 1632 (CHO), 1527, 1435, 1373.5, 1314, 1223.5, 1191, 1145, 1035, 993, 920, 865.5, 702, 617. ^{1}H-NMR (300 MHz): 10.210 (*s*, CHO); 9.350 (*s*, H–C(8)); 8.160 (*s*, H–C(2)); 7.999 (*s*, H–C(4)); 7.674 (br. *s*, H–C(6)); 2.730, 2.717 (2*s*, Me–C(5), Me–C(7)); 2.553 (*s*, Me–C(3)). CI-MS: 199.1 (100, $[M + 1]$). Anal. calc. for $C_{14}H_{14}O$ (198.27): C 84.81, H 7.12; found: C 84.57, H 7.34.

1.3.4. *Reduction of* **20** *to* **4**. The formylated azulene **20** (1.24 g, 6.25 mmol) was reduced with $NaBH_4$ (1.01 g, 26.8 mmol)/$BF_3 \cdot Et_2O$ (1.4 ml, 10.9 mmol) in diglyme to yield **4** (0.42 g, 37%) as blue crystals after chromatographic workup.

Data of **4**: m.p. 107–108° (hexane). R_f (petroleum ether, 30–60°): 0.56. UV (hexane). λ_{max} 375.1 (3.93), 365.6 (3.89), 339 sh (3.75), 284.6 (4.86), 253 (sh, 4.33), 245.2 (4.36), 221.0 (4.35); λ_{min} 365.0 (3.75), 321.0 (3.52), 257.0 (4.32), 231.0 (4.39), 214.0 (4.34). IR (KBr): 2920, 2851, 1734, 1684, 1653.5, 974, 921, 872, 615, 599. ^{1}H-NMR (300 MHz): 7.896 (*d*, ^4J(H,H–C(6)) = 1.5, H–C(4), H–C(8)); 7.472 (*s*, H–C(2)); 7.295 (br. *s*, H–C(6)); 2.561 (*s*, 4 Me). MS: 184.2 (100, $M^{+\cdot}$), 183.1 (48, $[M - 1]^+$), 169.1 (82). Anal. calc. for $C_{14}H_{16}$ (184.28): C 91.25, H 8.75; found: C 90.99, H 8.79.

2. Thermal Reactions of the Azulenes with Dimethyl Acetylenedicaboxylate (ADM). – 2.1. *Azulene* (**1**) *with ADM* (*cf.* [6]). Azulene (**1**; 0.500 g, 3.90 mmol) and ADM (2.22 g (1.92 ml), 15.6 mmol) were dissolved in decalin (5 ml) and heated under N_2 during 2.5 h at 200°. Chromatographic workup (silica gel; hexane/Et_2O 3:2) gave fractions containing *dimethyl heptalene-1,2-dicarboxylate* (**5**; 0.045 g, 4.3%), *dimethyl azulene-1,2-dicarboxylate* (**6**; 0.068 g, 7.2%), and *tetramethyl (1*RS,*2*RS,*5*SR,*8*RS*)-tetracyclo[6.2.2.2.^{2,5}.0^{1,5}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate* (*'anti'*-**7**; 0.025 g, 1.6%).

Data of **5**: orange crystals. M.p. 106–108° (hexane; [6]: m.p. 114–115°). R_f (hexane/Et_2O 3:2): 0.31. ^{1}H-NMR (300 MHz): 7.356 (br. *s*, H–C(3)); 6.52–5.73 (*m*, H–C(4–10)); 3.727 and 3.674 (2*s*, 2 MeOCO). Anal. calc. for $C_{16}H_{14}O_4$ (270.29): C 71.10, H 5.22; found: C 70.99, H 5.05.

Data of **6**: violet crystals. M.p. 46–47° (hexane; [6]: m.p. 49–50°). R_f (hexane/Et_2O 3:2): 0.21. ^{1}H-NMR (300 MHz, (D_6)acetone): 9.40 (*dd*, ^3J(H,H–C(7)) = 9.7, ^4J(H,H–C(6)) = 0.9, H–C(8)); 8.75 (*dd*, ^3J(H,H–C(5)) = 9.6, ^4J(H,H–C(6)) = 0.9, H–C(4)); 8.08 (*tt*, ^3J(H,H–C(5,7)) = 9.9, ^4J(H,H–C(4,8)) = 1.1, H–C(6)); 7.73 (*t*, ^3J(H,H–C(6,8)) = 9.8, H–C(7)); 7.68 (*t*, ^3J(H,H–C(4,6)) = 9.6, H–C(5)); 7.57 (*s*, H–C(3)); 3.92, 3.89 (2*s*, 2 MeOCO). Anal. calc. for $C_{14}H_{12}O_4$ (244.25): C 68.85, H 4.95; found: C 69.11, H 5.19.

