# 207. Thermal Reaction of Azulene-1-carbaldehydes with Dimethyl Acetylenedicarboxylate

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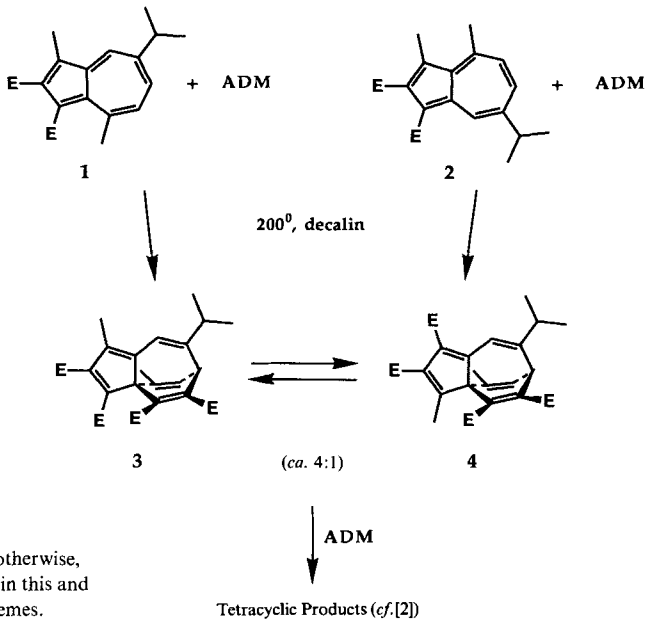
Azulene-1-carbaldehydes which have Me substituents at C(3) and C(8) and no substituent at C(6) react with excess dimethyl acetylenedicarboxylate (ADM) in decalin at 200° to yield exclusively the *Diels-Alder* adduct at the seven-membered ring (*cf. Scheme 3*). The corresponding 1-carboxylates behave similarly (*Scheme 4*). Azulene-1-carbaldehydes which possess no Me substituent at C(8) (*e.g.* **11**, **12** in *Scheme 2*) gave no defined products when heated with ADM in decalin. On the other hand, Me substituents at C(2) may also assist the thermal addition of ADM at the seven-membered ring of azulene-1-carbaldehydes (*Scheme 6*). However, in these cases the primary tricyclic adducts react with a second molecule of ADM to yield corresponding tetracyclic compounds. The new tricyclic aldehydes **16** and **17** which were obtained in up to 50% yield (*Scheme 3*) could quantitatively be decarbonylated with $[RhCl(PPh_3)_3]$ in toluene at 140° to yield a thermally equilibrated mixture of four tricycles (*Scheme 8*). It was found that the thermal isomerization of these tricycles occur at temperatures as low as 0° and that at temperatures > 40° the thermal equilibrium between the four tricycles is rapidly established *via* [1,5]-C shifts. The establishment of the equilibrium makes the existence of two further tricycles necessary (*cf. Scheme 8*). However, in the temperature range of up to 85° these two further tricycles could not be detected by $^1$H-NMR. When heated in the presence of excess ADM in decalin at 180°, the 'missing' tricyclic forms could be evidenced by their tetracyclic trapping products '*anti*'-**45** and '*anti*'-**48**, respectively (*Scheme 9*).

**1. Introduction.** – Recently, we showed that azulenes react thermally in apolar solvents such as decalin with dimethyl acetylenedicarboxylate (ADM) in a *Diels-Alder*-type addition at the five-membered ring in a HOMO(azulene)/LUMO(ADM)-controlled transformation as well as at the seven-membered ring in a SHOMO(azulene)/LUMO-(ADM)-controlled transformation [1–3]. $\pi$-Acceptor substituents such as a MeOCO group at C(2) of the azulene skeleton decrease the rate of the addition reaction as compared to a Me substituent at C(2); however, they do not change the site selectivity of the ADM addition, *i.e.* only products arising from the reaction at the five-membered ring of the azulenes are observed [1]. On the other hand, an additional $\pi$-acceptor substituent such as a MeOCO group at C(1) of the azulene skeleton does completely alter the site selectivity of the thermal ADM addition. In a slow reaction, only the addition of ADM at the seven-membered ring of the azulenes takes place [2]. *Scheme 1* shows the result of the addition of ADM to dimethyl 5-isopropyl-3,8-dimethyl- and to dimethyl 7-isopropyl-3,4-dimethylazulene-1,2-dicarboxylate (**1** and **2**, respectively) [2]. Both azulene-1,2-dicarboxylates yield the same mixture of the tricyclic compounds **3** and **4** which thermally equilibrate already slightly above room temperature, thus indicating that additional tricyclic compounds derived from **3** and **4**, respectively, by formal [1,5]-sigmatropic

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

*Scheme 1*[a])



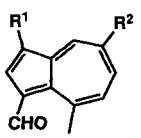

[a]) If not stated otherwise, E = MeOCO in this and following schemes.

C-shifts must be involved as intermediates. Some of them can be trapped at 200° by ADM in an *Diels-Alder*-type addition at the cyclopentadiene substructure of the tricyclic compounds. To gain further insight into the steric and electronic factors favoring the thermal addition of ADM at the seven-membered ring of the azulenes and thereby opening a synthetic path to this new class of tricyclic compounds, we studied the thermal reaction of azulene-1-carbaldehydes with ADM in decalin. The latter compounds are easily accessible by *Vilsmeier* formylation of the corresponding alkylated azulenes (*cf.* [4] as well as [1–3]).

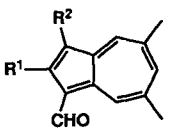
**2. Results and Discussions.** – Since we recognized already that substituents at C(6) of the azulene skeleton suppress or strongly depress at least the thermal addition of ADM at the seven-membered ring of the azulenes, mainly on steric grounds (*cf.* [1–3]), we investigated, in particular, those azulene-1-carbaldehydes (*Scheme 2*) whose reduced forms (*cf.* [2–3]) gave comparably high yields of addition products at the seven-membered ring or their follow-up products with ADM, *i.e.* the corresponding tetracyclic compounds (*cf. Scheme 1*). On grounds of comparison, we included in our investigation the azulene-carbaldehydes **13** and **14** bearing a Me or *t*-Bu group at C(6) as well as the azulene-1-carboxylate **15**. All azulenes were available from earlier work or synthesized by established procedures (*cf. Exper. Part*)[2]).

[2]) Lactaroviolin (*cf.* [5] and lit. cited there) that, on catalytic reduction of its isopropenyl group, yielded the azulene-1-carbaldehyde **11** (*cf.* [6]) was available from earlier work of *Karrer et al.* (*cf.* [7]). A crystalline probe (1 g) of lactaroviolin, sealed by Dr. *E. Schick* on November 20, 1946, in an ampoule, was still completely unchanged and showed no by-products at all. We thank Prof. Dr. *C. H. Eugster* for making several probes of lactaroviolin from *Karrer*'s work available to us.

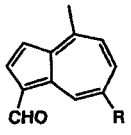
*Scheme 2*



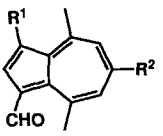
**5** $R^1$ = Me, $R^2$ = i-Pr
**6** $R^1$ = $R^2$ = Me
**7** $R^1$ = H, $R^2$ = Me



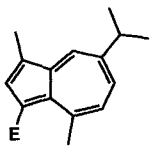
**8** $R^1$ = H, $R^2$ = Me
**9** $R^1$ = Me, $R^2$ = H
**10** $R^1$ = $R^2$ = Me



**11** R = i-Pr
**12** R = Me



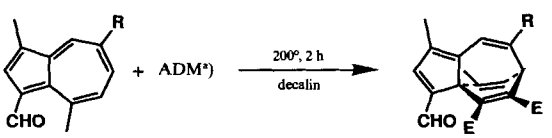
**13** $R^1$ = H, $R^2$ = Me
**14** $R^1$ = Me, $R^2$ = *t*-Bu



**15**

When the carbaldehyde **5** of guaiazulene or its 5-Me analogue **6** was heated with excess ADM in decalin at 200°, a single product was formed in both cases which was purified by chromatography and crystallization (*Scheme 3*). The spectroscopic data of both compounds **16** and **17** clearly showed that they possessed the tricyclic structure given in *Scheme 3* with the CHO group at C(2).

*Scheme 3*




**5** R = i-Pr
**6** R = Me

**16** (46%)[b])
**17** (39%)

[a]) The reactions were performed with a four-fold molar excess of ADM; yields are given for purified products.
[b]) With a three-fold molar excess of ADM at 180°/2 h, a yield of 51% for **16** was obtained. Under these conditions, the formation of the thermal-condensation product of ADM was avoided (*cf.* [8] as well as [1–3]).

The $^1$H-NMR spectrum ($CDCl_3$) of **16** reveals the presence of a CHO group in conjugation with C=C bonds, since the H-atom of the CHO group appears at 9.722 (9.739) ppm[3]). It shows a strong $^1$H-NOE with H–C(3) which absorbs at lowest field at 7.501 (7.497) ppm as *s*. This H-atom, in turn, exhibits a strong $^1$H-NOE with Me–C(4) at 2.058 (2.037) ppm which appears as *s* showing a further strong $^1$H-NOE with H–C(6) at 5.878 (5.905) ppm. Additional $^1$H-NOE of H–C(8), which shows an allylic coupling with H–C(6), with the i-Pr group, and with H–C(12) at 6.114 (6.172) ppm are in agreement with the proposed structure. Of further structural relevance is the fact that the vicinal

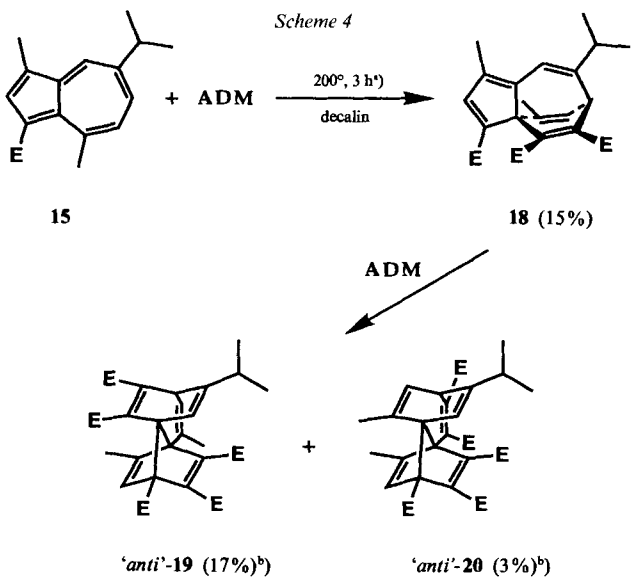
[3]) In parentheses are the values for the Me analogue **17**.

coupling constant of H–C(8) and H–C(12) amounts to 6.71 (6.68) Hz which shows that they form a dihedral angle of *ca.* 20° (*cf.* [1–3] and later). The coherent structural assignment is completed by an observed strong $^1$H-NOE between Me–C(11) at 1.531 (1.541) ppm, displaying an allylic coupling with H–C(12), and the H-atom of the CHO group at C(2).

The UV spectrum (hexane) of **16** shows the longest-wavelength absorption at 383 (381) nm[3]) ($\log \varepsilon = 4.01$ (3.97)) in good agreement with an estimated band position of 378 nm[4]). Both aldehydes, **16** and **17**, were stable when heated at temperatures > 100° in decalin. No new tricyclic aldehydes were formed under these conditions.

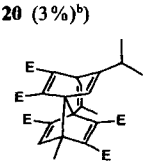
Similarly to the azulene-1-carbaldehyde **5** behaved the corresponding methyl azulene-1-carboxylate **15** when heated in decalin in the presence of an excess of ADM at 200° (*Scheme 4*). The tricyclic triester **18** showed $^1$H-NMR signals and coupling patterns nearly identical with those of the corresponding aldehyde **16** (*cf. Exper. Part*). The longest-wavelength UV maximum of **18** (367 nm) showed the expected hyposochromic shift in comparison to that of **16** (383 nm). The structures of '*anti*'-**19** and '*anti*'-**20** follow

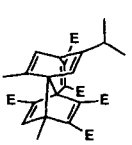
*Scheme 4*




[a]) The reaction was performed in the presence of a 4.4-fold molar excess of ADM; 12% of **15** were recovered.

[b]) Estimated yield ($^1$H-NMR) from a mixture of '*anti*'-**19**, '*anti*'-**20**, and the thermal condensation product of ADM (*cf.* [8] as well as [1–3]). '*anti*'-**19** and '*anti*'-**20** were further purified by HPLC (*cf. Exper. Part*). The purified fraction of '*anti*'-**20** (*ca.* 75%) showed in the $^1$H-NMR additional signals of two further, presumably tetracyclic compounds, to which tentatively the structures '*anti*'-**21** and '*anti*'-**22** can be assigned (*cf. Exper. Part*).


