

178. Thermal Reaction of Highly Alkylated Azulenes with Dimethyl Acetylenedicarboxylate: HOMO(Azulene) vs. SHOMO(Azulene) Control in the Primary Thermal Addition Step

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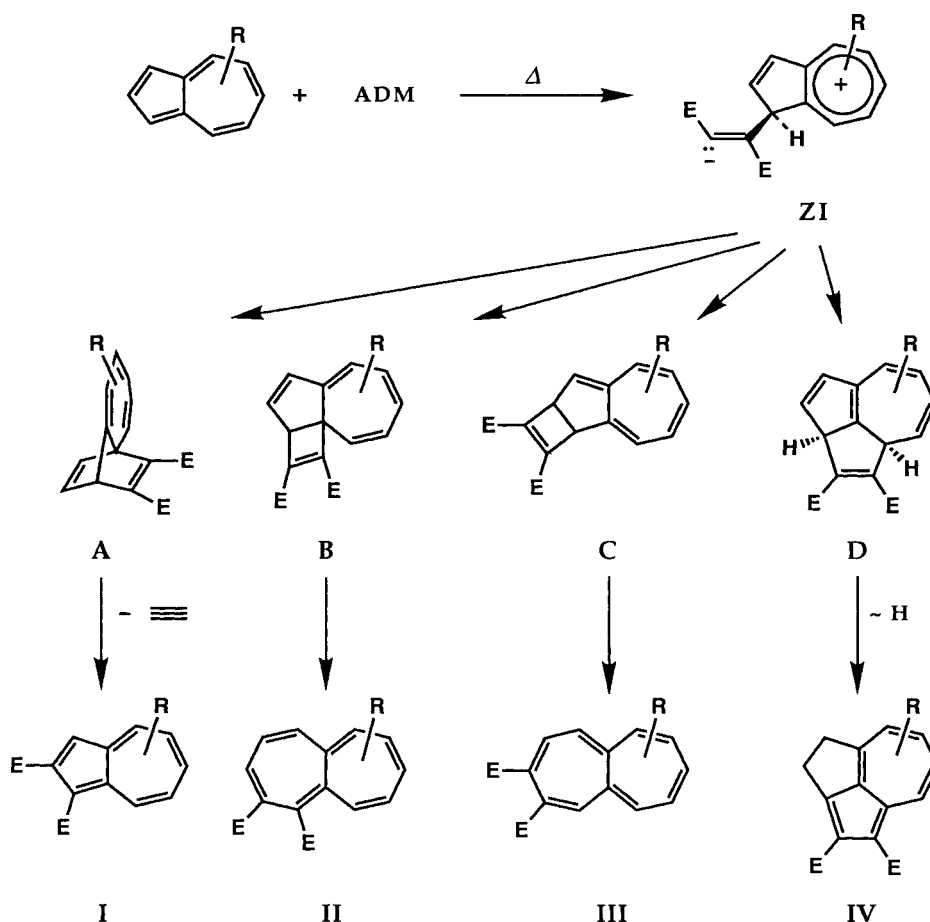
The reaction of highly alkylated azulenes with dimethyl acetylenedicarboxylate (ADM) in decalin or tetralin at 180–200° yields, beside the expected heptalene- and azulene-1,2-dicarboxylates, tetracyclic compounds of type 'anti'-V and tricyclic compounds of type E (cf. Schemes 2–4 and 8–11). The compounds of type 'anti'-V represent *Diels-Alder* adducts of the primary tricyclic intermediates A with ADM. In some cases, the tricyclic compounds of type E also underwent a consecutive *Diels-Alder* reaction with ADM to yield the tetracyclic compounds of type 'anti'- or 'syn'-VI (cf. Schemes 2 and 8–11). The tricyclic compounds of type E, namely 4 and 8, reversibly rearrange via [1,5]-C shifts to isomeric tricyclic structures (cf. 18 and 19, respectively, in Scheme 6) already at temperatures > 50°. Photochemically 4 rearranges to a corresponding tetracyclic compound 20 via a di- π -methane reaction. The observed heptalene- and azulene-1,2-dicarboxylates as well as the tetracyclic compounds of type 'anti'-V are formed from the primary tricyclic intermediates A via rearrangement ($\rightarrow$ heptalenedicarboxylates), *retro-Diels-Alder* reaction ($\rightarrow$ azulenedicarboxylates), and *Diels-Alder* reaction with ADM. The different reaction channels of A are dependent on the substituents. However, the main reaction channel of A is its *retro-Diels-Alder* reaction to the starting materials (azulene and ADM). The highly reversible *Diels-Alder* reaction of ADM to the five-membered ring of the azulenes is HOMO(azulene)/LUMO(ADM)-controlled, in contrast to the at 200° irreversible ADM addition to the seven-membered ring of the azulenes to yield the *Diels-Alder* products of type E. This competing reaction must occur on grounds of orbital-symmetry conservation under SHOMO(azulene)/LUMO(ADM) control (cf. Schemes 20–22). Several X-ray diffraction analyses of the products were performed (cf. Chapt. 4.1).

1. Introduction. – It has been well established over the past years by Hafner *et al.* (cf. [1] [2]) as well as by our own work (cf. [3–5]) that the thermal reaction of azulenes with dimethyl acetylenedicarboxylate (ADM) in apolar solvents such as tetralin or decalin at 180–200° represents the shortest and most versatile access to the heptalene skeleton, in particular, to heptalene-1,2-dicarboxylates. In addition, it has been shown that heptalene-1,2-dicarboxylates and their derivatives undergo thermal [2] [5–7] (see also [8] [9]) and photochemical double-bond shifts (DBS) [5] [6] as well as thermal σ -skeletal rearrangements [10] [11], and that heptalenes with substituents in the *peri*-positions can be resolved into their antipodes [2] [4] [7] [12]. In contrast, very little is known on the primary steps in the thermal reaction of azulenes with ADM. It has been postulated by Hafner *et al.* [1] [2] that azulenes and ADM yield as a first intermediate a zwitterionic species (ZI; cf. Scheme 1) from which all observed thermal products (I to IV) are derived.