Data of 'anti'-**7**: colorless crystals. M.p. 153–154° (hexane). R_f (hexane/Et_2O 1:2): 0.31. UV (hexane): λ_{max} 271.4 (4.07); λ_{min} 232.0 (3.78). IR (KBr): 2955, 1721 (H_3COOC), 1623, 1440, 1334, 1284, 1232, 1219, 1183, 1150, 1118.5, 1106, 1087, 1058, 955, 802, 751, 740, 722, 699, 682. ^{1}H-NMR (600 MHz; $CHCl_3$ at 7.258): 6.785 (*dd*, ^3J(H,H–C(13)) = 5.15, ^3J(H,H–C(2)) = 3.30, H–C(14)); 6.538 (*dd*, ^3J(H,H–C(14)) = 5.15, ^4J(H,H–C(2)) = 0.91, H–C(13)); 6.506 (*dd*, ^3J(H,H–C(11)) = 8.11, ^3J(H,H–C(8)) = 6.71, H–C(12)); 6.302 (*dd*, ^3J(H,H–C(6)) = 10.68, ^3J(H,H–C(8)) = 8.39, H–C(7)); 6.251 (*dd*, ^3J(H,H–C(12)) = 8.11, ^4J(H,H–C(8)) = 1.35, H–C(11)); 5.711 (*dt*-like, ^3J(H,H–C(7)) = 10.68, ^4J(H,H–C(8)) ≈ 2·^5J(H,H–C(2)), H–C(6)); 4.455 (*dt*, ^3J(H,H–C(14)) = 3.30, Σ^4J(H,H–C(13)) + ^5J(H,H–C(6)) = 1.86, *i.e.* ^5J(H,H–C(6)) = 0.95, H–C(2)); 3.788,

3.779, 3.736, 3.734 (4*s*, 4 MeOCO); 3.666 (*d'm'*, Σ^3J(H,H–C(7)) + ^3J(H,H–C(12)) = 15.10, H–C(8)). ^{1}H-NOE (400 MHz): 6.785 (H–C(14))→6.538 (*s*, H–C(13)), 4.455 (*s*, H–C(2)); 6.538 (H–C(13))→6.785 (*s*, H–C(14)), 5.711 (*s*, H–C(6)); 6.506 (H–C(12))→6.251 (*s*, H–C(11)), 3.666 (*s*, H–C(8)); 6.251 H–C(11))→6.506 (*s*, H–C(12)), 4.455 (*s*, H–C(2)). ^{1}H-DR (400 MHz): 3.666 (H–C(8))→5.711 (*dd*, ^3J(H,H–C(7)) = 10.7, ^5J(H,H–C(2)) = 1.0, H–C(6)), 6.251 (*d*, ^3J(H,H–C(12)) = 8.1, H–C(11)), 6.302 (*d*, ^3J(H,H–C(6)) = 10.7, H–C(7)), 6.506 (*d*, ^3J(H,H–C(11)) = 8.1, H–C(12)); 4.455 (H–C(2))→5.711 (br. *d*, ^3J(H,H–C(7)) = 10.7, H–C(6)), 6.538 (*d*, ^3J(H,H–C(14)) = 5.2, H–C(13)), 6.785 (*d*, ^3J(H,H–C(13)) = 5.2, H–C(14)). ^{1}H-NMR (300 MHz, C_6D_6; C_6D_5H at 7.159): 6.564 (*dd*, ^3J(H,H–C(13)) = 5.1, ^3J(H,H–C(2)) = 3.4, H–C(14)); 6.414 (*dd*, ^3J(H,H–C(14)) ≈ 4.9, ^4J(H,H–C(2)) ≈ 0.7, H–C(13)); 6.234 (*dd*, ^3J(H,H–C(12)) = 8.1, ^4J(H,H–C(8)) = 1.2, H–C(11)); 6.133 (*dd*, ^3J(H,H–C(6)) = 10.6, ^3J(H,H–C(8)) = 8.4, H–C(7)); 6.089 (*dd*, ^3J(H,H–C(11)) = 8.1, ^3J(H,H–C(8)) = 6.7, H–C(12)); 5.801 (br. *d*, ^3J(H,H–C(7)) = 10.7, H–C(6)); 4.708 (*d*-like, ^3J(H,H–C(14)) = 3.3, H–C(2)); 3.389, 3.342, 3.266 (3*s*, 2:1:1, 4 MeOCO); *ca.* 3.38 (*tt*-like, Σ^3J(H,H–C(7)) + ^3J(H,H–C(12)) = 15.2, H–C(8)). CI-MS: 413 (100, $[M + 1]^+$), 381 (10), 353 (6). Anal. calc. for $C_{22}H_{20}O_8$ (412.40): C 64.07, H 4.89; found: C 64.29, H 5.03.