'anti'-21

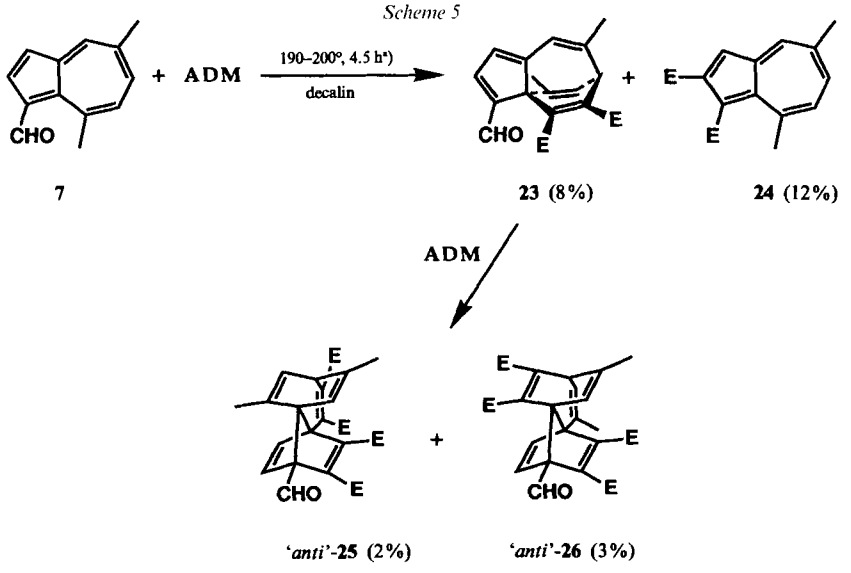

'anti'-22

[4]) For this estimation, we took the UV absorption band of cyclopentene-1-carbaldehyde at 237 nm (EtOH) [9] as parent value and an increment of 46 nm for the extension of conjugation in a five-membered ring (*cf.* Footnote 12 in [2]). The other increments for C=C bonds extending conjugation (30 nm) and $\gamma$-substituents (3 à 18 nm) as well as for solvent correction (EtOH→hexane, + 11 nm) were taken from *Scott* [10].

unequivocally from their $^1$H-NMR spectra and corresponding $^1$H-NOE measurements. Since irradiation of the signal of H–C(14) of '*anti*'-**19** caused no influence on the signal of H–C(11), but on the signals of two methyl-ester groups (MeOCO–C(2) and MeOCO–C(10)), we have to assign the '*anti*'-structure to **19**. On the other hand, irradiation of the signal of Me–C(11) of '*anti*'-**20** induced a strong $^1$H-NOE on the signal of H–C(14) and a weak $^1$H-NOE on the signal of Me–C(13). Therefore, there is little doubt that **20** has the ester group at C(3) and the Me group at C(11) in an '*anti*'-relation (*cf.* [1] for the use of the configurational descriptors '*anti*' and '*syn*'). Both tetracyclic compounds, '*anti*'-**19** as well as '*anti*'-**20**, cannot directly arise from a thermal addition of ADM to the cyclopentadiene substructure of **18**. Therefore, we have to assume that **18**, which is stable up to 150°, does rearrange at 200° *via* [1,5]-C shifts into isomeric tricyclic compounds which are trapped by ADM (*cf. Scheme 1* and [2]). The tentatively assigned structures of '*anti*'-**21** and '*anti*'-**22** (*cf. Scheme 4*) are in agreement with this mechanistic picture.

The thermal reaction of the azulene-1-carbaldehyde **7** with ADM at 190–200° in decalin was much more sluggish than of its 3-Me homologue **6** (*Scheme 5*)[5]). The blue azulene-1,2-dicarboxylate **24** could be separated from a mixture of aldehydes ($^1$H-NMR:

*Scheme 5*

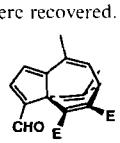



**7** **23** (8%) **24** (12%)

'*anti*'-**25** (2%) '*anti*'-**26** (3%)

[a]) Aldehyde **7** was reacted in total with a five-fold molar excess of ADM; 17% of aldehyde **7** were recovered.

[b]) Percentages of **23**, '*anti*'-**25**, and '*anti*'-**26** were estimated in the original reaction mixture by $^1$H-NMR spectroscopy (*s* of the CHO groups) after chromatographic separation of **24**. The tricyclic aldehyde **23** was accompanied by a second tricyclic aldehyde **27** and at least two further aldehydes of so far unknown structure (in total 18% of the fraction of structurally assigned aldehydes; see *Exper. Part*).



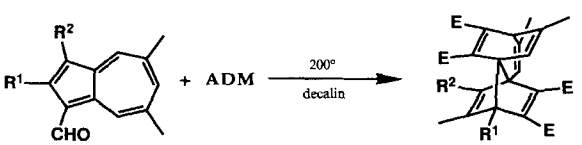

**27**

[5]) Aldehyde **7** was obtained as side-product (9%) in the *Vilsmeier* formylation of 4,7-dimethylazulene (*cf. Exper. Part*). Therefore, only one thermal experiment with a small amount of **7** and ADM was performed, *i.e.* the yields given in *Scheme 5* are not representative and do only reflect a tendency in the amount of product formation.

*s*, in the range of 10.3 to 9.6 ppm). From the latter one, two fractions were obtained by HPLC which mainly consisted of **23**, '*anti*'-**26**, and **27** as well as of the tetracycle '*anti*'-**25**. The assignment of the structures is based on a comparison of the $^1$H-NMR data of **23** and **27** with those of the tricyclic aldehydes **16** and **17** (*Scheme 3*). Characteristic for both new aldehydes is the low-field position of the signal for H–C(3) which appears as *d* with $^3J(3,4) = 2.62$ and 2.76 Hz, respectively, *i.e.* in the typical range for $J_{vic}$ of H–C(2) and H–C(3) in cyclopentadienes (*cf.* [11]). Aldehyde **23** shows a long-range coupling between H–C(4) and Me–C(7), which is not present in **27**. The $^1$H-NMR spectra of '*anti*'-**25** and '*anti*'-**26** resemble those of '*anti*'-**20** and '*anti*'-**19**, respectively. That the CHO group is located in both structures at the bridgehead position follows from the fact that its H-atom appears at low-field (10.25 and 10.15 ppm, respectively), and that H–C(13) and H–C(14) form an isolated *AB* system with $J_{AB} = 5.4$–5.5 Hz. The appearance of the azulene-1,2-dicarboxylate **24** shows that, in contrast to the thermal reaction of **6** – the Me homologue of **7** – with ADM, the aldehyde **7** reacts with ADM to some extent also at the five-membered ring of the azulene skeleton. The tetracyclic aldehyde '*anti*'-**26** can be considered as the direct thermal *Diels-Alder* product of **27** with ADM. On the other hand, the formation of '*anti*'-**25** requires, as precursor for the *Diels-Alder* reaction with ADM, a rearrangement of **23** as well as of **27** by [1,5]-C shifts (*vide supra*). The formation of **23** and **27** in the thermal reaction of **7** with ADM is of interest, since the isomeric 4,7-dimethylazulene-1-carbaldehyde (**12**) and its structural analogue **11** (*Scheme 2*) could not be reacted with ADM at 200°. Both aldehydes, when heated with excess ADM in decalin at 200°, decomposed slowly without distinct formation of products.

From the results so far described, it seems that a Me group at C(8) of the azulene-1-carbaldehyde is necessary to observe thermal ADM addition at the seven-membered ring of the azulene skeleton. The thermal addition experiments with ADM and the azulene-1-carbaldehydes **8**–**10** demonstrate, however, that a Me group at C(2) may act in the same way when C(8) is not substituted (*Scheme 6*). Indeed, whereas azulene-1-carbaldehyde **8** which carries the Me group at C(3) of the five-membered ring showed no distinct product formation at all when heated with an excess of ADM in decalin, its 2-Me isomer **9** reacted with ADM to yield the tetracyclic carbaldehyde '*anti*'-**28**. Similarly, the azulene-1-carbaldehyde **10**, bearing Me groups at C(2) and C(3), gave rise to the formation of the tetracycle '*anti*'-**29**. No tricyclic compounds could be observed in the latter two experi-

*Scheme 6*




9[a]) $R^1$ = Me, $R^2$ = H
10 $R^1 = R^2$ = Me

'*anti*'-**28** (25%) $R^1$ = H, $R^2$ = CHO (1.5 h)
'*anti*'-**29** (44%) $R^1$ = CHO, $R^2$ = Me (3.5 h)

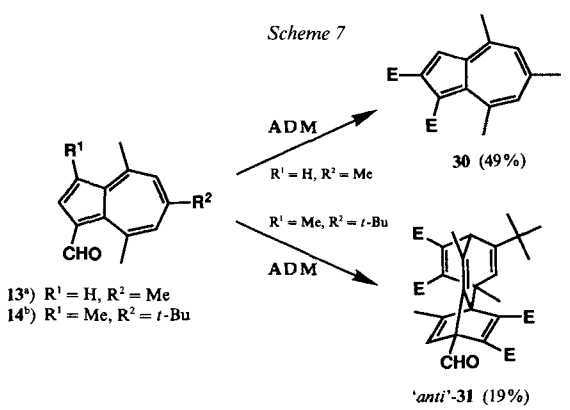
[a]) Carbaldehyde **9** was reacted in a 2:1 mixture with carbaldehyde **8** ($R^1$ = H, $R^2$ = Me) which gave no product when heated alone with an excess of ADM in decalin at 200° for 3.5 h. Yield of '*anti*'-**28** with respect to **9** in the 2:1 mixture.

[b]) Heated with a five-fold molar excess of ADM; '*anti*'-**29** crystallized from the reaction mixture after removal of decalin.

ments (*cf.* [3] for similar results obtained with 1,3,5,7-tetramethylazulene and related symmetrically substituted azulenes). However, the formation of *'anti'*-**28** and *anti'*-**29** can only be explained when the intermediate formation of tricyclic compounds of type **23** or **27** (*cf. Scheme 5*) is assumed. In this way, addition of ADM across C(3a), C(6) in **9** would lead to the formation of a tricycle whose further reaction with ADM from the sterically less hindered side will directly yield *'anti'*-**28**. Similarly, the addition of ADM across C(8a), C(6) in **10**, followed by addition of a second molecule of ADM, again from the sterically less hindered side, would give rise to the formation of *'anti'*-**29**. That both tetracycles, indeed, possess the shown *'anti'*-arrangement of their maleate substructures follows from $^1$H-NOE measurements. The tetracycle *'anti'*-**28** which shows the signal of the H-atom of its CHO group at 9.82 ppm exhibits to $^1$H-NOE at H–C(11) when Me–C(14) is irradiated. Conversely, $^1$H-NOE of strong and medium intensity are observed for the signal of the CHO group and one MeOCO group (at C(10)), respectively. Similar $^1$H-NOE were observed in *'anti'*-**29** which showed the H-atom of its CHO group at 10.23 ppm, *i.e.* in the bridgehead position at C(2).

The last experiments which we performed in the context of evaluating the influence of Me groups – or alkyl group, in general – on the formation of seven-ring adducts of azulene-1-carbaldehydes and ADM are shown in *Scheme 7*. They clearly demonstrate

*Scheme 7*




**13**[a]) $R^1$ = H, $R^2$ = Me
**14**[b]) $R^1$ = Me, $R^2$ = *t*-Bu

*'anti'*-**31** (19%)

[a]) The aldehyde was reacted with a 4.5-fold molar excess of ADM in decalin at 200° for 3.5 h. After this time, 18% of **13** were recovered.

[b]) The aldehyde was reacted with a 4.4-fold molar excess of ADM in decalin at 200° for 2.5 h. After this time, in total 38% of **14** were recovered. The tetracycle *'anti'*-**31** was accompanied by a second product in 22% yield. It represented a (1 + 1) adduct, but decomposed during HPLC. Therefore, its structures could not be elucidated (*cf. Exper. Part*).

[c]) Yield of purified crystalline material. The $^1$H-NMR analysis of the chromatographic fractions indicated a total yield of 29% for *'anti'*-**31** (*cf. Exper. Part*).

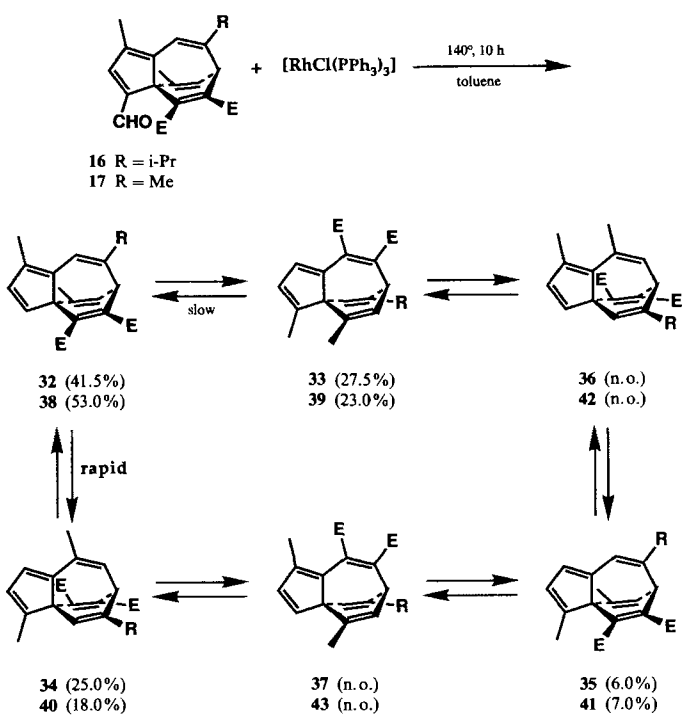
that the favorable effect of a Me substituent at C(8), as we have seen in the preceding experiments, can completely be overruled by an alkyl substituent at C(6) (*cf.* [1]).