Very recently, we have shown that in apolar solvents the tricyclic compounds A must represent the sole primary intermediate in the thermal reaction of azulenes with ADM

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

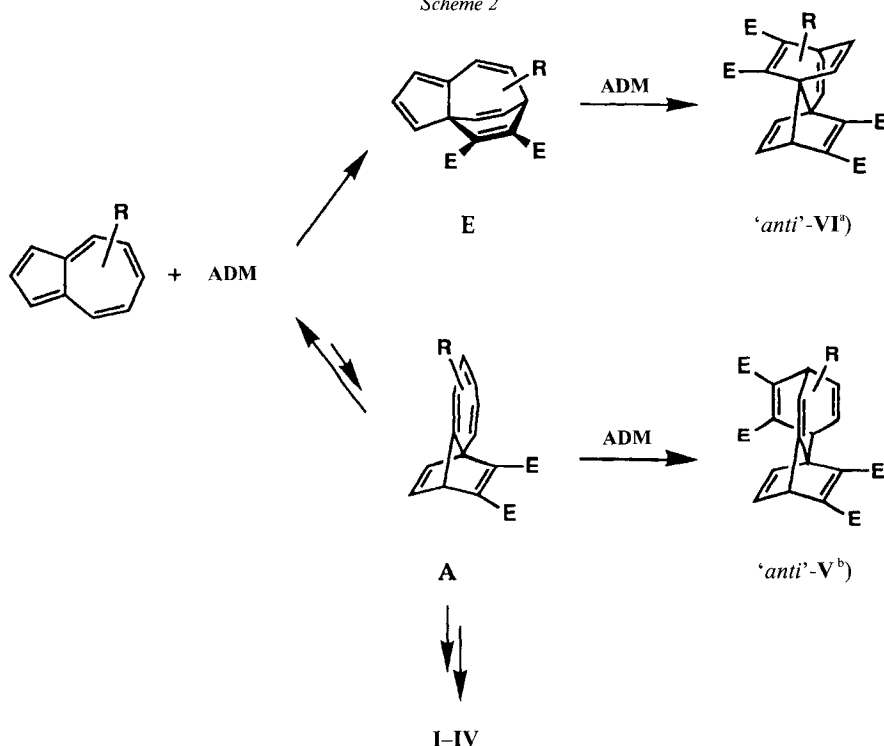
²⁾ Part of the Ph. D. thesis of R.H.W., University of Basle, 1988; present address: Rohner AG, CH-4132 Muttenz BL.

Scheme 1^{a)}

^{a)} In this and the following schemes, E represents the methoxycarbonyl group. R stands for substituents at the five- and/or seven-membered ring of the azulenes or at one or both seven-membered rings of the heptalenes.

yielding heptalenes [13]. In apolar solvents such as decane, intermediates A (*cf.* [14]) revert mainly ($> 95\%$) to the starting materials, and only a small part ($< 5\%$) rearranges *via* the zwitterionic species ZI to the corresponding heptalenes. On the other hand, in polar aprotic solvents such as MeCN intermediates A are mainly ($> 70\%$) transformed *via* ZI into heptalene-1,2-dicarboxylates II. The *retro-Diels-Alder* reaction yielding the starting materials *via* a concerted transition state showing little or no polarity occurs only to a small extent ($< 30\%$). In this and the following two contributions [15] [16], we want to show that azulenes and ADM yield at $180\text{--}200^\circ$ in apolar solvents such as decalin in a HOMO(azulene)/LUMO(ADM) controlled highly reversible reaction tricyclic intermediates of type A which may be trapped by excess ADM in a consecutive *Diels-Alder* reaction leading to the formation of the tetracyclic compounds V (Scheme 2).

Scheme 2



^a) 'anti' refers to the relative position of the two maleic ester fragments with respect to the original azulene skeleton. The 'syn'-structures may also be formed (see later). ^b) See ^a). The 'syn'-structures have not been observed so far (see later).

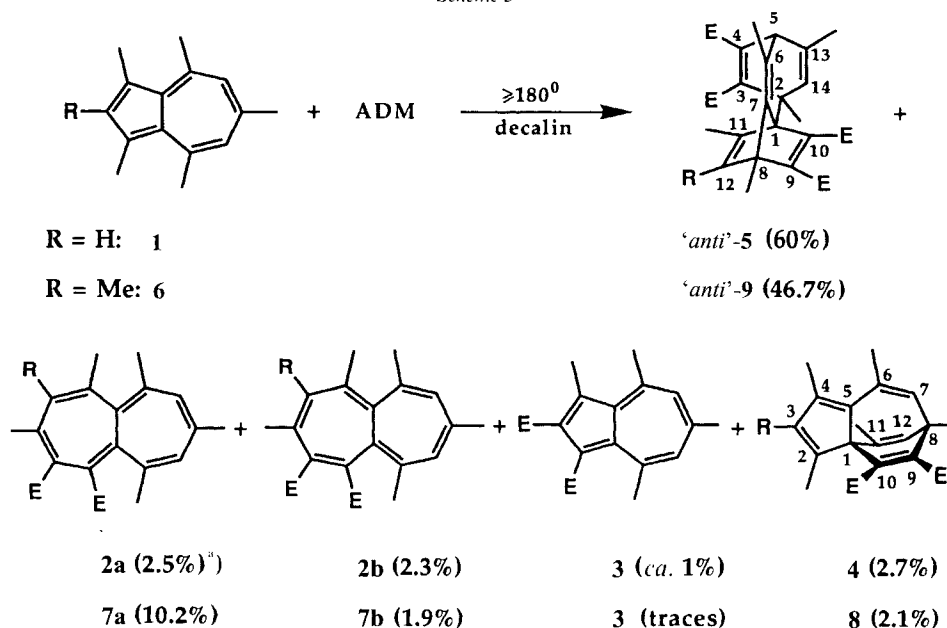
However, with this expected azulene/ADM reactivity competes a second intrinsic and so far uncovered reactivity of the azulene/ADM system governed by a SHOMO(azulene)/LUMO(ADM)³) interaction which results in the (under the applied conditions) irreversible formation of tricyclic structures of type **E**. The latter one may also be trapped by excess ADM in a following *Diels-Alder* reaction yielding the tetracyclic compounds **VI** which are 'isoskeletal' with **V**.