The structure of '*anti*'-**7** was confirmed by an X-ray structure analysis. *Crystal data:* triclinic *P*1 (2) with a = 707.7, b = 1077.9, c = 1377.9 pm, and α = 72.14°, β = 87.60°, γ = 77.76°; calc. density: 1.401 Mgm^{-3}, Z = 2; $\mu(MoK_\alpha)$ = 1.004 cm^{-1}; measured reflexions (at −60°): 4834, observed 4471; R = 0.016.

Data of the skeleton (in parentheses the corresponding data taken from an MM3 [15] calculation of the parent tetracyclic structure (*cf.* [1])); C,C bond lengths [pm]: C(1)–C(2), 155.2 (155.5); C(2)–C(3), 153.3 (153.5); C(2)–C(14), 153.8 (153.5); C(1)–C(10), 152.6 (152.4); C(1)–C(5), 159.1 (157.3); C(1)–C(11), 152.1 (152.4); C(9)–C(10), 133.2 (134.1); C(8)–C(9), 152.8 (151.9); C(7)–C(8), 152.2 (152.0); C(8)–C(12), 152.3 (151.9); C(6)–C(7), 132.3 (134.4); C(5)–C(6), 149.5 (150.5); C(4)–C(5), 155.9 (154.0); C(5)–C(13), 154.0 (154.0), C(3)–C(4), 133.8 (134.8); C(13)–C(14), 131.4 (134.8); C(11)–C(12), 131.3 (134.1).

Valence angles [°]: C(2)–C(1)–C(10), 116.9 (116.1); C(2)–C(1)–C(5), 92.3 (94.1); C(2)–C(1)–C(11), 118.1 (116.1); C(1)–C(10)–C(9), 116.7 (116.6); C(1)–C(5)–C(4), 96.8 (97.1); C(1)–C(5)–C(13), 98.4 (97.1); C(8)–C(9)–C(10), 117.1 (116.3); C(7)–C(8)–C(9), 109.9 (111.1); C(9)–C(8)–C(12), 107.7 (108.4); C(6)–C(7)–C(8), 124.6 (122.9); C(8)–C(12)–C(11), 118.3 (116.3); C(5)–C(6)–C(7), 125.3 (125.7); C(1)–C(5)–C(6), 117.9 (117.3); C(4)–C(5)–C(6), 117.3 (118.3); C(6)–C(5)–C(13), 117.9 (118.3); C(5)–C(1)–C(10), 109.9 (111.4); C(3)–C(4)–C(5), 107.3 (108.3); C(5)–C(13)–C(14), 108.2 (108.3); C(2)–C(3)–C(4), 107.6 (107.3); C(1)–C(2)–C(3), 98.6 (97.9); C(3)–C(2)–C(14), 105.5 (106.2); C(2)–C(14)–C(13), 107.8 (107.3); C(1)–C(2)–C(14), 99.3 (97.9); C(1)–C(11)–C(12), 116.5 (116.6); C(10)–C(1)–C(11), 108.1 (107.2); C(5)–C(1)–C(11), 110.2 (111.4).