In the case of aldehyde **13**, thermal addition of ADM across C(3), C(8a) at the five-membered ring leads to a tricyclic intermediate which, at least at 200°, can undergo the *retro-Diels-Alder* reaction under loss of propiolaldehyde to yield the azulene-1,2-di-

carboxylate **30.** This energetically most favorable pathway is also observed with other 1-alkyl-substituted 4,6,8-trimethylazulenes (*cf.* [12] [13]) or conjugative substituents such as Ph or styryl groups [14]. The thermal behavior of aldehyde **14** in the presence of ADM shows that it reacts in a similar way as its 1-Me analogue due to the elevation of the ground-state energy, since all four *peri*-positions are occupied by substituents (*cf.* [1]). This means that the relative concentration of the tricyclic intermediate resulting from addition of ADM across C(1), C(3a) is augmented, and, therefore, it can be trapped by addition of a second molecule of ADM leading to '*anti*'-**31**. The structure of '*anti*'-**31** follows from a comparison of the $^1$H-NMR shifts and coupling constants of '*anti*'-**31** and its 8-Me analogue [1] whose structure has been established by $^1$H-NOE measurements and an X-ray structure analysis of the corresponding 13-Me derivative [1].

The tricyclic aldehydes **16** and **17** offer the opportunity to obtain, by decarbonylation, a series of further tricyclic compounds. Indeed, when **16** was heated in toluene in the presence of a slight molar excess of the *Wilkinson* catalyst [$RhCl(PPh_3)_3$] (*cf.* [15] [16]), a quantitative decarbonylation of **16** was observed, and a mixture of the four tricycles **32**–**35** was isolated in a total yield of 86% (*Scheme 8*). In a similar way, aldehyde **17** was decarbonylated to yield a mixture of the four analogous tricycles **38**–**41** (*Scheme 8*).

*Scheme 8*[a])




[a]) The percentages given in parentheses refer to the equilibrium mixture in toluene at 85° (R = i-Pr) and 55° (R = Me), respectively. n.o. = not observed, *i.e.* relative amount must be < 0.5%.

Qualitative UV spectra of the four tetracycles **32–35** which were recorded in the course of an HPLC analysis showed that three tricycles possess very similar electronic structures (*cf. Fig. 1*) with the longest-wavelength maximum at 305–307 nm and comparable with

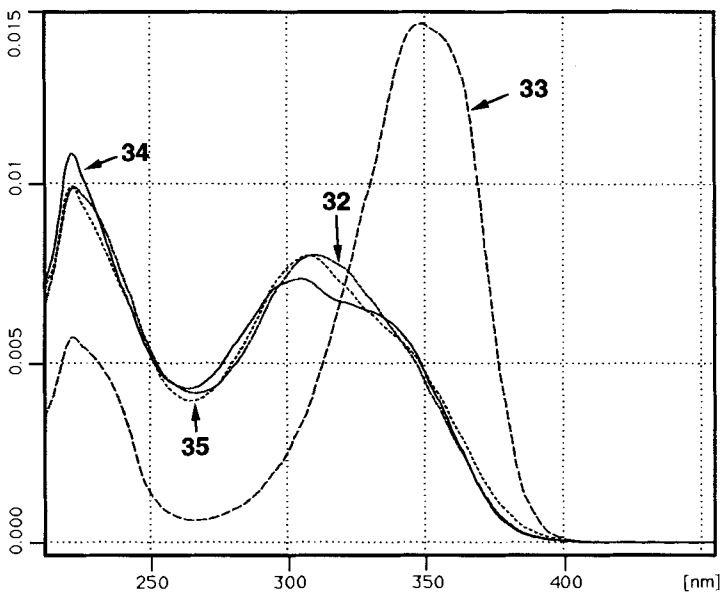



Fig. 1. *Comparison of the qualitative UV spectra of the tricycles* **32–35** (hexane + 2% i-PrOH) *taken in the course of an analytical HPLC separation* (*cf. Exper. Part*)

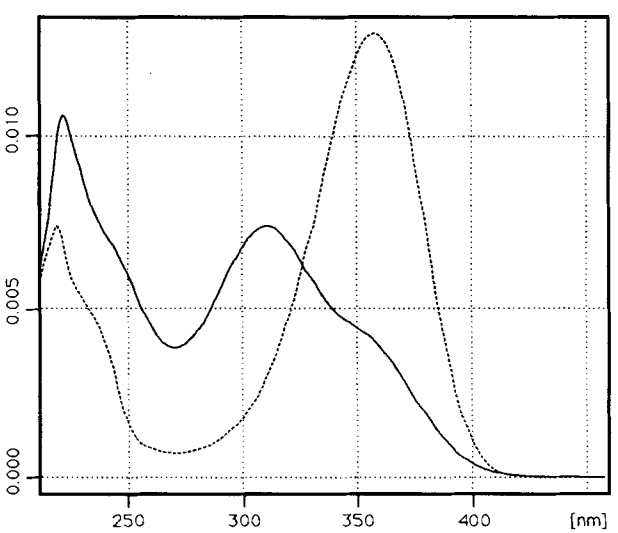



Fig. 2. *Qualitative UV spectra of the 2-Me and 4-Me homologues of* **32** *and* **33** (*cf.* [2]) *taken under the same conditions as given in* Fig. 1

those of the 2-Me homologue of **32** which have it at 312 nm (*Fig. 2*) [2]. On the other hand, the fourth tetracycle showed the longest-wavelength maximum, bathochromically shifted, at 346 nm (*Fig. 1*). This is the region where tricycles with MeOCO substituents at C(6) and C(7) show their longest-wavelength maximum, *e.g.* the 4-Me homologue exhibits its UV maximum at 357 nm (*Fig. 2*) [2]. Preparative HPLC separations allowed to obtain the tricycle **33** in pure form. In addition, a 1.7:1 mixture of the tricycles **32** and **34** was obtained. When this mixture was dissolved in a minimum amount of $Et_2O$ and kept at −20°, crystals of pure **32** slowly formed. The following observations were made: *1*) At −20°, the tricycle **32** was stable in $CDCl_3$ solution. Already at 0°–20°, it reversibly rearranged into a *ca.* 1.7:1 mixture of **32** and **34.** Neither tricycle **33** nor tricycle **35** could be detected in this temperature range. However, when the 1.7:1 mixture of **32** and **34** was heated ≥ 50° the equilibrium mixture of all four tricycles **32**–**35** as shown in *Scheme 8* was rapidly established. *2*) Tricycle **33** was stable at temperatures ≤ 40° in $CDCl_3$ solution. At temperatures > 40°, it rearranged reversibly into the tricycles **32**, **34**, and **35** which were formed in their relative equilibrium ratio.

These results demonstrate that the tricycles **32** and **34** easily undergo [1,5]-C shifts of the MeOCO-substituted C(10). On the other hand, the [1,5]-C shifts of Me–C(11) or H–C(10) in **33** seem to be loaded with a higher activation energy, but this may be due to the interruption of a stronger conjugation in the transition state leading to **32** or **36**[6]). The appearance of **35** in the equilibrium mixture of the tricycles shows that two further tricycles, namely **36** and **37**, must be involved in the establishment of the equilibrium (*cf. Scheme 8*). Both tricycles, **36** and **37**, could not be detected in the equilibrium mixture by $^1$H-NMR measurements, *i.e.* their equilibrium concentration must be much smaller than 0.5% which represents the limits of $^1$H-NMR detection. We obtained almost the same results with the Me analogues **38**–**41**. Again, the necessary additional tricyclic compounds **42** and **43** could not be detected in the equilibrium mixture (*cf. Scheme 8*).

The tricycles **32**–**37** are the postulated intermediates in the thermal reaction of guaiazulene and excess ADM in decalin at 190° [2]. The intermediate appearance of five of these tricycles, namely **32**–**34** as well as **36** and **37**, could be deduced from the structures of six tetracyclic compounds (*cf.* '*anti*'-**44** to '*anti*'-**48** in *Scheme 9*) that were isolated in a total yield of 20–30% from the reaction mixture [2]. The tricycle **35** which is found in the equilibrium mixture in an amount of 6% and whose structure is unequivocally established by $^1$H-NOE measurements (*cf. Exper. Part*) represents the 'missing link' in the evidence of all six possible tricyclic structures that can arise by thermal addition of ADM at the seven-membered ring of guaiazulene followed by rearrangement. Indeed, when the equilibrium mixture of **32**–**35** was heated with an excess of ADM in decalin, the mixture of the already characterized [2] six tetracyclic compounds '*anti*'-**44** to '*anti*'-**48** was isolated in a total yield of 85% (*Scheme 9*). No additional tetracyclic adduct derived from the tricycle **35** could be detected by $^1$H-NMR spectroscopy as well as by HPLC (*cf. Exper. Part*). We suppose that the two sites of the cyclopentadiene substructure in **35** are well shielded by the flanking substituents E–C(10) and Me–C(11) against an approaching ADM molecule which is further hindered by the Me substituent at C(2). A similar flanking is present in the tricycle **32**. However, in this case, the Me substituent is located at

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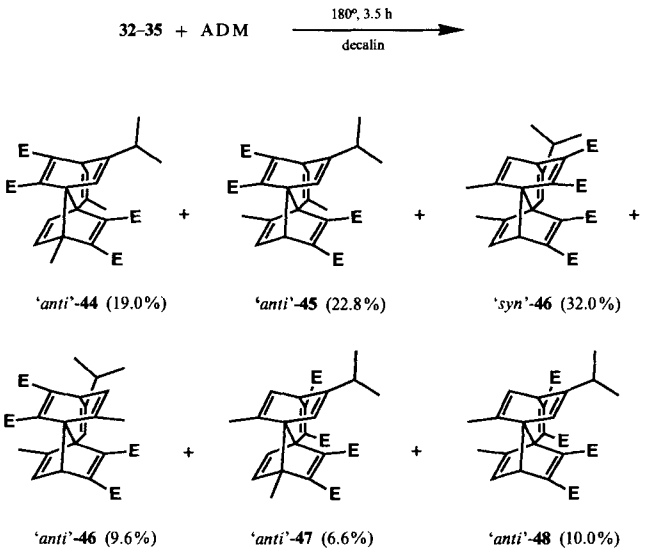
[6]) We will report on the kinetics of [1,5]-C shifts in tricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-dicarboxylates later in this journal.

*Scheme 9*[a])




[a]) The mixture of the tricycles **32–35** was reacted with a 5.7-fold molar excess of ADM. The total yield of the tetracyclic compounds amounted to 85%. The yields in parentheses are relative yields.

C(4), and '*syn*'- as well as '*anti*'-addition of ADM is observed (*cf.* '*syn*'- and '*anti*'-**46** in (*Scheme 9*). All the other tricycles **33**, **34**, **36**, and **37** show sterically well differentiated sites (H–C(10/11) *vs.* Me–C(11) or E–C(10)), and only '*anti*'-products are formed (*Scheme 9*).

We thank Prof. *M. Hesse* and his coworkers for mass spectra, Prof. *W. von Philipsborn* and his coworkers for NMR support and numerous $^1$H-NOE measurements, and *H. Frohofer* for elemental analyses. The financial support of this work by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* as well as *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged.

## Experimental Part

*General.* See [1–3] [12a].

**1. Synthesis of Azulene-1-carbaldehydes.** – 1.1. *5-Isopropyl-3,8-dimethylazulene-1-carbaldehyde* (**5**). See [2] [4].

1.2. *3,5,8-Trimethylazulene-1-carbaldehyde* (**6**). 1.2.1. *4,7-Dimethylazulene* (**49**; *cf.* [4a] [17]). It was synthetized in the usual way in 10% yield (*cf.* [3] [8]) by refluxing 1-butyl-2,5-dimethylpyridinium bromide (13 g, 0.053 mol; prepared in 50% yield by heating 2,5-lutidine in the presence of BuBr in toluene) with cyclopentadiene (*ca.* 6 g) in the presence of NaH (0.06 mol, dispersed in mineral oil) in DMF during 5 h. Two CC (1. *Alox B*, act. IV/hexane; 2. silica gel/hexane) yielded **49** as a blue oil. UV (hexane): $\lambda_{max}$ 357 (3.20), 345 (sh, 3.52), 341 (3.55), 333 (3.45), 327 (sh, 3.40), 320 (sh, 3.30), 303 (3.82), 285 (4.51), 281 (4.52), 278 (sh, 4.49), 243 (4.26); $\lambda_{min}$ 354 (3.01), 337 (3.41), 314 (3.25), 300 (3.76), 284 (4.51), 256 (3.93), 222 (3.96). $^1$H-NMR: 8.293 (*d*, $^4J(6,8) \approx 1.4$, H–C(8)); 7.812 (*t*-like, $^3J(1,2) \approx {}^3J(3,2) \approx 3.8$, H–C(2)); 7.456 (*dd*, $^3J(5,6) = 10.6$, $^4J(8,6) = 1.6$, H–C(6)); 7.319 (br. *d*, $^3J(2,1) = 3.7$, H–C(1)); 7.256 (*dd*, $^3J(3,2) = 3.8$, $^4J(1,3) \approx 1.2$, H–C(3)); 7.071 (*d*, $^3J(6,5) = 10.5$, H–C(5)); 2.888 (*s*, Me–C(4)); 2.633 (*s*, Me–C(7)).