2. Thermal Reactions of Alkylated Azulenes with ADM. – All described thermal reactions were performed in 0.1–0.5M solutions of the corresponding azulene in freshly, under Ar distilled decalin in the presence of a three- to five-fold molar excess of ADM at 180–200°. The separation of products was realized by column chromatography (CC) or TLC on silica gel or on Al₂O₃ (Act. III) with hexane/Et₂O mixtures. For further separation or purification of the products, crystallization or HPLC were applied (see *Exper. Part*). All yields, given in the following schemes, refer to purified compounds.

2.1. Azulenes with Me Groups in All Four peri-Positions. The reaction of 1,3,4,6,8-pentamethylazulene (**1**) with ADM in decalin (*Scheme 3*) yielded only small amounts of

³) SHOMO = subjacent HOMO.

Scheme 3



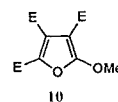
^{a)} The pure mixture of **2a/2b** and **4** amounted to 11%.

the expected heptalene-1,2-dicarboxylate **2a** and its DBS (double-bond-shift) isomer **2b** as well as of the azulene-1,2-dicarboxylate **3**⁴⁾. The heptalene fractions contained in small amounts (isolated yield 2.7%) an additional (1 + 1) adduct which behaved thermally similar to **2a/2b** (see later). It was separated from **2a/2b** by HPLC and further purified by crystallization. It turned out to be the tricyclic compound **4**. The dominating product, however, which was isolated in 60% yield represented the (1 + 2) adduct 'anti'-**5**. In a similar manner the thermal reaction of 1,2,3,4,6,8-hexamethylazulene (**6**) and ADM in decalin led to the formation of the (1 + 2) adduct 'anti'-**9** as the main product accompanied by the two heptalenes **7a** and **7b**, the azulene-1,2-dicarboxylate **3** as well as the tricyclic (1 + 1) adduct **8** (Scheme 3).

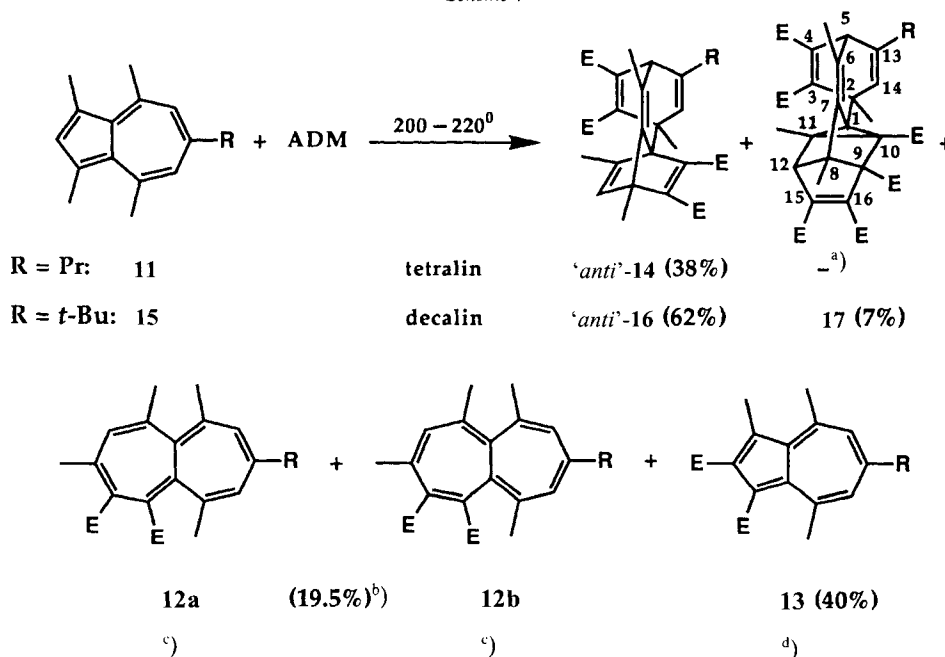
When the steric encumbrance at C(6) of the azulenes was augmented by exchanging the Me group at this position in **1** by a Pr or *t*-Bu group the formation of the corresponding tricyclic (1 + 1) adducts was not observed⁵⁾. Thus, the thermal reaction of 1,3,4,8-tetramethyl-6-propylazulene (**11**) with excess ADM (4.8 mol-equiv.) in decalin yielded the expected two heptalenes **12a** and **12b**, the azulene-1,2-dicarboxylate **13** as well as the (1 + 2) adduct 'anti'-**14** (Scheme 4). On the other hand, 6-(*tert*-butyl)-1,3,4,8-tetramethyl-

⁴⁾ Similar results were obtained when **1** was heated with an excess of ADM in tetralin at 150° (cf. Footnote 2 and Exper. Part).

⁵⁾ The level of detection of products in the chromatographic runs was ca. 0.5% of an unknown compound. In most of the thermal reactions of the azulenes with ADM in decalin at 200°, especially over longer reaction periods, we observed the known thermal condensation product of ADM, namely trimethyl 5-methoxyfuran-2,3,4-tricarboxylate (**10**; cf. [17]).