Torsional angles [°]: C(2)–C(1)–C(10)–C(9), 178.0 (179.6); C(2)–C(1)–C(5)–C(4), −54.5 (−53.0); C(2)–C(1)–C(5)–C(13), 52.0 (53.0); C(1)–C(10)–C(9)–C(8), −0.1 (−1.2); C(7)–C(8)–C(9)–C(10), 74.6 (76.2); C(10)–C(9)–C(8)–C(12), −44.3 (−46.0); C(6)–C(7)–C(8)–C(9), −59.5 (−60.3); C(9)–C(8)–C(12)–C(11), 44.1 (46.0); C(5)–C(6)–C(7)–C(8), 0.4 (0.0); C(7)–C(8)–C(12)–C(11), 75.3 (76.2); C(1)–C(5)–C(6)–C(7), −0.5 (0.0); C(4)–C(5)–C(6)–C(7), −115.5 (−115.8); C(7)–C(6)–C(5)–C(13), 117.3 (115.8); C(2)–C(1)–C(5)–C(6), 179.7 (180.0); C(6)–C(5)–C(1)–C(10), 60.0 (59.8); C(3)–C(4)–C(5)–C(6), 162.5 (160.7); C(5)–C(1)–C(10)–C(9), −74.6 (−74.2); C(2)–C(3)–C(4)–C(5), −0.6 (0.5); C(2)–C(14)–C(13)–C(5), −0.3 (0.5); C(4)–C(5)–C(13)–C(14), 65.1 (64.9); C(1)–C(2)–C(3)–C(4), −36.5 (−35.8); C(4)–C(3)–C(2)–C(14), 65.8 (64.9); C(3)–C(2)–C(1)–C(10), 168.7 (170.2); C(3)–C(2)–C(1)–C(5), 55.0 (53.8); C(3)–C(2)–C(1)–C(11), −59.5 (−62.5); C(1)–C(2)–C(14)–C(13), 36.0 (35.8); C(3)–C(2)–C(14)–C(13), −65.7 (−64.9); C(10)–C(1)–C(2)–C(14), 61.3 (62.5); C(11)–C(1)–C(2)–C(14), −166.9 (−170.2); C(2)–C(1)–C(11)–C(12), 177.8 (179.6); C(10)–C(1)–C(11)–C(12), −46.5 (−47.9); C(5)–C(1)–C(11)–C(12), 73.7 (74.2); O=C–C(10)–C(9), −119.0; O–C–C(10)–C(9), 62.5; O=C–C(9)–C(10), 30.5; O–C–C(9)–C(10), −150.4; O=C–C(4)–C(3), 127.6; O–C–C(4)–C(3), −51.6; O=C–C(3)–C(4), 145.7; O–C–C(3)–C(4), −36.1.

2.2. *Azulene* **2** *and ADM* (*cf.* [7]). The azulene (0.390 g, 2.48 mmol) and ADM (2.22 ml, 18.1 mmol) were dissolved in decaline (8 ml) and heated under N_2 during 4.5 h at 200°. Chromatographic workup (silica gel; hexane/Et_2O 3:2) gave *dimethyl 3-methylazulene-1,2-dicarboxylate* (**8**; 0.124 g, 19.4%) and *tetramethyl (1*RS,*2*RS,*5*SR,*8*RS*)-2,13-dimethyltetracyclo[6.2.2.2^{2,5}.0^{1,5}]tetradeca-3,6,9,11,13-pentaene-3,4-9,10-tetracarboxylate* ('*anti*'-**9**; 0.220 g, 20.1%). Heptalenes, such as dimethyl 3,5-dimethylheptalene-1,2-dicarboxylate, could not be detected in isolable amounts.

Data of **8**: blue crystals. M.p. 105–105.5° (hexane). R_f (hexane/Et_2O 3:2): 0.24. UV (hexane): λ_{max} 378.8 (3.74), 360.0 (3.67), 347 (sh, 3.58), 303.2 (4.68), 292.2 (4.62), 238.6 (4.31); λ_{min} 368.0 (3.58), 322.0 (3.33), 298.0 (4.58), 262.0 (4.19), 220.0 (4.11). IR (KBr): 2996.5, 2951, 1731 (H_3COOC), 1681, 1576, 1455, 1422, 1389, 1320, 1251, 1224, 1068, 970, 950, 846, 798, 782, 732. ^{1}H-NMR (300 MHz): 9.507 (br. *d*, ^3J(H,H–C(7)) = 10.0, H–C(8)); 8.434 (*dd*,

^3J(H,H–C(5)) = 9.7, ^4J(H,H–C(6)) = 1.0, H–C(4)); 7.814 (*tt*, ^3J(H,H–C(5,7)) = 9.8, ^4J(H,H–C(4,8)) = 1.0, H–C(6)); 7.508 (*t*, ^3J(H,H–C(6,8)) = 10.0, H–C(7)); 7.454 (*t*, ^3J(H,H–C(4,6)) = 9.7, H–C(5)); 4.009, 3.933 (2*s*, 2 MeOCO); 2.593 (*s*, Me). MS: 258 (82, $M^{+\cdot}$), 226 (100). Anal. calc. for $C_{15}H_{14}O_4$ (258.28): C 69.76, H 5.46; found: C 69.47, H 5.63.