1.2.2. *4,7- and 5,8-Dimethylazulene-1-carbaldehyde* (**12** and **7**, resp.; *cf.* [4a]). Azulene **49** (0.82 g, 5.25 mmol) was formylated with DMF/$POCl_3$ in the usual manner (*cf.* [1–4]). HPLC (*Spherisorb CN*, hexane +5% i-PrOH; *cf.* [1]) of the isolated mixture indicated the formation of **12** and **7** in a ratio of 85:15. CC (silica gel; $Et_2O$ + 0.1% of

*Hünig*'s base) yielded pure **12** (0.441 g; 45.6%), then a mixture **12**/**7** (0.088 g; 9.1%), and, at last, nearly pure (83%) **7** (0.025 g; 2.6%). The fraction of pure **12** was crystallized from $Et_2O$ at −20° to yield violet needles, m.p. 45.6–46.8° (47–48° [4a]). The middle fraction was separated by prep. HPLC (*cf.* [1]) to yield pure **7** (0.030 g) which crystallized from $Et_2O$ at −20° also in violet needles, m.p. 90.8–91.8°.

*Data of* **12**: $R_f$ (hexane/AcOEt 3:2) 0.29. UV (hexane): $\lambda_{max}$ 390 (3.98), 375 (3.97), 314 (sh, 4.35), 308 (4.54), 302 (sh, 4.50), 297 (sh, 4.47), 241 (4.37), 225 (4.35), 208 (sh, 4.34); $\lambda_{min}$ 381 (3.92), 338 (3.57), 264 (3.76), 233 (4.31), 218 (4.26). IR ($CHCl_3$; only bands with > 50% absorbance): 3006, 1641, 1501, 1442, 1408, 1355, 1048. $^1$H-NMR: 10.285 (*s*, CHO); 9.629 (*d*, $^4J(6,8) = 1.3$, H–C(8)); 8.157 (*d*, $^3J(3,2) = 4.3$, H–C(2)); 7.677 (*dd*, $^3J(5,6) = 10.6$, $^4J(8,6) = 1.5$, H–C(6)); 7.410 (*d*, $^3J(6,5) = 10.6$, H–C(5)); 7.241 (*d*, $^3J(2,3) = 4.3$, H–C(3)); 2.914 (*s*, Me–C(4)); 2.748 (*s*, Me–C(7)).

*Data of* **7**: $R_f$ (hexane/AcOEt 3:2) 0.21. UV (hexane): $\lambda_{max}$ 383 (4.08), 370 (sh, 3.99), 355 (sh, 3.83), 309 (4.53), 306 (sh, 4.52), 271 (sh, 3.96), 247 (4.25), 227 (4.27); $\lambda_{min}$ 336 (3.67), 275 (3.95), 237 (4.20), 212 (4.22). IR ($CHCl_3$; only bands with > 50% absorbance): 3006, 1623, 1501, 1441, 1372, 1320. $^1$H-NMR: 10.663 (*s*, CHO); 8.395 (*d*, $^3J(3,2) = 4.4$, H–C(2)); 8.360 (*d*, $^4J(6,4) = 2.0$, H–C(4)); 7.592 (*dd*, $^3J(7,6) = 10.8$, $^4J(4,6) = 1,8$, H–C(6)); 7.418 (*d*, $^3J(6,7) = 10.8$, H–C(7)); 7.174 (*d*, $^3J(2,3) = 4.4$, H–C(3)); 3.175 (*s*, Me–C(8)); 2.673 (*s*, Me–C(5)).

1.2.3. *Reduction and Consecutive Formylation of* **12**. Aldehyde **12** (0.44 g, 2.39 mmol) was reduced in the usual manner with $NaBH_4/BF_3 \cdot OEt_2$ (0.29 g/0.42 ml, 7.6/3.3 mmol) in diglyme (*cf.* [1–3] [19]) to yield 1,3,7-trimethylazulene [4a] [20]. This azulene was formylated without further purification in the usual way with DMF/$POCl_3$ (*cf.* [1–4]) to yield the expected carbaldehyde **6** (*cf.* [4a]) in a total amount of 0.21 g (45%, with respect to aldehyde **12**) after chromatography (*Alox B*, act. III; $Et_2O$) and recrystallization from acetone/hexane. M.p. 144.2–146.1° ([4a]: 148–149°). $R_f$ ($Et_2O$) 0.36. UV (hexane): $\lambda_{max}$ 399 (4.04), 383 (3.98), 315 (4.50), 310 (sh, 4.47), 304 (sh, 4.45), 278 (4.05), 247 (4.27), 240 (sh, 4.24), 219 (sh, 4.19); $\lambda_{min}$ 388 (3.97), 341 (3.48), 280 (4.04), 269 (3.99), 226 (4.17). IR ($CHCl_3$; only bands with ⩾ 50% absorbance): 3006, 1619, 1546, 1435, 1393, 1366, 1093, 1024. $^1$H-NMR: 10.659 (*s*, CHO); 8.269 (*d*, $^4J(6,4) = 1.9$, H–C(4)); 8.245 (*s*, H–C(2)); 7.581 (*dd*, $^3J(7,6) = 10.8$, $^4J(4,6) \approx 1.8$, H–C(6)); 7.370 (*d*, $^3J(6,7) = 10.7$, H–C(7)); 3.165 (*s*, Me–C(8)); 2.712 (*s*, Me–C(5)); 2.581 (*s*, Me–C(3)).

1.3. *2,5,7- and 3,5,7-Trimethylazulene-1-carbaldehyde* (**9** and **8**, resp.). 1.3.1. *Mixture of 1,5,7- and 2,5,7-Trimethylazulene* (**50** and **51**, resp.). The reaction of 1-butyl-3,5-dimethylpyridinium bromide (30 g, 0.123 mol) [3] with an excess of methylcyclopentadiene in the presence of NaH (0.134 mol, dispersed in mineral oil) in boiling DMF (*cf.* [3] [18]) yielded a mixture of 76% of **50** [3] and 24% of **51**. The mixture was purified by CC (*Alox B*, act III; hexane) to yield 15.3 g (73%) of **50** and **51** as a blue oil.

*Data of* **50**: see [3].

*Data of* **51**: $^1$H-NMR (taken from the 76:24 mixture **50**/**51**): 7.997 (br. *s*, H–C(4,8)); 7.358 (br. *s*., H–C(6)); 6.933 (*s*, H–C(1,3)); 2.625 (*s*, Me–C(5,7)); 2.599 (*s*, Me–C(2)).

1.3.2. *Formylation of* **50**/**51**. The afore-mentioned mixture (15.3 g, 0.09 mol) was reacted with $POCl_3$ (0.135 mol)/DMF (80 ml). Several CC (silica gel; $Et_2O$) and recrystallization from $Et_2O$/hexane as well as from AcOEt/hexane yielded 4.5 g (25%) pure **8** [3] and 2.6 g (15%) of a crystalline 1:2 mixture **8**/**9** which could not be further enriched in **9** by crystallization.

*Data of* **8**: identical with those reported in [3].

*Data of* **9**: $R_f$ ($Et_2O$) 0.47. UV (hexane + 3% i-PrOH; qual.): $\lambda_{max}$ 402.5 (0.19), 387 (0.21), 316.7 (1.00), 306 (sh, 0.77), 265 (sh, 0.23), 245 (sh, 0.33); 227.4 (0.46); $\lambda_{min}$ 395 (0.18), 343 (0.09), 277.5 (0.17). $^1$H-NMR (taken from the 1:2 mixture **8**/**9**): 10.374 (*s*, CHO); 9.365 (br. *s*, H–C(8)); 8.090 (br. *s*, H–C(4)); 7.592 (br. *s*, H–C(6)); 6.830 (*s*, H–C(3)); 2.796 (*s*, Me–C(2)); 2.724 (*s*, Me–C(7)); 2.657 (*s*, Me–C(5)).

1.4. *2,3,5,7-Tetramethylazulene-1-carbaldehyde* (**10**). 1.4.1. *Mixture of 1,2,5,7- and 1,3,5,7-tetramethylazulene* (**52** and **53**, resp.). The 1:2 mixture **8**/**9** (1.74 g, 8.78 mmol) was reduced in the usual manner with $NaBH_4$ (1.07 g, 28 mmol)/$BF_3 \cdot OEt_2$ (1.54 ml, 12 mmol) in diglyme (*cf.* [1–3] [19]). Workup of the mixture and filtration through a short column (silica gel; hexane/$Et_2O$ 4:1) yielded 1 g (62%) of the mixture **52**/**53** [3] as a blue oil.

1.4.2. *Formylation of* **52**/**53**. It was performed in the usual manner (*cf.* [1–4]) with $POCl_3$ (8.25 mmol)/DMF (5 ml). CC (*Alox B*, act. III; $Et_2O/CH_2Cl_2$ 2:1) yielded pure **10** which was recrystallized from toluene (0.55 g, 44% with respect to **9**). M.p. 166.1–167.2°. $R_f$ ($Et_2O$/hexane 4:1) 0.29. UV (hexane): $\lambda_{max}$ 415 (3.86), 397 (3.91), 381 (sh, 3.75), 361 (sh, 3.52), 319 (4.66), 307 (4.53), 301 (sh, 4.47), 274 (4.06), 249 (4.20), 220 (4.31); $\lambda_{min}$ 407 (3.82), 346 (3.43), 310 (4.51), 282 (4.01), 264 (4.04), 236 (4.16), 209 (4.25). IR ($CHCl_3$; 4 most intensive bands). 3006, 1624 (CHO), 1441, 1371. $^1$H-NMR: 10.406 (*s*, CHO); 9.302 (br. *s*, H–C(8)); 8.052 (br. *s*, H–C(4)); 7.555 (*s*, H–C(6)); 2.733 (*s*, Me–C(2)); 2.703, 2.684 (2*s*, Me–C(5,7)); 2.410 (*s*, Me–C(3)). EI-MS: 212.2 (100, $M^+$), 211.2 (92.5), 197.2 (18), 183.2 (19), 165.1 (12), 153.1 (15), 149.1 (27). Anal. calc. for $C_{15}H_{16}O$ (212.29): C 84.87, H 7.60; found: C 84.94, H 7.82.

1.5. *7-Isopropyl-4-methylazulene-1-carbaldehyde* (**11**; dihydrolactaroviolin, *cf.* [6]). Lactaroviolin[2]) (0.50 g, 2.38 mmol) was dissolved in dioxan (25 ml) and hydrogenated at 20° in the presence of Pd/C (0.060 g; 10% Pd) under slight excess pressure of $H_2$. CC (*Alox B*, act. IV; hexane/$Et_2O$ 3:2) yielded pure **11** (0.426 g, 84%) as a violet oil. $R_f$ ($Et_2O$/hexane 3:2) 0.38. UV (hexane): $\lambda_{max}$ 390 (3.60), 375 (3.58), 308 (4.13), 301 (sh, 4.09), 296 (sh, 4.06), 241 (3.99), 226 (3.97); $\lambda_{min}$ 381 (3.53), 343 (3.18), 264 (3.43), 232 (3.95), 217 (3.90). VIS (hexane): $\lambda_{max}$ 570 (2.44), 531 (2.50), *ca.* 495 (sh, 2.30); $\lambda_{min}$ 560 (2.50). IR ($CHCl_3$; only bands with > 50% absorbance): 3006, 2965, 1641 (CHO), 1501, 1446, 1406, 1358. $^1$H-NMR: 10.320 (*s*, CHO), 9.728 (*d*, $^4J(6,8) = 1.8$, H–C(8)); 8.174 (*d*, $^3J(3,2) = 4.3$, H–C(2)); 7.724 (*dd*, $^3J(5,6) = 10.6$, $^4J(8,6) = 2.0$, H–C(6)); 7.505 (*d*, $^3J(6,5) = 10.6$, H–C(5)); 7.266 (*d*, $^3J(2,3) \approx 4$, H–C(3)); 3.239 (*sept.*, $Me_2CH$–C(7)); 2.937 (*s*, Me–C(4)); 1.412 (*d*, $J = 6.8$, $Me_2$CH–C(7)). EI-MS: 212.3 (100, $M^{+\cdot}$), 197.2 (77), 169.2 (33.5), 165.1 (31), 154.1 (43), 153.2 (56), 152.1 (47).

1.6. *4,6,8-Trimethylazulene-1-carbaldehyde* (**13**). See [4] [12a].

1.7. *6-(*tert*-Butyl)-3,4,8-trimethylazulene-1-carbaldehyde* (**14**). See [1].