Scheme 4



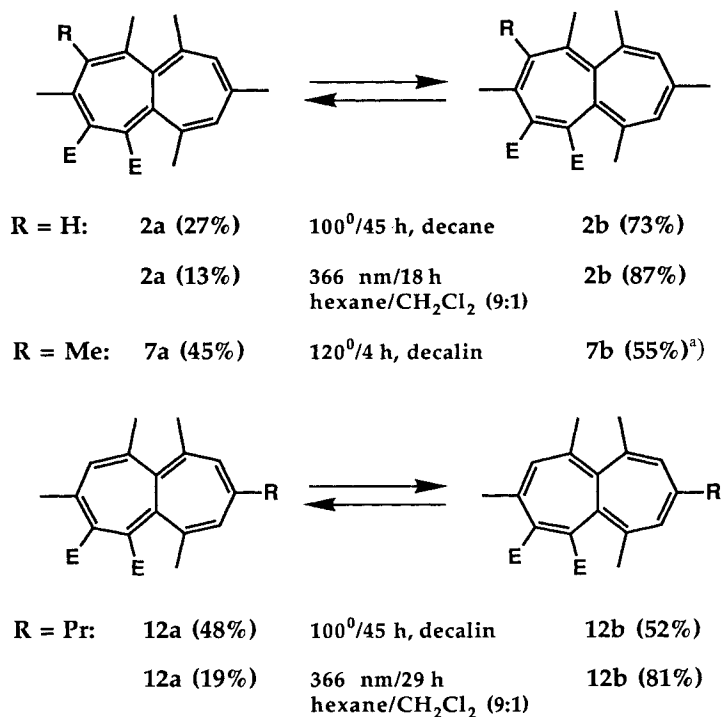
^{a)} Not observed in the case of R = Pr (*cf. Footnote 5*). ^{b)} Pure mixture of **12a/12b** which was separated by HPLC and further purified by crystallization. ^{c)} Only very small amounts. Identified as heptalenes by their characteristic pale yellow color and their typical R_f values under standard conditions. ^{d)} Only small amounts. Identified by its typical blue 'azulene color' and R_f value.

azulene (**15**) and ADM (5 mol-equiv.) led to the formation of only traces of heptalenes and dimethyl 6-(*tert*-butyl)-3,4,8-trimethylazulene-1,2-dicarboxylate. The predominant product was the (1 + 2) adduct 'anti'-**16** which was accompanied by its homo-*Diels-Alder* adduct with ADM, namely **17** (*Scheme 4*).

The structure of the heptalenes **2a/2b**, **7a/7b**, and **12a/12b** follows from their spectroscopic data (*cf. Exper. Part* as well as [4] [5]) and their thermal and photochemical reversible interconversions (*Scheme 5*). The structures of **7b** and **12b** were confirmed by an X-ray diffraction analysis (*cf. Chapt. 4.1*), since it was especially difficult in the case of the pair of heptalenes **7a/7b** to assign unambiguously the position of the π bonds. It is of interest to note that as compared to dimethyl 5,6,8,10-tetramethylheptalene-1,2-dicarboxylate (**23a**; *cf. Scheme 8*) and its DBS isomer **23b** which show at 100° (tetralin) an equilibrium ratio of 88.7%/11.3% ($\Delta G_{100} = -6.4$ kJ mol⁻¹; *cf. [5]*) the additional Me group at C(3) in **2a** shifts the equilibrium ratio in favor of **2b** ($\Delta G_{100} = +3.1$ kJ mol⁻¹).

The new tricyclic structure of **4** and **8** was established on the basis of an X-ray diffraction analysis of **4** (*cf. Chapt. 4.1*). ¹H-NOE measurements (400 MHz) allowed the assignment of the skeletal positions of all Me groups in **4** and **8** (*cf. Chapt. 4.2*). We were surprised when we found that **4** as well as **8** rearranged reversibly into a second tricyclic compound (**18** and **19**, respectively; *Scheme 6*) already at temperatures slightly above

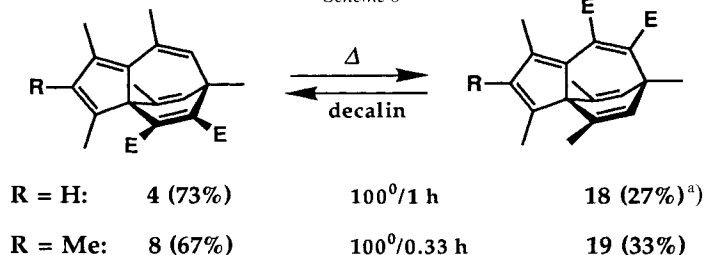
Scheme 5



^{a)} Prolonged heating of the mixture of **7a** and **7b** at 120° yielded an unknown additional product.

room temperature (*cf. Exper. Part*). At 100° the equilibrium ratios given in *Scheme 6* were rapidly established. The structural assignment of **18** and **19** is based on the similarity of their ¹H-NMR spectra with those of **4** and **8** and by the plane of symmetry that is reflected in the identical chemical shifts for H–C(9,12) and CH₃–C(10,11) which show strong ¹H-NOE with CH₃–C(8) and CH₃–C(2), respectively. We suppose that the thermal equilibria **4** ⇌ **18** and **8** ⇌ **19** are established by easily occurring sigmatropic [1,5]-C shifts in the cyclopentadiene substructures (see later).

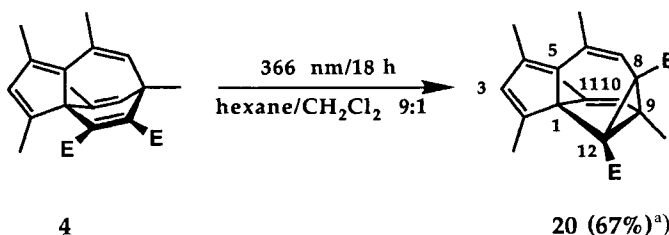
Scheme 6



^{a)} MM2 Calculations for 100° *in vacuo* gave an equilibrium ratio of 77%/23%.

When the photochemical behavior of **4** was routinely checked, we observed a nearly quantitative rearrangement into a new tetracyclic compound **20** by irradiating **4** at 366 nm. The structure of **20**, which is based on its $^1\text{H-NMR}$ spectrum and on corresponding $^1\text{H-NOE}$ measurements, shows that **4** must have undergone a di- π -methane rearrangement (*Scheme 7*)⁶. Characteristic for the structural change in going photochemically from **4** to **20** is the alteration in the chemical shift (CDCl_3) of $\text{CH}_3\text{-C}(11)$ in **4** (1.487 ppm) and the corresponding $\text{CH}_3\text{-C}(11)$ in **20** (1.071 ppm). The latter one is well displaced above the cyclopentadiene substructure and, thus, in the shielding area of this π system.