Data of 'anti'-**9**: colorless crystals. M.p. 78.5–80.0° (hexane). R_f (hexane/Et_2O 3:2): 0.16. UV (hexane): λ_{max} 242 (sh, 3.85). IR (KBr): 2953.5, 1715 (MeOCO), 1646, 1610, 1435, 1383, 1257, 1191.5, 1149.5, 1127, 1087, 1060, 1024, 976, 846, 773, 727, 706. ^{1}H-NMR (300 MHz; $CHCl_3$ at 7.270): 6.515 (*dd*, ^3J(H,H–C(11)) = 8.2, ^3J(H,H–C(8)) = 6.8, H–C(12)); 6.300 (*dd*, ^3J(H,H–C(6)) = 10.9, ^3J(H,H–C(8)) = 8.2, H–C(7)); 6.266 (*dd*, ^3J(H,H–C(12)) = 8.2, ^4J(H,H–C(8)) = 1.4, H–C(11)); 6.018 (*q*, ^4J(H,Me–C(13)) = 1.8, H–C(14)); 5.875 (*dd*, ^3J(H,H–C(7)) = 10.9, ^4J(H,H–C(8)) ≈ 0.7, H–C(6)); 3.834, 3.736, 3.695 (3*s*, 1:1:2, 4 MeOCO); *ca.* 3.74 (*tt*, Σ^3J(H,H–C(7)) + ^3J(H,H–C(12)) = 15.0, ^4J(H,H–C(6)) ≈ 0.5·^4J(H,H–C(11)), H–C(8)); 1.761 (*d*, ^4J(Me,H–C(14)) = 1.8, Me–C(13)); 1.642 (*s*, Me–C(2)). ^{1}H-NMR (600 MHz, C_6D_6; C_6D_5H at 7.156): 6.446 (*dd*, ^3J(H,H–C(12)) = 8.26, ^4J(H,H–C(8)) = 1.37, H–C(11)); 6.229 (*dd*, ^3J(H,H–C(6)) = 10.92, ^3J(H,H–C(8)) = 8.23, H–C(7)); 6.174 (*dd*, ^3J(H,H–C(11)) = 8.26, ^3J(H,H–C(8)) = 6.78, H–C(12)); 6.083 (*dd*, ^3J(H,H–C(7)) = 10.92, ^4J(H,H–C(8)) = 0.68, H–C(6)); 5.950 (*q* ^4J(H,Me–C(13)) = 1.84, H–C(14)); 3.561 (*ddt*, ^3J(H,H–C(7)) = 8.23, ^3J(H,H–C(12)) = 6.78, ^4J(H,H–C(6)) ≈ 0.5·^4J(H,H–C(11)), H–C(8)); 3.441, 3.411, 3.249, 3.235 (4*s*, 4 MeOCO); 1.947 (*s*, Me–C(2)); 1.678 (*d*, ^4J(Me,H–C(14)) = 1.84, Me–C(13)). CI-MS (NH_3): 458 (100, $[M + NH_3 + 1]^+$), 441 (26, $[M + 1]^+$), 426 (4), 409 (8), 381 (7). MS: 440 (0.1, $M^{+\cdot}$), 381 (69), 349 (100), 321 (28), 289 (35), 261 (18). Anal. calc. for $C_{24}H_{24}O_8$ (440.46): C 65.45, H 5.49; found: C 65.33, H 5.40.

2.3. *Azulene* **3** *and ADM*. The azulene (0.680 g, 4.35 mmol) and ADM (2.14 ml, 17.4 mmol) were dissolved in decalin (5 ml) and heated under N_2 during 2.5 h at 120°. Chromatographic workup (silica gel; hexane/Et_2O 3:2) gave *dimethyl 7,9-dimethylheptalene-1,2-dicarboxylate* (**10**; 0.200 g, 15.4%), *dimethyl 5,7-dimethylazulene-1,2-dicarboxylate* (**11**; 0.027 g, 2.3%), and *tetramethyl (1*RS*,2*RS*,5*SR*,8*RS*)-7,12-dimethyltetracyclo[6.2.2.2^{2,5}.0^{1,5}]-tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate* ('*anti*'-**12**; 0.020 g, 1.0%).