**2. Methyl 5-Isopropyl-3,8-dimethylazulene-1-carboxylate** (**15**). – The corresponding azulene-1-carbaldehyde **5** (0.71 g, 3.14 mmol) [2] [4] was dissolved in MeOH, and KCN (1.22 g, 18.8 mmol), AcOH (0.3 ml), and $MnO_2$ (16 g) were added (*cf.* [21]). The mixture was stirred during 24 h and then worked up. CC (silica gel; $Et_2O$/hexane 3:2) yielded **15** (0.174 g, 76% with respect to reacted **5**) as a blue oil and the starting aldehyde **5** (0.51 g, 72%). $R_f$ ($Et_2O$/hexane 3:2) 0.49. UV (hexane): $\lambda_{max}$ 380 (3.88), 372 (sh, 3.86), 354 (sh, 3.72), 312 (sh, 4.35), 299 (4.53), 247 (4.40), 220 (sh, 4.17); $\lambda_{min}$ 332 (3.55), 268 (3.99), 206 (410). IR ($CHCl_3$; bands with > 50% absorbance): 3006, 2964, 2870, 1695, 1524, 1440, 1408, 1375, 1176, 1134, 1034, 864. $^1$H-NMR: 8.246 (*d*, $^4J(6,4) = 2.1$, H–C(4)); 7.945 (br. *s*, H–C(2)); 7.529 (*dd*, $^3J(7,6) = 10.9$, $^4J(4,6) = 2.1$, H–C(6)); 7.273 (*d*, $^3J(6,7) = 10.8$, H–C(7)); 3.914 (*s*, MeOCO–C(1)); 3.118 (*sept.*, $Me_2CH$–C(5)); 2.968 (*s*, Me–C(8)); 2.591 (*s*, Me–C(3)); 1.370 (*d*, $J = 6.9$, $Me_2$CH–C(5)).

**3. Thermal Reactions of the Azulene-1-carbaldehydes with Dimethyl Acetylenedicarboxylate (ADM).** – 3.1. *Carbaldehyde* **5** *with ADM*. The aldehyde (1.012 g, 4.47 mmol) and ADM (2.24 ml, 18 mmol) were dissolved in decalin (20 ml) and heated at 200° during 2 h under $N_2$. Decalin and ADM were removed at 50°/high vacuum. The residue was dissolved in acetone (5 ml) and kept over weekend at ambient temp. The supernatant soln. was decanted from the yellow-brown crystals which were washed with $Et_2O$ and pentane and recrystallized from AcOEt/hexane to yield a first crop of pure dimethyl *2-formyl-7-isopropyl-4,11-dimethyltricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**16**; 0.236 g). CC (silica gel; $Et_2O$/hexane 19:1) of the decanted soln. gave a fraction which mainly contained **16** and traces of **5** as well as trimethyl 5-methoxyfuran-2,3,4-tricarboxylate (*cf.* [1] [8]). Crystallization from $Et_2O$ and recrystallization from AcOEt/hexane yielded a second crop of pure **16** (0.419 g). A further CC of all combined mother liquors, followed by the crystallization, yielded a third amount (0.108 g) of pure **16**, *i.e.* the total yield of pure, recrystallized **16** amounted to 0.763 g (46%).

In later runs, we reacted **5** (0.452 g, 2.0 mmol) with ADM (0.852 g, 6.0 mol) in decalin (10 ml) in a *Schlenk* reaction vessel under Ar at 180° during 2 h. Under these conditions, we avoided the formation of the thermal ADM condensation product, and a single CC (silica gel; $Et_2O$/hexane 9:1) was sufficient to obtain pure **16** (0.378 g, 51%) as a light brown crystal powder.

*Data of* **16**: Amber-colored leaflets. M.p. 158.0–160.3° (AcOEt/hexane). $R_f$ ($Et_2O$/hexane 9:1) 0.32. UV (hexane): $\lambda_{max}$ 383 (4.01), 314 (sh, 3.46), 224 (sh, 4.27); $\lambda_{min}$ 268 (3.30). IR ($CHCl_3$; bands with > 50% absorbance): 3030, 2964, 1718, 1651, 1508, 1436, 1357, 1159, 1106, 1075, 1047. $^1$H-NMR: 9.722 (*s*, CHO); 7.501 (*s*, H–C(3)); 6.114 (*dq*, $^3J(8,12) = 6.71$, $^4J(Me$–C(11),12) = 1.59, H–C(12)); 5.878 (*t*-like, $^4J(8,6) \approx {}^4J(Me_2CH$–C(7),6), H–C(6)); 4.316 (*dd*, $^3J(12,8) = 6.69$, $^4J(6,8) = 1.44$, H–C(8)); 3.716, 3.615 (2*s*, MeOCO–C(9,10)); 2.503 (br. *sept.*, $Me_2CH$–C(7)); 2.058 (*s*, Me–C(4)); 1.531 (*d*, $^4J(12$, Me–C(11)) = 1.53, Me–C(11)); 1.100, 1.085 (2*s*, $J = 6.73$, 6.82, $Me_2$CH–C(7)). $^1$H-NOE (400 MHz, $CDCl_3$): 2.058 (Me–C(4))→7.503 (*s*), 5.878 (*s*); 7.503 (H–C(3))→9.722 (*s*), 2.058 (*m*); 1.531 (Me–C(11))→9.722 (*s*), 6.114 (*s*); 4.316 (H–C(8))→6.114 (*s*), 2.503 (*s*). EI-MS: 368.2 (48, $M^{+\cdot}$), 336.1 (29), 321.1 (71), 293.0 (100), 65 (78). Anal. calc. for $C_{22}H_{24}O_5$ (368.43): C 71.72, H 6.57; found: C 71.88, H 6.48.

3.2. *Carbaldehyde* **6** *with ADM*. The aldehyde (0.132 g, 0.663 mmol) and ADM (0.424 g, 2.98 mmol) were heated in decalin (3 ml) at 200° during 2 h under $N_2$. The workup was the same as described under *3.1* to yield in total 0.089 g (39.4%) of crystallized, pure *dimethyl 2-formyl-4,7,11-trimethyltricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**17**).

*Data of* **17**: Amber-colored platelets. M.p. 150.0–152.5° ($Et_2O$/hexane). $R_f$ ($Et_2O$) 0.25. UV (hexane): $\lambda_{max}$ 381 (3.97), 305 (3.54), 224 (4.25), 207 (sh, 4.27); $\lambda_{min}$ 319 (3.53), 271 (3.46), 218 (4.25). IR ($CHCl_3$; bands with > 50% absorbance): 3011, 2953, 1718, 1653, 1507, 1436, 1380, 1355, 1164, 1107, 1077. $^1$H-NMR: 9.739 (*s*, CHO); 7.497 (*s*, H–C(3)); 6.172 (*dq*, $^3J(8,12) = 6.73$, $^4J(Me$–C(11),12) = 1.61, H–C(12)); 5.905 (*quint.*-like,

$^4J(8,6) \approx {}^4J(Me\text{–}C(7),6)$, H–C(6)); 4.235 (*dd*, $^3J(12,8) = 6.68$, $^4J(6,8) = 1.40$, H–C(8)); 3.729, 3.623 (2*s*, MeOCO–C(9,10)); 2.080 (br. *s*, Me–C(7)); 2.037 (*s*, Me–C(4)); 1.541 (*d*, $^4J(12, Me\text{–}C(11)) = 1.57$, Me–C(11)). EI-MS: 340.1 (64, $M^+$), 308.1 (25), 293.0 (100), 281.0 (39), 280.0 (36), 279.0 (31), 265.1 (48). Anal. calc. for $C_{20}H_{20}O_5$ (340.38): C 70.57, H 5.92; found: C 70.39, H 6.11.

3.3. *Mixture* **8**/**9** *with ADM*. The 1:2 mixture **8**/**9** (*cf. 1.3*; 0.213 g, 1.07 mmol) and ADM (0.694 g, 4.88 mmol) were heated in decalin (5 ml) during 15 h at 200°. CC (siliga gel; $Et_2O$/hexane 9:1) yielded in a first fraction starting material (0.091 g, 43%) which mainly consisted of **8** (see later). A second fraction (0.145 g) contained mainly *tetramethyl (1*RS,*2*RS,*5*RS,*8*RS*)-13-formyl-7,12,14-trimethyltetracyclo[6.2.2.2$^{2,5}$0$^{1,5}$]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate* (*'anti'*-**28**) which was crystallized from acetone/hexane to yield pure *'anti'*-**28** (0.085 g, 25% with respect to **9**).

*Data of* 'anti'-**28**: brownish crystals. M.p. 150–155°. $R_f$ ($EtO_2$) 0.35. UV (EtOH): $\lambda_{max}$ 289 (sh, 3.25), 237 (4.14); $\lambda_{min}$ 224 (4.10). IR ($CHCl_3$; bands with absorbance > 40%): 3028, 2954, 1717, 1670, 1633, 1436, 1112, 1084. $^1$H-NMR: 9.820 (*s*, CHO); 5.816 (*sext.*-like, $^4J(8,6) \approx {}^4J(Me\text{–}C(7),6) \approx {}^5J(2,6)$, H–C(6)); 5.772 (*quint.*-like, $^4J(8,11) \approx {}^4J(Me\text{–}C(12),11)$, H–C(11)); 4.230 (*d*, $^5J(6,2) \approx 0.6$, H–C(2)); 3.788, 3.786, 3.737 (3*s*, 1:1:2, MeOCO–C(3,4,9,10)); 3.329 (*t*-like, $^4J(6,8) \approx {}^4J(11,8)$, H–C(8)); 2.218 (*s*, Me–C(14)); 1.989 (*d*, $^4J(6, Me\text{–}C(7)) = 1.52$, Me–C(7)); 1.855 (*d*, $^4J(11, Me\text{–}C(12)) = 1.60$, Me–C(12)). $^1$H-NOE (400 MHz, $CDCl_3$): 2.218 (Me–C(14))→9.820 (*s*), 4.230 (*s*), 3.737 (*m*, MeOCO–C(10)); 1.989 (Me–C(7))→5.816 (*s*), 3.329 (*s*); 1.855 (Me–C(12))→5.772 (*s*), 3.329 (*s*). EI-MS: 482.3 (1.7, $M^+$), 450.2 (6), 435.2 (5), 423.2 (100), 391.1 (18), 363.1 (33), 331.1 (29), 303.1 (20). Anal. calc. for $C_{26}H_{26}O_9$ (482.49): C 64.72, H 5.43; found: C 64.45, H 5.72.

In a control experiment, pure **8** (0.215 g, 1.08 mmol) and ADM (0.55 ml, 4.48 mmol) were heated in decalin (5 ml) at 200° during 3.5 h. No product, except the thermal condensation product of ADM (*cf.* [1] [8]), could be isolated from this run. The starting aldehyde **8** was mainly recovered.

3.4. *Carbaldehyde* **10** *with ADM*. The aldehyde (0.172 g, 0.808 mmol) and ADM (0.50 ml, 4.07 mmol) were heated in decalin (5 ml) at 200° during 3.5 h. Decalin and excess ADM were removed at 50°/high vacuum. The residue was crystallized from acetone to yield a first crop (0.102 g) of *tetramethyl (1*RS,*2*RS,*5*RS,*8*RS*)-2-formyl-7,12,13,14-tetramethyltetracyclo[6.2.2.2$^{2,5}$0$^{1,5}$]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate* (*'anti'*-**29**). CC (silica gel; AcOEt/hexane 3:2) of the mother liquor yielded further amounts of *'anti'*-**22** as well as some thermal condensation product of ADM. In total, 0.178 g (44.3%) of crystallized *'anti'*-**29** were obtained.

*Data of* 'anti'-**29**: pale-yellow crystals. M.p. 202–205° (with some melting already at 192°). $R_f$ ($Et_2O$) 0.33. UV (EtOH): $\lambda_{max}$ 242 (sh, 3.73), 201 (4.22). IR ($CHCl_3$; bands with absorbance > 40%): 3028, 2953, 1715, 1625, 1436, 1127, 1097, 1065. $^1$H-NMR ($CDCl_3/C_6D_6$): 10.231/10.616 (*s*, CHO); 6.195/6.155 (*quint.*-like, $^4J(8,11) \approx {}^4J(Me\text{–}C(12),11)$, H–C(11)); 5.353/5.731 (*quint.*-like, $^4J(8,6) \approx {}^4J(Me\text{–}C(7),6)$, H–C(6)); 3.754, 3.727, and 3.674/3.372, 3.325, 3.274, and 3.231 (3*s*, (2:1:1)/4*s*, MeOCO–C(3,4,9,10)); 3.294/3.264 (*t*-like, $^4J(6,8) \approx {}^4J(11,8)$, H–C(8)); 2.013/1.945 (*d*, $^4J(6, Me\text{–}C(7)) = 1.55/1.54$, Me–C(7)); 1.870/1.812 (*q*-like, $^5J(Me\text{–}C(13), Me\text{–}C(14)) = 1.34/1.40$, Me–C(14)); 1.855/1.429 (*d*, $^4J(11, Me\text{–}C(12)) = 1.66/1.57$, *Me*–C(12)); 1.632/1.557 (*q*-like, $^4J(Me\text{–}C(14), Me\text{–}C(13)) = 1.27/1.29$, Me–C(13)). $^1$H-NOE (400 MHz, $C_6D_6$): 1.945 (Me–C(7))→5.731 (*s*), 3.264 (*s*), 1.429 (*w*); 1.812 (Me–C(14))→10.616 (*s*), 3.325 (*m*, MeOCO–C(10)), 1.557 (*m*, Me–C(13)); 1.557 (Me–C(14))→5.731 (*s*), 1.812 (*m*, Me–C(13)); 1.429 (Me–C(12))→6.155 (*s*), 3.264 (*s*), 1.945 (*w*, Me–C(6)). EI-MS: 496.3 (8, $M^+$), 465.3 (5), 464.3 (4), 437.2 (100), 405.2 (13), 377.2 (40), 345.1 (29), 317.2 (24). Anal. calc. for $C_{27}H_{28}O_9$ (496.52): C 65.31, H 5.68; found: C 65.42, H 5.81.