Scheme 7



^{a)} Yield of purified material (> 90% yield of isolated material).

On the other hand, $\text{CH}_3\text{-C}(8)$ in **4** (1.423 ppm) is changed into $\text{CH}_3\text{-C}(9)$ in **20** (1.596 ppm) which shows a pronounced $^1\text{H-NOE}$ with $\text{H-C}(10)$ at 5.491 ppm which, in turn, is coupled ($^4J = 1.4 \text{ Hz}$) with $\text{CH}_3\text{-C}(11)$. Indicative for the presence of the three-membered ring in **20** is the observation of weak $^1\text{H-NOE}$ with both CH_3OOC groups when $\text{CH}_3\text{-C}(9)$ is irradiated.

Whether **4/18** nor **8/19** were changed when heated at 200° in decalin. Tricycle **8** showed also no change when heated at 200° in decalin in the presence of excess ADM (*cf.* [15]).

The structure of 'anti'-**5**, 'anti'-**9**, 'anti'-**14**, and 'anti'-**16** has been elucidated by an X-ray diffraction analysis of 'anti'-**5** (*cf.* *Chapt. 4.1* as well as *Footnote 2*) and extensive $^1\text{H-NMR}$ as well as $^1\text{H-DR}$ and $^1\text{H-NOE}$ measurements (*cf.* *Chapt. 4.2*). That all compounds possess the 'anti'-configuration follows from the nearly identical chemical shifts (CDCl_3), observed especially for $\text{CH}_3\text{-C}(2)$ ($1.56 \pm 0.03 \text{ ppm}$) and $\text{CH}_3\text{-C}(11)$ ($2.04 \pm 0.01 \text{ ppm}$; 1.90 ppm for 'anti'-**9**) as well as for all CH_3OOC groups (3.82 ± 0.01 , 3.79 ± 0.01 , 3.74 ± 0.01 , and $3.68 \pm 0.01 \text{ ppm}$). In addition, no $^1\text{H-NOE}$ is observed between $\text{CH}_3\text{-C}(11)$ and $\text{H-C}(14)$ for all 'anti'-structures (*cf.* also [15]).

The structure of the pentacyclic compound **17** is secured by its thermal formation from 'anti'-**16** and ADM at 200° in decalin (*cf.* *Exper. Part*). That the homo-*Diels-Alder* reaction had occurred with the norbornadiene part of 'anti'-**16** follows from the fact that the allylic coupling of $\text{H-C}(5)$ and $\text{H-C}(14)$ is still present in the $^1\text{H-NMR}$ spectrum (CDCl_3) of **17**, and that $\text{CH}_3\text{-C}(2)$ (1.313 ppm) and $\text{CH}_3\text{-C}(8)$ (1.093) are remarkably shifted upfield in comparison to 'anti'-**16** (1.592 and 1.715 ppm, respectively) due to shielding effects of the three-membered ring and the $\text{C}(15)=\text{C}(16)$ bond in **17**.

⁶⁾ We will report on this type of rearrangement in detail later in this journal.

five-fold molar excess of ADM in decalin. However, in this case, the two (1 + 2) adducts 'anti'-**29** and 'anti'-**30**, 'isoskeletal' with 'syn'-**24**, were isolated, beside the known products **26** and **27a/27b** [5], and small amounts of the phthalic diester **28** and the pentacyclic compound **31** (Scheme 8).

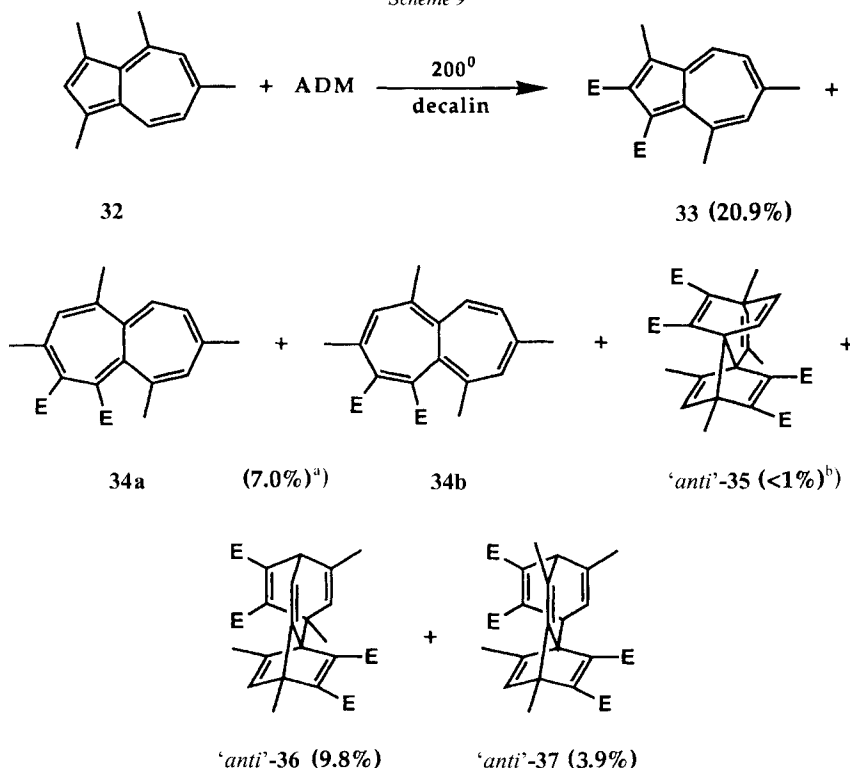
The structures of 'anti'-**29** and 'anti'-**30** could easily be assigned by comparison of their ¹H-NMR data (CDCl₃) with those of 'anti'-**16**. The main product showed for H–C(12) (6.658 ppm) and H–C(11) (7.104 ppm) an *AB* system with $J_{AB} = 5.4$ Hz which is quite typical for norbornadiene structures (*cf.* [18]). CH₃–C(8) appeared as *s* at 1.755 ppm. In contrast, the isomeric structure of 'anti'-**30** exhibited at 4.096 ppm a *d* with $^3J = 3.4$ Hz for an H-atom (at C(8)) in, at least, bisallylic position. The coupling partner (H–C(12)) showed a *sext.*-like signal at 6.490 ppm due to a further coupling ($^4J = 1.7$ Hz) with the adjacent Me group at C(11). The pentacyclic compound **31** showed in the ¹H-NMR spectrum (CDCl₃) no signal in the region of 1.1 ppm (CH₃–C(8) in **17**). However, an *AB* system at 3.184 ppm (H–C(12)) and 2.947 ppm (H–C(8)) shielded by the C(15)=C(16) bond indicated that the Me group in the precursor ('anti'-**30**) must have been located at C(11). Indeed, this Me group appeared in **17** at 1.557 ppm and in **31** at 1.530 ppm.