Data of **10**: orange crystals. M.p. 99.0–99.5° (hexane). R_f (hexane/Et_2O 3:2): 0.41. UV (hexane): λ_{max} 343.2 (3.70), 275.6 (4.31), 205.5 (4.47); λ_{min} 317.0 (3.59), 237.0 (4.20). IR (KBr): 2945.5, 1723 (MeOCO), 1575, 1436, 1256, 1226, 1199, 1158, 1136, 1106, 1047, 898, 814.5, 748. ^{1}H-NMR (300 MHz): 7.265 (br. *s*, H–C(3)); 6.179 (*dd*, ^3J(H,H–C(5)) = 10.2, ^3J(H,H–C(3)) = 6.7, H–C(4)); 6.117 (br. *s*, H–C(10)); 5.845 (*d*, ^3J(H,H–C(4)) = 10.2, H–C(5)); 5.711 (br. *s*, H–C(8)); 5.540 (*s*, H–C(6)); 3.715, 3.670 (2*s*, 2 MeOCO); 1.963 (*s*, 2 Me). CI-MS: 299 (100, $[M + 1]^+$). Anal. calc. for $C_{18}H_{18}O_4$ (298.34): C 72.47, H 6.08; found: C 72.39, H 6.29.

Data of **11**: blue crystals. M.p. 111–113° (hexane). R_f (hexane/Et_2O 3:2): 0.33. UV (hexane): λ_{max} 371.8 (3.82), 344.5 (3.81), 305.6 (4.71), 297.0 (4.65), 246.8 (4.36), 218.4 (4.26); λ_{min} 326.0 (3.75), 325.8 (3.67), 300.0 (4.65), 267.0 (4.09), 229.0 (4.20). IR (KBr): 2934, 2853, 1723 (MeOCO), 1685.5, 1653, 1506, 1472, 1404, 1388.5, 1331, 1304, 1234, 1167, 1120, 1040, 930, 866, 800, 769. ^{1}H-NMR (300 MHz): 9.334 (br. *s*, H–C(8)); 8.285 (*d*, ^4J(H,H–C(6)) = 1.4, H–C(4)); 7.714 (br. *s*, H–C(6)); 7.200 (*s*, H–C(3)); 3.969, 3.919 (2*s*, 2 MeOCO); 2.733, 2.678 (2*s*, 2 Me). CI-MS: 273 (100, $[M + 1]^+$), 272 (14, $M^{+\cdot}$), 267 (5), 241 (37). Anal. calc. for $C_{16}H_{16}O_4$ (272.30): C 70.57, H 5.92; found: C 70.78, H 6.05.

Data of 'anti'-**12**: colorless crystals. M.p. 119–121° (hexane). R_f (hexane/Et_2O 2:3): 0.40. UV (hexane): λ_{max} 296 (sh, 3.38). IR (KBr): 2953, 1724 (MeOCO), 1634, 1436, 1285, 1214, 1168.5, 1105, 1062.5, 948, 840.5, 774, 723.5. ^{1}H-NMR (300 MHz, $CDCl_3/C_6D_6$; $CHCl_3$ at 7.260/C_6D_5H at 7.159): 6.733/6.591 (*dd*, ^3J(H,H–C(13)) = 5.15/5.15, ^3J(H,H–C(2)) = 3.30/3.29, H–C(14)); 6.495/6.480 (*dd*, ^3J(H,H–C(14)) = 5.15/5.16, ^4J(H,H–C(2)) = 0.86/0.85, H–C(13)); 5.821/5.983 (*quint.*-like, ^4J(H,Me–C(12)) ≈ ^4J(H,H–C(8)) = 1.65/1.64, H–C(11)); 5.414/5.662 (*sext.*-like, ^4J(H,Me–C(7)) ≈ ^4J(H,H–C(8)) ≈ ^5J(H,H–C(2)) ≈ 1.2/1.2, H–C(6)); 4.372/4.726 (*dt*-like, ^3J(H,H–C(14)) = 3.30/3.28, ^4J(H,H–C(13)) ≈ ^5J(H,H–C(6)), H–C(2)); 3.782, 3.778, 3.737, 3.727/3.406, 3.387, 3.353, 3.277 (4*s*, 4 MeOCO); 3.279/3.248 (*t*, ^4J(H,H–C(6)) ≈ ^4J(H,H–C(11)) ≈ 1.4/1.4, H–C(8)); 1.978/1.896 (*d*, ^4J(Me,H–C(6)) = 1.53/1.54, Me–C(7)); 1.824/1.465 (*d*, ^4J(Me, H–C(11)) = 1.56/1.56, Me–C(12)). ^{1}H-DR (400 MHz, $CDCl_3$): 5.420 (H–C(6))→4.376 (*dd*, ^3J(H,H–C(14)) = 3.29, ^4J(H,H–C(13)) = 0.85, H–C(2)), 3.283 (*d*, ^4J(H,H–C(11)) = 1.50, H–C(8)), 1.984 (*s*, Me–C(7)); 4.376 (H–C(2))→6.737 (*d*, ^3J(H,H–C(13)) = 5.15, H–C(14)), 6.500 (*d*, ^3J(H,H–C(14)) = 5.16, H–C(13)), 5.422 (*quint.*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me–C(7)) ≈ 1.3, H–C(6)); 3.284 (H–C(8))→5.827 (*q*, ^4J(H,Me–C(12)) = 1.70, H–C(11)), 5.421 (*quint.*-like, ^5J(H,H–C(2)) ≈ 0.5·^4J(H,Me–C(7)) ≈ 1.3, H–C(6)). CI-MS: 441 (100, $[M + 1]^+$), 409 (8), 381 (2). Anal. calc. for $C_{24}H_{24}O_8$ (440.46): C 65.45, H 5.49; found: C 65.46, H 5.32.