3.5. *Carbaldehyde* **7** *with ADM*. The aldehyde (0.0336 g, 0.182 mmol) and ADM (0.065 g, 0.457 mmol) were heated in decalin (1 ml) at 190° during 2 h. Since *ca.* 70% of **7** was still present after this time (TLC control) heating was continued for 1.5 h at 200° (TLC indicated *ca.* 50% **7**). Additional ADM (0.065 g, 0.457 mmol) was added and heating prolonged at 200° for a further h. Filtration over silica gel ($Et_2O$ + 1% MeOH) and separation on a *Lobar* column (*Si 60*) with hexane/AcOEt 1:1 yielded starting **7** (0.006 g, 17%), *dimethyl 5,8-dimethylazulene-1,2-dicarboxylate* (**24**; 0.005 g, 12%), and a mixture (0.0132 g) of tri- and tetracyclic compounds. According to the $^1$H-NMR signals ($CDCl_3$) of the CHO groups, it consisted of 12% of *'anti'*-**25** (CHO at 10.25), 18% of *'anti'*-**26** (CHO at 10.15), 11% of an unknown aldehyde (CHO at 9.93), 15% of the tricycle **27** (CHO at 9.775), 37% of the tricycle **23** (CHO at 9.770), and 7% of a second unknown aldehyde (CHO at 9.65). HPLC yielded two fractions which mainly contained the tetracyclic compound *'anti'*-**25** (enrichment 60%) and the tricycle **23** (enrichment 55%), accompanied by *'anti'*-**26** (15%), and the second unknown aldehyde (22%).

*Data of* **24**: M.p. 145.9–146.9° ($Et_2O$/hexane). $R_f$ (hexane/AcOEt 3:2) 0.29. UV (hexane): $\lambda_{max}$ 360 (3.55), 349 (3.87), 334 (3.79), 306 (sh, 4.45), 294 (4.63), 265 (4.22), 247 (4.44), 218 (4.18); $\lambda_{min}$ 357 (3.53), 340 (3.75), 322 (3.67), 269 (4.21), 260 (4.21), 225 (4.13). IR ($CHCl_3$; absorbance > 40%): 3022, 2953, 1718, 1476, 1438, 1401, 1334, 1148, 1105, 1058, 1016. $^1$H-NMR (300 MHz, $CDCl_3$; $CHCl_3$ at 7.262); 8.342 (*d*, $^4J(6,4) = 1.97$, H–C(4)); 7.577 (*s*,

H–C(3)); 7.543 (*dd*, $^3J$(7,6) = 10.80, $^4J$(4,6) = 1.74, H–C(6)); 7.138 (*d*, $^3J$(6,7) = 10.71, H–C(7)); 4.009, 3.936 (2*s*, MeOCO–C(1,2)); 2.862 (*s*, Me–C(8)); 2.609 (*s*, Me–C(5)).

*Dimethyl 2-Formyl-7,11-dimethyltricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**23**): $R_f$ ($Et_2O$) 0.29. $^1$H-NMR (300 MHz, $CDCl_3$; $CHCl_3$ at 7.260): 9.770 (*s*, CHO); 7.626 (*d*, $^3J$(4,3) = 2.62, H–C(3)); 6.272 (*dquint.*-like, $^3J$(3,4) = 2.60, H–C(4)); 6.224 (*dq*, $^3J$(8,12) = 6.68, $^4J$(*Me*–C(11),12) = 1.67, H–C(12)); 5.915 (*quint.*-like, $^4J$(8,6) ≈ $^4J$(*Me*–C(7),6), H–C(6)); 4.287 (*dd*, $^3J$(12,8) = 6.78, $^4J$(6,8) = 1.48, H–C(8))[7]; 3.742, 3.635 (2*s*, MeOCO–C(9,10)); 2.073 (*dd*, $^4J$(6, *Me*–C(7)) = 1.5, $^6J$(4, *Me*–C(7)) = 0.7, Me–C(7)); 1.560 (*d*, $^4J$(12, *Me*–C(11)) = 1.67, Me–C(11)).

*Dimethyl 2-Formyl-6,12-dimethyltricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**27**): $^1$H-NMR (300 MHz, $CDCl_3$; $CHCl_3$ at 7.260): 9.775 (*s*, CHO); 7.518 (*d*, $^3J$(4,3) = 2.76, H–C(3)); *ca.* 6.23 (H–C(4)); *ca.* 6.15 (H–C(7)); 5.710 (*quint.*-like, $^4J$(8,11) ≈ $^4J$(*Me*–C(12),11), H–C(11)); 4.162 (*dd*, $^3J$(7,8) = 8.50, $^4J$(11,8) = 1.85, H–C(8)); 3.737, 3.641[8]) (2*s*, MeOCO–C(9,10)); 1.921 (*d*, $^4J$(11, *Me*–C(12)) = 1.58, Me–C(12)); 1.885 (*d*, $^4J$(7, *Me*–C(6)) = 1.44, Me–C(6)).

*Tetramethyl (1RS,2RS,5RS,8RS)-2-Formyl-9,11-dimethyltetracyclo[6.2.2.2$^{2,5}$0$^{1,5}$]tetradeca-2,4,6,9,11-pentaene-3,4,6,7-tetracarboxylate* (*'anti'*-**25**): $^1$H-NMR (300 MHz, $CDCl_3$; $CHCl_3$ at 7.260): 10.250 (*s*, CHO); 7.263 (*d*, $^3J$(13,14) ≈ 5.3, H–C(14)); 6.779 (*d*, $^3J$(14,13) = 5.47 H–C(13)); 6.198 (*dq*, $^3J$(8,12) = 6.94, $^4J$(*Me*–C(11),12) = 1.62, H–C(12)); 6.126 (*quint.*-like, $^4J$(8,10) ≈ $^4J$(*Me*–C(9),10), H–C(10)); 3.218 (*dd*, $^3J$(12,8) = 6.95, $^4J$(10,8) = 1.67, H–C(8)); 3.863, 3.787, 3.645 (4*s*, MeOCO–C(3,4,6,7)); 1.904 (*d*, $^4J$(10, *Me*–C(9)) = 1.64, Me–C(9)); 1.766 (*d*, $^4J$(12, *Me*–C(11)) = 1.64, Me–C(11)).

*Tetramethyl (1RS,2RS,5RS,8RS)-2-Formyl-6,12-dimethyltetracyclo[6.2.2.2$^{2,5}$0$^{1,5}$]tetradeca-2,4,6,9,11-pentaene-3,4,9,10-tetracarboxylate* (*'anti'*-**26**): $^1$H-NMR (300 MHz, $CDCl_3$; $CHCl_3$ at 7.260): 10.154 (*s*, CHO); 7.142 (*d*, $^3J$(13,14) = 5.42, H–C(14)); 6.637 (*d*, $^3J$(14,13) = 5.42, H–C(13)); 6.154 (*dq*, $^3J$(8,7) = 8.5, $^4J$(*Me*–C(6),7) = 1.5, H–C(7)); H–C(11) not discernible, 3.782, 3.713, 3.671 (3*s*; fourth *s* not discernible; MeOCO–C(3,4,9,10)); 3.430 (*dd*, $^3J$(7,8) = 8.6, $^4J$(11,8) = 1.84, H–C(8)); 1.870 (*d*, $^4J$(11, *Me*–C(12)) = 1.70, Me–C(12)); 1.667 (*d*, $^4J$(7, *Me*–C(6) = 1.61, Me–C(6)).

3.6. *Carbaldehyde* **13** *with ADM.* The aldehyde (0.126 g, 0.594 mmol) and ADM (0.384 g, 2.70 mmol) were heated in decalin (3 ml) at 200° during 3.5 h. TLC (silica gel; $Et_2O$/hexane 9:1) indicated the presence of starting **13** and a slightly faster-moving blue spot of *dimethyl 4,6,8-azulene-1,2-dicarboxylate* (**30**) [12b]. Workup by prep. TLC (silica gel; $Et_2O$/hexane 4:1) yielded 0.092 g of a 3:1 mixture ($^1$H-NMR evidence) **30** (49%) and **13** (18%). No additional product could be detected.

3.7. *Carbaldehyde* **14** *with ADM.* The aldehyde (0.159 g, 0.625 mmol) and ADM (0.390 g, 2.74 mmol) were heated in decalin (5 ml) at 200° during 1.5 h. TLC (silica gel; hexane/AcOEt 3:2) revealed the presence of starting **14** as fastest-moving red spot, followed by a yellow spot and a continuous band of colored materials. Prep. TLC (silica gel; hexane/AcOEt 1:1) yielded a fraction which contained mainly yellow material. Crystallization from $Et_2O$/hexane yielded 0.040 g (14%) of orange crystals of *'anti'*-**31**. The mother liquor contained in an amount of 75% an additional compound, accompanied by 14% of *'anti'*-**31** and 11% of aldehyde **14** (in total 0.033 g). This fraction was further purified by prep.TLC (see later). A second fraction (0.054 g) was a mixture of 55% of **14**, 28% of *'anti'*-**31**, and 17% of the additional product. A third fraction contained pure **14** (0.027 g; 17%). The total yields of **14**, *'anti'***31**, and the additional compound were 38%, 29%, and 22%, respectively.

*Tetramethyl (1RS,2RS,5RS,8RS)-13-(*tert*-Butyl)-8-formyl-2,6,11-trimethyltetracyclo[6.2.2.2$^{2,5}$0$^{1,7}$]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate* (*'anti'*-**31**). M.p. 174–184°. $R_f$ (hexane/AcOEt 3:2) 0.30. UV (EtOH); $\lambda_{max}$ 314 (sh, 2.95), 245 (sh, 3.79), 224 (sh, 4.06). IR ($CHCl_3$; bands with ≥ 40% absorbance): 3018, 2955, 1723, 1436. $^1$H-NMR($CDCl_3/C_6D_6$; $CHCl_3$ at 7.260/$C_6D_5H$ at 7.160): 10.072/10.233 (*s*, CHO); 6.779/6.994 (*q*-like, $^4J$(*Me*–C(11),12) = 1.69/1.68, H–C(11)); 5.738/6.048 (*d*, $^4J$(5,14) = 2.00/2.03, H–C(14)); 3.717/3.851 (*d*, $^4J$(14.5) = 2.15/2.08, H–C(5)); 3.888, 3.791, 3.744, and 3.707/3.491, 3.482, 3.208, and 3.076 (4*s*, MeOCO–C(3,4,9,10)); 2.089/2.149 (*d*, $^4J$(11, *Me*–C(12)) = 1.65/1.68, Me–C(12)); 1.716/1.786 (*s*, Me–C(6)); 1.566/1.689 (*s*, Me–C(2)); 1.065/1.007 (*s*, *t*-Bu). EI-MS: 538 (6, $M^{+\cdot}$), 506 (12), 479 (6), 449 (19), 391 (17), 274 (15), 259 (51), 242 (36), 57 (100). Anal. calc. for $C_{30}H_{34}O_9$ (538.60): C 66.90, H 6.36; found: C 67.24, H 6.16.

The content of the mother liquor which readily decomposed in an attempt of purification by CC on silica gel could be enriched to up to 77% in the presence of 23% of *'anti'*-**31** by TLC. Its $^1$H-NMR (see below) was in

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[7]) A weak *dd* (*J* = 7.0 and 1.5) at 4.33 would be compatible with the presence of dimethyl 2-formyl-9,11-dimethyltricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-6,7-dicarboxylate in small amounts.

[8]) Signals of the MeOCO groups are not secured.

agreement with a (1 + 1) adduct whose structure could be dimethyl (1*RS*,8*RS*)-12-(*tert*-butyl)-5-formyl-1,3,7-trimethyltetracyclo[6.2.2.0$^{2,6}$]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate. $^1$H-NMR (300 MHz, $CDCl_3$; $CHCl_3$ at 7.260): 9.546 (*s*, CHO); 6.889 (*s*, H–C(4)); 5.746 (*d*, $^4J$(8,11) = 2.17, H–C(11); 4.497 (*d*, $^4J$(11,8) = 2.16, H–C(8)); 3.826, 3.762 (2*s*, MeOCO–C(9,10)); 2.700 (*s*, Me–C(7)); 2.221 (*s*, Me–C(3)); 1.755 (*s*, Me–C(1)). The observed $^1$H-NMR signals are not in agreement with the two possible (1 + 1) adducts arising from ADM addition at the five-membered ring of azulene **14**. They are also not in agreement with tricycles resulting from addition of ADM across C(3a),C(6) or C(8a),C(6) in **14**.