The establishment of the fact that the (1 + 2) adduct, isolated from the reaction mixture of **21** and ADM, was not an analogue of 'anti'-**29** or 'anti'-**30** with R = Me (Scheme 8) was easy since 'syn'-**24** showed in its ¹H-NMR spectrum (CDCl₃) the presence of three olefinic Me groups that appeared as *d* ($^4J = 1.4$ to 1.8 Hz). The analogues of 'anti'-**29** or 'anti'-**30** should show only one or two olefinic Me groups that appear as *d* due to allylic couplings with adjacent olefinic H-atoms. The other structural features of 'syn'-**24** follow from ¹H-NOE measurements. Typical for the 'syn'-arrangement of the two maleic ester substructures in the molecule is an observed strong ¹H-NOE of H–C(14) (6.503 ppm) when CH₃–C(11) (1.821 ppm) is irradiated. In this case, further strong ¹H-NOE are observed with H–C(1) (4.377 ppm) and H–C(12) (5.761 ppm).

All tetracyclic and pentacyclic compounds, so far described, were stable when heated at 200° in solutions of decalin. This also means that tetracyclic structures of type **29** or **30** or the pentacyclic structures of type **31** do not undergo a thermal 1,4-fragmentation to yield phthalic ester derivatives such as **28** (however, *cf. Chapt. 4.3*).

It was of interest to study also the thermal reactivity of 1,3,4,6-tetramethylazulene (**32**) in which, in comparison to **21**, one of the *peri*-located Me groups is formally shifted from the seven- to the five-membered ring of the azulene skeleton (Scheme 9). When **32** was heated in the presence of a four-fold molar excess of ADM at 200° in decalin, it was transformed into the azulene-1,2-dicarboxylate **33** and a mixture of the heptalene-dicarboxylates **34a** and **34b** which rapidly equilibrate already at r.t. From the fraction of the (1 + 2) adducts, the tetracyclic compounds 'anti'-**36** and 'anti'-**37** were obtained in pure crystalline form. The third tetracycle, 'anti'-**35** could only be enriched in the mother liquors of the crystallization of 'anti'-**37**. However, its structure could unequivocally be assigned by the ¹H-NMR spectrum (C₆D₆) of a *ca.* 1:1 mixture of both compounds. Characteristic for 'anti'-**35** was the observed *AB* system for H–C(14) (6.195 ppm) and H–C(13) (5.942) with $J_{AB} = 8.40$ Hz (*cf.* [16]). The absence of a ¹H-NOE between H–C(14) (irradiated proton) and H–C(11) (6.088 ppm; observed signal) allows to attribute the 'anti'-relation to the maleic ester substructures in **35**. The assignment of the structures of 'anti'-**36** and 'anti'-**37** is based on the comparison of their ¹H-NMR spectra

Scheme 9



^{a)} Heptalenes **34a** and **34b** equilibrate already at r.t. to a mixture of 61 % of **34a** and 39 % of **34b**. ^{b)} Only obtained in a 1:1 mixture with 'anti'-**37** (cf. *Exper. Part*).

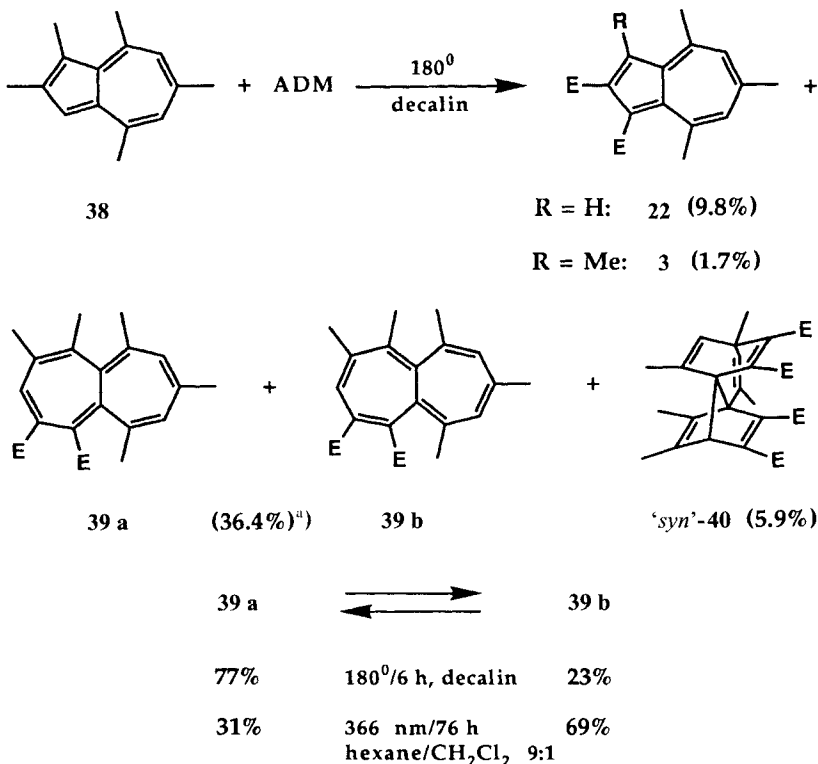
with that of 'anti'-**5** which comprises an additional Me substituent. The differentiation between 'anti'-**36** and 'anti'-**37** on the basis of their ¹H-NMR spectra (CDCl₃) causes no problem, since 'anti'-**36** possesses only one H-atom in bisallylic position (H-C(5) at 3.581 ppm) the signal of which shows a *dd* splitting pattern according to a vicinal (³*J* = 8.3 Hz) and an allylic coupling (⁴*J* = 1.7 Hz; with H-C(6) (4.339 ppm) and H-C(14) (5.677 ppm), respectively). In contrast, 'anti'-**37** has two H-atoms (H-C(2) and H-C(5)) which are placed in bisallylic positions. Thus, H-C(2) appears as *d* at 4.329 ppm (³*J* = 6.23 Hz), since it couples with H-C(14) (5.877 ppm) and H-C(5) also as *d* at 3.063 ppm showing an allylic coupling (⁴*J* = 1.8 Hz) with H-C(14)).