In a second run, the reaction of azulene **3** with ADM (4 mol-equiv.) in decalin was performed at 200° (1 h). Compounds **10** and **11** were obtained in a yield of 10.7% and 2.4%, respectively. The tetracycle '*anti*'-**12** could not be detected. However, tetramethyl naphthalene-1,2,3,4-tetracarboxylate and tetramethyl azulene-1,2,4,5- and 1,2,7,8-tetracarboxylate as well as some further (1 + 2)-, (1 + 3)-, and (1 + 4)-addition products were isolated in yields of 1–3% [8].

2.4. *Azulene* **4** *and ADM*. The azulene (0.390 g, 2.12 mmol) and ADM (1.0 ml, 8.48 mmol) were dissolved in decalin (5 ml) and heated under N_2 during 1 h at 200°. The chromatographic workup (silica gel; hexane/Et_2O 3:2) yielded *dimethyl 3,5,7,9-tetramethylheptalene-1,2-dicarboxylate* (**13**) in a mixture with its DBS isomer (in total 0.007 g, 1%), *dimethyl 3,5,7-trimethylazulene-1,2-dicarboxylate* (**14**); 0.029 g, 4.8%), and *tetramethyl (1*RS,*2*RS,*5*SR,*8*RS*)-2,7,12,13-tetramethyltetracyclo[6.2.2.2^{2,5}.0^{1,5}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate* ('*anti*'-**15**; 0.370 g, 37.2%).

Data of **13**. Yellow crystals. M.p. 127–130° (hexane). R_f (hexane/Et_2O 3:2): 0.38. UV (hexane): λ_{max} 344 (3.65), 265 (4.34), 211 (4.33); λ_{min} 319 (3.58), 236 (4.20). IR (KBr): 2944, 1716.5 (MeOCO), 1581, 1431, 1284.5, 1258, 1222, 1192, 1138, 1081, 1023, 882, 846, 797, 772. ^{1}H-NMR (300 MHz; when dissolved in $CDCl_3$ at r.t., an equilibrium mixture of *ca.* 87% of **13** and 13% of its DBS isomer was established; signals of **13** are given); 6.199 (*q*-like, ^4J(H,Me–C(5)) = 1.4, H–C(4)); 5.956 (br. *s*, H–C(8)); 5.916 (br. *s*, H–C(10)); 5.779 (*s*, H–C(6)); 3.645, 3.634 (2*s*, 2 MeOCO); 2.200 (*s*, Me–C(3)); 2.01 (br. *s*, Me–C(5,7,9)). CI-MS: 327 (100, $[M+1]^+$). Anal. calc. for $C_{20}H_{22}O_4$ (326.40): C 73.60, H 6.79; found: C 73.85, H 6.71.