**4. Thermal Reaction of Azulene-1-carboxylate 15 with ADM.** – The ester (0.163 g, 0.636 mmol) and ADM (0.400 g, 2.81 mmol) were heated in decalin (3 ml) at 200° during 3 h. Two consecutive prep. TLC (silica gel; $Et_2O$/hexane 4:1 and then toluene/$Et_2O$ 4:1) yielded three fractions. The first one consisted of starting material (0.020 g, 12%), the second one mainly of the tricycle **18** which was recrystallized from hexane/AcOEt (0.034 g, 15%), and the third one (0.121 g) of at least two tetracyclic compounds accompanied by the thermal condensation product of ADM (*ca.* 40%). HPLC (*cf.* [2]) of the latter fraction allowed to remove the ADM condensation product and yielded almost pure '*anti*'-**19** as main product and '*anti*'-**20** in a purity of at least 75%.

*Trimethyl 7-Isopropyl-4,11-dimethyltricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-2,9,10-tricarboxylate* (**18**): M.p. 143–144.5°. $R_f$ ($Et_2O$/hexane 4:1) 0.28. UV (hexane): $\lambda_{max}$ 380 (weak sh, 3.93) 367 (3.99), 319 (sh, 3.63), 216 (sh, 4.33); $\lambda_{min}$ 266/3.38). IR ($CHCl_3$; bands with > 40% absorbance): 3026, 2954, 1717, 1631, 1518, 1436, 1357, 1330, 1130, 1090, 1061, 1009. $^1$H-NMR: 7.522 (*s*, H–C(3)); 6.050 (*dd*, $^3J$(8,12) = 6.66, $^4J$(*Me*–C(11),12) = 1.63, H–C(12)); 5.853 (*t*-like, $^4J$(8,6) ≈ $^4J$(Me$_2$C*H*–C(7),6), H–C(6)); 4.233 (*dd*, $^3J$(12,8) = 6.64, $^4J$(6,8) = 1.46, H–C(8)); 3.754, 3.719, 3.607 (3*s*, MeOCO–C(2,9,10)); 2.480 (br. *sept.*, Me$_2$C*H*–C(7)); 2.009 (*s*, Me–C(4)); 1.554 (*d*, $^4J$(12,*Me*–C(11)) = 1.51, Me–C(11)); 1.088, 1.072 (2*d*, *J*(6.73, 6.80, *Me*$_2$CH–C(7)). EI-MS: 398 (28, $M^{+\cdot}$), 366 (48), 351 (71), 323 (100), 307 (61), 279 (38), 265 (53). Anal. calc. for $C_{23}H_{26}O_6$ (398.46): C 69.33, H 6.58; found: C 69.09, H 6.58.

*Pentamethyl (1*RS*,2*RS*,5*RS*,8*RS*)-12-Isopropyl-6,13-dimethyltetracyclo[6.2.2.2$^{2,5}$0$^{1,5}$]tetradeca-3,6,9,11,13-pentaene-2,3,4,9,10-pentacarboxylate* ('*anti*'-**19**). Present in the third fraction in *ca.* 49% (17% yield in total ). $R_f$ ($Et_2O$/hexane 4:1) 0.20. $^1$H-NMR (300 MHz; $CDCl_3/C_6D_6$; $CHCl_3$ at 7.260 and $C_6D_5H$ at 7.160): 6.600/6.844 (*q*-like, $^4J$(*Me*–C(13),14) = 1.81/1.81, H–C(14)); 6.181/6.639 (*t*-like, $^4J$(Me$_2$C*H*–C(12,11) ≈ $^4J$(8,11) = 1.53/1.53, H–C(11)); 6.164/6.138 (*dq*-like, $^3J$(8,7) = 8.85/8.75, $^4J$(*Me*–C(6),7) = 1.46/1.47, H–C(7)); 3.589/3.738 (*dd*, $^3J$(7,8) = 8.70/8.82, $^4J$(11,8) = 1.91/1.82, H–C(8)); 3.845, 3.765, 3.732, 3.703, and 3.675/3.707, 3.465, 3.394, 3.293, and 3.239 (5*s*, MeOCO–C(2,3,4,9,10)); 2.369/2.169 (*sept.d*, Me$_2$C*H*–C(12)); 1.855 (*d*, $^4J$(14, *Me*–C(13)) = 1.77/1.80, Me–C(13)); 1.654/1.589 (*d*, $^4J$(7, *Me*–C(6)) = 1.36/1.41, Me–C(6)); 1.030 and 1.008/0.970 and 0.929 (2*d*, *J*(6.61 and 6.69/6.75 and 6.77, *Me*$_2$CH–C(12)). $^1$H-NOE (400 MHz, $C_6D_6$): 6.844→3.707 (*w*, MeOCO–C(2)), 3.465 (*m*, MeOCO–C(10)), 1.697 (*m*, Me–C(13)); 6.639→3.707 (*w*, MeOCO–C(2)), 2.169 (*s*, Me$_2$C*H*–C(12)), 0.970/0.929 (*m*/*w*, *Me*$_2$CH–C(12)).

*Pentamethyl (1*RS*,2*RS*,5*RS*,8*RS*)-9-Isopropyl-11,13-dimethyltetracyclo[6.2.2.2$^{2,5}$0$^{1,5}$]tetradeca-3,6,9,11,13-pentaene-2,3,4,6,7-pentacarboxylate* ('*anti*'-**20**). Present in the third fraction in *ca.* 8%. (2.8% yield in total). $^1$H-NMR (300 MHz; $CDCl_3/C_6D_6$; $CHCl_3$ at 7.260 and $C_6D_5H$ at 7.160): 6.803/6.881 (*q*-like, $^4J$(*Me*–C(13),14) = 1.84/1.84, H–C(14)); 6.246/6.173 (*dq*-like, $^3J$(8,12) = 7.05/7.02, $^4J$(*Me*–C(11),12) = 1.59/1.63, H–C(12)); 6.210/6.684 (*t*-like, $^4J$(8,10) ≈ $^4J$(*Me*$_2$CH–C(9),10), H–C(10)); 3.373/3.526 (*dd*, $^3J$(12,8) = 7.00/7.0, $^4J$(10.8) = 1.84/1.8, H–C(8)); 3.816/3.812, 3.767, 3.696, and 3.617/3.511, 3.484, 3.446, 3.454, and 3.202 (5*s*, MeOCO–C(2,3,4,6,7)); 2.37/2.35 (*sept.d*, Me$_2$C*H*–C(9)); 1.755/1.827 (*d*, $^4J$(12, *Me*–C(11)) = 1.60/1.63, Me–C(11)); 1.642/1.493 (*d*, $^4J$(14, *Me*–C(13)) = 1.82/1.81, Me–C(13)); 1.001 and 1.000/1.083 and 1.072 (2*d*, *J* = 6.65/6.80 and 6.81, *Me*$_2$CH–C(9)). $^1$H-NOE (400 MHz, $C_6D_6$): 1.827→6.881 (*s*, H–C(14)), 6.173 (*s*, H–C(12)), 1.493 (*w*, Me–C(13)).

The solution of '*anti*'-**20** (*ca.* 75%) showed in the $^1$H-NMR signals of two further tetracyclic compounds which – so far as their structure could be deduced – are in agreement with the presence of '*anti*'-**21** (*ca.* 18% with respect to '*anti*'-**20**) and '*anti*'-**22** (only traces).

$^1$H-NMR signals (300 MHz, $C_6D_6$) of '*anti*'-**21**: 7.566 (*s*, H–C(14)); 6.128 (*dq*, $^3J$(8,7) = 8.79, $^4J$(*Me*–C(6),7) = 1.43, H–C(7)); 5.884 (*t*-like, $^4J$(8,11) ≈ $^4J$(Me$_2$C*H*–C(12),11), H–C(11)); 3.907 (*dd*, $^3J$(7,8) = 8.72, $^4J$(11,8) = 1.83, H–C(8)); 2.027 (*d*, $^4J$(7, *Me*–C(6)) = 1.38, Me–C(6)); 2.035 (*s*, Me–C(2). Signals for MeOCO and for *Me*$_2$C*H*–C(12) were not discernible.

$^1$H-NMR signals (300 MHz, $C_6D_6$) of '*anti*'-**22**: 7.435 (*s*, H–C(14)); 6.511 (*t*-like, $^4J$(8,10) ≈ $^4J$(Me$_2$C*H*–C(9),10), H–C(10)); 6.062 (*dq*-like, $^3J$(8,12) = 7.0, $^4J$(*Me*–C(11),12) = 1.6, H–C(12)); 2.088 (*d*, $^4J$(12, *Me*–C(11)) = 1.6, Me–C(11)); 2.015 (*s*, Me–C(2)). Signals for MeOCO, *Me*$_2$C*H*–C(9) as well as for H–C(8) were not discernible.

**5. Decarbonylation of the Tricyclic Carbaldehydes** (*cf.* [15] [16]). – 5.1. *Carbaldehyde* **16** *with* $[RhCl(PPh_3)_3]$. The aldehyde (0.440 g, 1.19 mmol) and the Rh catalyst (1.20 g, 1.30 mmol) were dissolved in dry toluene (10 ml) and heated under a slight excess of pressure in a *Schlenk* reaction vessel at 140° during 10 h. Upon cooling, most of the formed $[RhCl(CO)(PPh_3)_2]$ crystallized and was filtered off. The toluene was distilled off in high vacuum and the residue dissolved in EtOH. The residual Rh complex was removed, and the reaction products were subjected to CC (silica gel; $Et_2O$/hexane 9:1) to yield a yellow-brownish oil (0.349 g, 86%) with $R_f$ ($Et_2O$/hexane 9:1) 0.63 which consisted according to HPLC and $^1$H-NMR of the 4 tetracycles **32**–**35** in a ratio of *ca.* 7 (**32**): 4.6 (**33**): 4.2 (**34**): 1 (**35**). Prep. HPLC (*Spherisorb CN*, hexane + 2% i-PrOH; *cf.* [1]) at 20° allowed to obtain tricycle **33** in pure form. Tricycles **32** and **34** could only be obtained as a *ca.* 1.7 (**32**): 1 (**34**) mixture, since they thermally equibrated already at ambient temp. (see later). The fourth tricycle (**35**) could only by enriched in a fraction with **32** and **34**. When the pure mixture **32**/**34** was dissolved in a minimum amount of $Et_2O$ and the soln. kept at −20°, crystals of pure **32** slowly formed. They were separated from the mother liquor at −20° and kept at −20°. From the mother liquor, upon standing at −20°, further crystals of pure **32** separated.

*Dimethyl 7-Isopropyl-4,11-dimethyltricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**32**): Soft, waxy, and pale-yellow crystals; m.p. could not be determined due to the ease of isomerization. $t_R$ (*Spherisorb CN* column, hexane + 2% i-PrOH; flow rate: 1 ml/min; *cf.* [1]) 8.7 min. UV (*cf. Fig. 1*): $\lambda_{max}$ 340 (weak sh, 3.62), 306 (3.71), 232 (sh, 3.81); $\lambda_{min}$ 265 (3.45). $^1$H-NMR ($CDCl_3$, 295 K; $CHCl_3$ at 7.260; taken from the 1.7:1 mixture with **34**[9]): 6.756 (br. *d*, $^3J$(3,2) = 5.42, H–C(2)); 6.556 (*d*, $^3J$((2,3) = 5.42, H–C(3)); 6.007 (*dq*, $^3J$(8,12) = 6.82, $^4J$(*Me*–C(11),12) = 1.60, H–C(12)); 5.839 (*t*-like, $^4J$(8,6) ≈ $^4J$($Me_2CH$–C(7),6), H–C(6)); 4.221 (*dd*, $^3J$(12,8) = 6.79, $^4J$(6,8) = 1.42, H–C(8)); 3.708, 3.682 (2*s*, MeOCO–C(9, 10)); 2.513 (br. *sept.*, $Me_2CH$–C(7)); 1.967 (*s*, Me–C(4)); 1.594 (*d*, $^4J$(12, *Me*–C(11)) = 1.55, Me–C(11)); 1.121, 1.111 (2*d*, *J* = 6.83, 6.72, $Me_2CH$–C(7)). $^1$H-NOE (400 MHz; measured at the original 7 (**32**): 4.6 (**33**): 4.2 (**34**): 1 (**35**) mixture): 1.967 Me–C(4))→6.556 (*s*), 5.839 (*s*); 1.594 (Me–C(11))→6.756 (*s*), 6.007 (*s*).

Tricycle **32**, dissolved in $CDCl_3$, rearranged slowly already at temp. < 0° to yield an equilibrium mixture with **34**. The other two tricycles, **33** and **35**, were not formed under these conditions ($^1$H-NMR analysis).