The exclusion of the structure of an isomeric heptalene-1,2-dicarboxylate with the Me groups at C(3), C(5), C(6), and C(8) instead of the positions assigned for **34a** is based on an observed strong ¹H-NOE between CH₃-C(5) at 2.03 ppm (irradiated group) and H-C(6) at 5.97 ppm as well as H-C(4) at 6.04 ppm. H-C(6) shows a vicinal coupling with H-C(7) at 6.34 ppm of 6.5 Hz (cf. [3–5]). Finally, an isomeric structure for **33** with the Me groups at C(3), C(4), and C(6) can be excluded since the H-atom at the seven-membered ring, showing only a vicinal coupling (³*J* = 9.7 Hz), appears at 8.285 ppm in

the ^1H -NMR spectrum (CDCl_3). In the isomeric azulene-1,2-dicarboxylate, the analogous $\text{H}-\text{C}(8)$ is expected at much lower field (*ca.* 9.7 ppm⁷).

The thermal reactivity pattern of 1,2,4,6,8-pentamethylazulene (**38**) in the presence of excess ADM (4 mol-equiv.) at 180 and 190° in decalin turned out to be very similar to that of its 2-demethyl analogue **21** (*cf. Scheme 8* as well as [2] [4]). However, the yield of the heptalenedicarboxylates **39a** and **39b** is slightly higher and, correspondingly, the amount of azulene-1,2-dicarboxylates reduced. Both possible azulenedicarboxylates **3** and **22** are formed in this case. Again, only one (1 + 2) adduct, namely 'syn'-**40**, is found. It must have the shown 'syn'-configuration, since the Me groups at C(13) (1.720 ppm) and at C(11) (1.591 ppm) show reciprocal ¹H-NOE when irradiated. All other observed ¹H-NOE (*cf. Exper. Part*), H,H-coupling patterns, and chemical shifts clearly demonstrate that 'syn'-**40** and 'syn'-**24** possess the same tetracyclic skeleton with the shown positions of the Me substituents.

Scheme 10

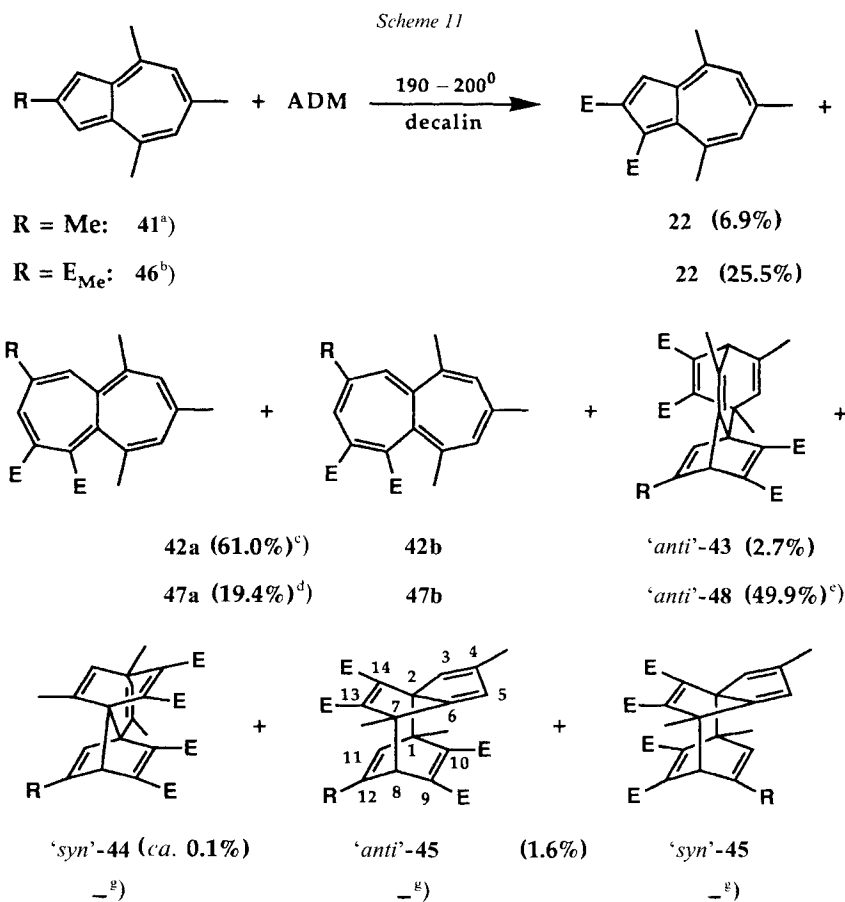


a) Mixture of both isomers. In a second run at 180°, the mixture of **39a**/**39b** was obtained in a yield of 58.5%. Compound **22** was isolated in 7.3% yield.

7) In dimethyl 5-isopropyl-3,8-dimethylazulene-1,2-dicarboxylate, the $^1\text{H-NMR}$ signal for H-C(4) appears at 8.39 ppm, whereas H-C(8) in dimethyl 7-isopropyl-3,4-dimethylazulene-1,2-dicarboxylate resonates at 9.70 ppm [15].