Data of the DBS Isomer of **13**: ^{1}H-NMR (300 MHz; in the mixture with *ca.* 87% **13** in $CDCl_3$): 6.386 (br. *s*, H–C(2)); 6.069 (br. *s*, H–C(8)); 5.595 (br. *s*, H–C(6)); 5.557 (br. *s*, H–C(10)); 3.844, 3.693 (2*s*, 2 MeOCO); 2.006, 1.983, 1.968 (3 br. *s*, Me–C(3,7,9)); 1.732 (*s*, Me–C(1)).

Data of **14**: blue crystals. M.p. 171–172° (hexane). R_f (hexane/Et_2O 3:2): 0.34. UV (hexane): λ_{max} 385.6 (3.83), 373 (sh, 3.76), 352 (sh, 3.58), 309.2 (4.61), 297.8 (4.57), 248.8 (4.30), 213.0 (4.19); λ_{min} 330.0 (3.42), 303.0 (4.54), 264.2 (4.18), 219.0 (4.16). IR (KBr): 2954, 1726 (MeOCO), 1686, 1441, 1395, 1244, 1205, 1144, 1069, 1007, 934, 869, 792, 780.5. ^{1}H-NMR (300 MHz): 9.381 (br. *s*, H–C(8)); 8.195 (*d*, ^4J(H,H–C(6)) = 1.6, H–C(4)); 7.667 (br. *s*, H–C(6)); 3.991, 3.894 (2*s*, 2 MeOCO); 2.711, 2.695 (2*s*, Me–C(5,7)); 2.507 (*s*, Me–C(3)). CI-MS: 287 (100, $[M+1]^+$), 255 (34). Anal. calc. for $C_{17}H_{18}O_4$ (286.33): C 71.31, H 6.34; found: C 71.28, H 6.53.

Data of 'anti'-**15**: colorless crystals. M.p. 165–166° (hexane). R_f (hexane/Et_2O 1:1): 0.33. UV (hexane): λ_{max} 244 (sh, 3.78). IR (KBr): 2955, 1716 (MeOCO), 1643, 1618, 1438, 1315, 1262, 1241, 1192, 1146, 1101.5, 1074, 1011, 974, 838, 781, 726. ^{1}H-NMR (300 MHz, $CDCl_3/C_6D_6$; $CHCl_3$ at 7.264/C_6D_5H at 7.162): 5.972/5.976 (*q*, ^4J(H, Me–C(13)) = 1.8/1.6, H–C(14)); 5.823/6.140 (*quint.*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me–C(12)) ≈ 1.6/1.7, H–C(11)); 5.578/5.979 *quint.*-like, ^4J(H,H–C(8)) ≈ ^4J(H, Me–C(7)) ≈ 1.3/-, H–C(6)); 3.819, 3.738, 3.695, 3.678/3.443, 3.420, 3.249, 3.237 (4*s*, 4 MeOCO); 3.355/3.394 (*t*-like, ^4J(H,H–C(6)) ≈ ^4J(H,H–C(11)) ≈ 1.4/1.4, H–C(8)); 2.000/2.002 (*d*, ^4J(Me,H–C(6)) = 1.5/1.4, Me–C(7)); 1.835/1.500 (*d*, ^4J(Me,H–C(11)) = 1.6/1.55, Me–C(12)); 1.738/1.733 (*d*, ^4J(Me,H–C(14)) = 1.8/1.80, Me–C(13)); 1.618/2.004 (*s*, Me–C(2)). ^{1}H-NOE (400 MHz, $CDCl_3$): 5.972 (H–C(14))→3.678 (*m*, MeOCO–C(10)), 1.738 (*s*, Me–C(13)), 1.618 (*s*, Me–C(2)); 5.823 (H–C(11))→1.835 (*s*, Me–C(12)), 1.618 (*s*, Me–C(2)); 5.578 (H–C(6))→2.000 (*s*, Me–C(7)), 1.738 (*s*, Me–C(13)); 3.355 (H–C(8))→2.000 (*s*, Me–C(7)), 1.835 (*s*, Me–C(12)); 1.835 (Me–C(12))→5.823 (*s*, H–C(11)), 3.355 (*s*, H–C(8)); 1.738 (Me–C(13))→5.972 (*s*, H–C(14)), 5.578 (*s*, H–C(6)); 1.618 (Me–C(2))→5.972 (*s*, H–C(14)), 5.823 (*s*, H–C(11)). CI-MS: 469 (100, $[M+1]^+$), 437 (16), 409 (2), 277 (5), 246 (4), 190 (4). Anal. calc. for $C_{26}H_{28}O_8$ (468.51): C 66.66, H 6.02; found: C 66.89, H 5.88.

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