*Dimethyl 9-Isopropyl-2,11-dimethyltricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-6,7-dicarboxylate* (**33**). Obtained as a pale-yellow oil which was thermally stable at ambient temp. over shorter periods. $t_R$ (*cf.* **32**) 9.3 min. UV (*cf. Fig. 1*): $\lambda_{max}$ 357 (weak sh, 4.07), 346 (4.10), 288 (3.72), 228 (sh, 3.79); $\lambda_{min}$ 298 (3.70), 250 (3.52). $^1$H-NMR ($CDCl_3$, 295 K; $CDCl_3$ at 7.260): 6.406 (*d*, $^3J$(3,4) = 2.39, H–C(4)); 6.357 (*sext.*-like, ½·$^3J$(4,3) ≈ $^4J$(*Me*–C(2),4), H–C(3)); 6.032 (*dq*, $^3J$(8,12) = 6.70, $^4J$(*Me*–C(11),12) = 1.57, H–C(12)); 5.523 (*t*-like, $^4J$(8,10) ≈ $^4J$($Me_2CH$–C(9),10), H–C(10)); 4.417 (*dd*, $^3J$(12,8) = 6.64, $^4J$(10,8) = 1.76, H–C(8)); 3.805, 3.784 (2*s*, MeOCO–C(6,7)); 2.404 (*sept. d*, $Me_2CH$–C(9)); 2.178 (*d*, $^4J$(3, *Me*–C(2)) = 1.29, Me–C(2)); 1.537 (*d*, $^4J$(12, *Me*–C(11)) = 1.60, Me–C(11)); 1.015, 1.004 (2*d*, *J* = 6.80, 6.77, $Me_2CH$–C(9)). $^1$H-NOE (400 MHz; *cf.* **32**): 2.178 (Me–C(2))→6.357 (*s*), 5.523 (*s*), 1.537 (*m*); 1.537 (Me–C(11))→6.032 (*s*), 2.178 (*m*).

Tricycle **33**, when warmed above 50° in toluene soln., rearranged into the thermal equilibrium mixture **32**/**34** as well as **35**. At 85°, the equilibrium mixture consisted of 41.5% of **32**, 27.5% of **33**, 25.0% of **34**, and 6.0% of **32** ($^1$H-NMR at 295 K). No other tricyclic compound could be recognized (limit of detection by $^1$H-NMR: ≥ 0.5%).

The equilibrium mixture (0.015 g, 0.044 mmol) and ADM (0.035 g, 0.25 mmol) were heated in decalin (0.5 ml) at 180° during 3.5 h. Prep. TLC (silica gel; hexane/AcOEt 3:2) yielded two fractions (0.0105 g and 0.0076 g; in total 85%) of 6 tetracyclic compounds, namely '*anti*'-**46** and '*syn*'-**46**, '*anti*'-**44**, '*anti*'-**45**, '*anti*'-**47**, and '*anti*'-**48**, *i.e.* the same compounds that were isolated from the thermal reaction of guaiazulene with ADM in decalin at 190° [2]. The identification of the tetracyclic compounds in the two TLC fractions was unambiguous on the basis of their individual $^1$H-NMR signals. On the other hand, further signals, attributable to tetracyclic structures, were not discernible (limit of secure detection ≥ 0.5%). HPLC combined with $^1$H-NMR gave the following relative yields: 9.6% of '*anti*'-**46**, 32% of '*syn*'-**46**, 19% of '*anti*'-**44**, 22.8% of '*anti*'-**45**, 6.6% of '*anti*'-**47**, and 10% of '*anti*'-**48**, in good agreement with the results obtained earlier [2].

*Dimethyl 12-Isopropyl-2,6-dimethyltricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**34**). Only obtained in the 1.7:1 equilibrium mixture with **32** (see there). $t_R$ (*cf.* **32**) 7.9 min UV (*cf. Fig. 1*): $\lambda_{max}$ 330 (sh, 0.61), 305 (0.70), 223 (1.00); $\lambda_{min}$ 263 (0.40). $^1$H-NMR (*cf.* **32**): 6.265 (*A* of *ABX*$_3$, $^3J_{AB}$ ≈ 2.5, H–C(4)); *ca.* 6.255 (*B m*, H–C(3)); 5.728 (br. *d*, $^3J$(8,7) = 8.38, $^4J$(*Me*–C(6),7) not discernible, H–C(7)); 5.517 (*t*-like, $^4J$(8,10) ≈ $^4J$($Me_2CH$–C(12),10), H–C(11)); 4.169 (*dd*, $^3J$(7,8) = 8.38, $^4J$(10,8) = 1.82, H–C(8)); 3.737, 3.680 (2*s*, MeOCO–C(9,10)); 2.176 (*sept. d*, $Me_2CH$–C(12)); 2.092 (*d*, $^4J$(3, *Me*–C(2)) = 0.93, Me–C(2)); 1.798

[9]) When crystals of **32** were dissolved in $CDCl_3$ at 230 K and the $^1$H-NMR measured at this temperature, only the signals of **32** were present.

(*d*, $^4J$(7, *Me*–C(6)) = 1.35, Me–C(6)); 1.037, 1.036 (2*s*, *J* = 6.9, $Me_2$CH–C(12)). $^1$H-NOE (*cf.* **32**): 2.092 (Me–C(2))→6.255 (*s*), 5.517 (*s*), 3.680 (*m*, MeOCO–C(10)); 1.798 (Me–C(6))→6.265 (*s*), 5.728 (*s*).

*Dimethyl 7-Isopropyl-2,11-dimethyltricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**35**). Degree of enrichment *ca.* 20%; in a mixture with *ca.* 35% of **32** and 22.5% of **33** as well as **34**. $t_R$ (*cf.* **32**) 8.2 min. UV (*cf. Fig. 1*): $\lambda_{max}$ 345 (sh, 0.58), 307 (0.87), 223 (1.00); $\lambda_{min}$ 265 (0.41). $^1$H-NMR ($CDCl_3$, 295 K; $CHCl_3$ at 7.260): 6.385 (*sext.*-like, $\frac{1}{2} \cdot {}^3J(Me\text{–}C(4),3) \approx {}^4J(Me\text{–}C(2),3)$, H–C(3)); 6.088 (*d*, $^3J(3,4) = 2.26$, H–C(4)); 6.052 (*dq*, $^3J(8,12) = 6.84$, $^4J(Me\text{–}C(11),12) = 1.64$, H–C(12)); 5.767 (*t*-like, $^4J(8,6) \approx {}^4J(Me_2CH\text{–}C(7),6)$, H–C(6)); 4.207 (*dd*, $^3J(12,8) = 6.64$, $^4J(6,8) = 1.67$, H–C(8)); 3.725, 3.694 (2*s*, MeOCO–C(9,10)); *ca.* 2.35 (*sept.*, $Me_2CH$–C(7)); 2.094 (2.100 in $C_6D_6$) (*d*, $^4J(3, Me\text{–}C(2)) \approx 1.3$, Me–C(2)); 1.595 (1.492 in $C_6D_6$) (*d*, $^4J(12, Me\text{–}C(11)) = 1.57$ (1.52), Me–C(11)); 1.066, 1.063 (2*d*, *J* = 6.8, $Me_2$CH–C(7)). $^1$H-NOE (400 MHz; *cf.* **32**): 2.094 (Me–C(2))→6.385 (*s*), 1.595 (*s*); 1.595 (Me–C(11))→6.052 (*s*), 2.094 (*m*).

5.2. *Carbaldehyde* **17** *with [RhCl(PPh$_3$)$_3$]*. The aldehyde (0.060 g, 0.18 mmol) and the Rh catalyst (0.19 g, 0.20 mmol) were heated in dry toluene (3 ml) in a *Schlenk* reaction vessel at 140° during 10 h under a slight excess of pressure. Workup (*cf. 5.1*) yielded 0.040 g (71%) of a mixture of **38**–**41** in a ratio of *ca.* 8.4:3.1:1.8:1 ($^1$H-NMR). At 55°, the thermal equilibrium mixture amounted to 53% of **38**, 23% of **39**, 18% of **40**, and 7% of **41**. The mixture was not further separated.

*Dimethyl 4,7,11-Trimethyltricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**38**): Present in an amount of 53% in the thermal equilibrium mixture. $t_R$ (*cf. 5.1*) 8.7 min. UV (hexane + 2% i-PrOH; qual.): $\lambda_{max}$ 335 (weak sh, 0.60), 308 (0.76), 223 (1.00); $\lambda_{min}$ 267 (0.46). $^1$H-NMR ($CDCl_3$; $CHCl_3$ at 7.260): 6.794 (br. *d*, $^3J(3,2) = 5.37$, H–C(2)); 6.555 (*d*, $^3J(2,3) = 5.44$, H–C(3)); 6.075 (*dq*, $^3J(8,12) = 6.81$, $^4J(Me\text{–}C(11),12) = 1.64$, H–C(12)); 5.884 (*quint.*-like, $^4J(8,6) \approx {}^4J(Me\text{–}C(7),6)$, H–C(6)); 4.110 (*dd*, $^3J(12,8) = 6.82$, $^4J(6,8) = 1.44$, H–C(8)); 3.737, 3.690 (2*s*, MeOCO–C(9,10)); 2.072 (br. *s*, Me–C(7)); 1.961 (*s*, Me–C(4)); 1.616 (*d*, $^4J(12, Me\text{–}C(11)) = 1.68$, Me–C(11)).

*Dimethyl 2,9,11-Trimethyltricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-6,7-dicarboxylate* (**39**). Present in an amount of 23% in the thermal equilibrium mixture. $t_R$ (*cf. 5.1*) 9.7 min. UV (hexane + 2% i-PrOH; qual.): $\lambda_{max}$ 349 (1.00), 222 (0.39); $\lambda_{min}$ 266 (0.04). $^1$H-NMR ($CDCl_3$; $CHCl_3$ at 7.260): 6.411 (br. *d*, $^3J(3,4) = 2.47$, H–C(4)); 6.350 (*sext.*-like, $\frac{1}{2} \cdot {}^3J(4,3) \approx {}^4J(Me\text{–}C(2),3)$, H–C(3)); 6.039 (*dq*, $^3J(8,12) = 6.64$, $^4J(Me\text{–}C(11),12) = 1.58$, H–C(12)); 5.556 (*quint.*-like, $^4J(8,10) \approx {}^4J(Me\text{–}C(9),10)$, H–C(10)); 4.286 (*dd*, $^3J(12,8) = 6.56$, $^4J(10,8) = 1.68$, H–C(8)); 3.830, 3.797 (2*s*, MeOCO–C(6,7)); 2.180 (*d*, $^4J(3, Me\text{–}C(2)) = 1.41$, Me–C(2)); 1.901 (*d*, $^4J(10, Me\text{–}C(9)) = 1.57$, Me–C(9)); 1.559 (*d*, $^4J(12, Me\text{–}C(11)) = 1.57$, Me–C(11)).

*Dimethyl 2,6,12-Trimethyltricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**40**). Present in an amount of 18% in the thermal equilibrium mixture. $t_R$ (*cf. 5.1*) 7.7 min. UV (hexane + 2% i-PrOH; qual.): $\lambda_{max}$ 329 (sh, 0.61), 304 (0.67), 222 (1.00); $\lambda_{min}$ 263 (0.41). $^1$H-NMR ($CDCl_3$; $CHCl_3$ at 7.260): 6.292 (br. *d*, $^3J(3,4) = 2.26$, H–C(4)); 6.255 (*sext.*-like, $\frac{1}{2} \cdot {}^3J(4,3) \approx {}^4J(Me\text{–}C(2),3)$, H–C(3)); 5.795 (br. *d*, $^3J(8,7) = 8.4$, H–C(7)); 5.569 (*quint.*-like, $^4J(8,11) \approx {}^4J(Me\text{–}C(12),11)$, H–C(11)); 4.062 (*dd*, $^3J(7,8) = 8.41$, $^4J(11,8) = 1.80$, H–C(8)); 3.747, 3.697 (2*s*, MeOCO–C(9,10)); 2.097 (*d*, $^4J(3, Me\text{–}C(2)) = 1.54$, Me–C(2)); 1.926 (*d*, $^4J(12, Me\text{–}C(11)); 1.830$ (*d*, $^4J(7, Me\text{–}C(6)) = 1.42$, Me–C(6)).

*Dimethyl 2,7,11-Trimethyltricyclo[6.2.2.0$^{1,5}$]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**41**). Present in an amount of 7% in the thermal equilibrium mixture. $t_R$ (*cf. 5.1*) 8.0 min. UV (hexane + 2% i-PrOH; qual.): $\lambda_{max}$ 339 (sh, 0.57), 305 (0.80), 222 (1.00); $\lambda_{min}$ 266 (0.44). $^1$H-NMR ($CDCl_3$; $CHCl_3$ at 7.260): 6.383 (*sext.*-like, $\frac{1}{2} \cdot {}^3J(4,3) \approx {}^4J(Me\text{–}C(2),3)$, H–C(3)); 6.123 (*dq*, $^3J(8,12) = 6.66$, $^4J(Me\text{–}C(11),12) = 1.55$, H–C(12)); *ca.* 6.055 (*d*, covered by signals of **38** and **39**, H–C(4)); *ca.* 5.793 (*quint.*-like, $^4J(8,6) \approx {}^4J(Me\text{–}C(7),6)$, H–C(6)); 4.116 (*dd*, $^3J(12,8) = 6.6$, $^4J(6,8) = 1.6$, H–C(8)); 3.752, 3.705 (2*s*, MeOCO–C(9,10)); 2.127 (*d*, $^4J(3, Me\text{–}C(2)) \approx 1.2$, Me–C(2)); 2.002 (br. *s*, Me–C(7)); 1.616 (*d*, $^4J(12, Me\text{–}C(11)) = 1.6$, Me–C(11)).

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