It is of interest to note that the thermal process in the heptalenedicarboxylates **39a** and **39b** could only be induced at temperatures above 150° (*Scheme 10*), in contrast to the thermal behavior of their 4- or 2-demethyl analogues **23a** and **23b**, respectively, which undergo the DBS process already at 100° [4] (*cf.* also [7]). The additional Me group seems to exert a pronounced buttressing effect in the transition state of the DBS process. On the other hand, the free energy differences (ΔG_{180}) are very similar for **39a/39b** (−4.6 kJ mol^{−1}) and for **23a/23b** (−5.6 kJ mol^{−1}).

2.3. Azulenes with Two Me Groups in peri-Positions. We have investigated the thermal addition reaction of ADM with 2,4,6,8-tetramethylazulene and methyl 4,6,8-trimethyl-



^{a)} A second run at 180° with 3.1 molar excess of ADM yielded 83.9% of the heptalenes **42a/42b** and 10.3% of azulenedicarboxylate **22**. (1 + 2) Adducts were not isolated. ^{b)} After heating in the presence of a 4.1 molar excess of ADM at 200° during 7.5 h, 48% of the starting material was recovered. The yields of products are given with respect to the reacted starting material. ^{c)} The equilibrium mixture at 25° consisted of 72.5% of **42a** and 27.5% of **42b**. ^{d)} The equilibrium mixture at r.t. amounted to 82% of **47a** and 18% of **47b**. ^{e)} Yield of pure 'anti'-**48** contaminated with 20% of **10**⁵⁾ (*cf. Exper. Part*). The yield of pure recrystallized 'anti'-**48** amounted to 37%. ^{f)} Only observed as a by-product (*ca.* 5%) in mixtures with 'anti'/'syn'-**45**. The structural assignment is only based on the chemical shifts of the ¹H-NMR signals (C_6D_6) in comparison with those of 'syn'-**24** and 'syn'-**40**. ^{g)} Not observed⁵⁾.

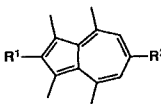
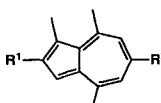
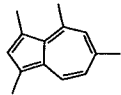
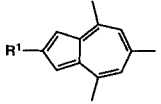
azulene-2-carboxylate (**41** and **46**, respectively; *cf.* Scheme 11). The tetramethylazulene yielded the corresponding heptalenes at 190° in up to 84%. The azulene-dicarboxylate **22** was formed in up to 10% yield. From a second run, where we looked carefully for (1 + 2) adducts, we isolated small amounts of 'anti'-**43** and observed traces of 'syn'-**44**. The latter one was only identified by its ¹H-NMR signals that could be detected in ¹H-NMR spectra (C₆D₆) of 3:1 mixtures of two new structural types of (1 + 2) adducts, namely 'anti'- and 'syn'-**45**, which were isolated in a yield of 1.6%. The corresponding thermal reaction between **46** and ADM at 200° occurred much slower due to the σ - and π -acceptor substituent at C(2). Nevertheless, the main product was the (1 + 2) adduct 'anti'-**48** which was obtained in 50% yield with respect to reacted **46**. The expected heptalenetricarboxylates **47a** and **47b** as well as the azulenedicarboxylate **22** were isolated in much lower yields. Both pairs of heptalenes (**42a/42b** and **47a/47b**, respectively) exhibited the DBS process already at 25° to yield equilibrium mixtures of similar composition, *i.e.* ΔG_{25} amounts to -2.4 and -3.8 kJ mol⁻¹, respectively.

The structure of 'anti'-**43** and 'anti'-**48** follows from their ¹H-NMR spectra and, in the case of 'anti'-**43** from corresponding ¹H-NOE measurements. The chemical ¹H-shifts of 'anti'-**43** are in perfect agreement with those of its analogues 'anti'-**5**, 'anti'-**9**, 'anti'-**36**, and 'anti'-**37**. The assignment of the 'anti'-configuration is also based on the absence of an ¹H-NOE at H–C(14) (5.604 ppm), when H–C(11) (6.540 ppm) was irradiated. However, strong ¹H-NOE were observed in this case with CH₃–C(2) (1.368 ppm) and CH₃–C(12) (1.918 ppm). H–C(8) appears at 3.921 ppm as *d* ($^4J \approx 1.2$ Hz), since it couples with H–C(11). Its analogue, 'anti'-**48**, shows H–C(8) at 4.611 ppm as *d* (4J with H–C(11) = 1.2 Hz). The other H-atom in bisallylic position C(5) appears at 3.456 ppm (*cf.* 3.413 ppm for 'anti'-**43**) as *d* (4J with H–C(14) = 1.7 Hz (1.6 Hz in 'anti'-**43**)). Therefore, there is no doubt that both structures exhibit the 'anti'-orientation of the two maleic substructures.

The structure proposal for 'anti'- and 'syn'-**45** is based on their ¹H-NMR spectra in CDCl₃ and C₆D₆, on corresponding ¹H-NOE measurements in both solvents as well as on the fact that the other two tetracyclic skeletons have already been assigned to 'anti'-**43** and 'syn'-**44**. Both isomers show the presence of three H-atoms in olefinic and one in bisallylic position. The latter one has two vicinal Me groups which are linked to an olefinic C-atom and to a C-atom in a bridgehead position. It appears as a clear *d* with an allylic coupling constant (4J) of 1.86 and 1.67 Hz, respectively. One of the H-atoms in olefinic position appears in both isomers also as a *d* with an allylic coupling constant (4J) of 1.24 and 1.27 Hz, respectively, which is quite typical for allylic coupling between olefinic H-atoms in cyclopentadienes (*cf.* [18]). The 'anti'-configuration for the main isomer follows from observed medium ¹H-NOE at C(13)–COOCH₃ in both solvents when CH₃–C(12) or CH₃–C(7) is irradiated.

3. Discussion. – Table 1 presents a survey of the described results. It is quite obvious that the amount of the tetracyclic compounds of type 'anti'-**V** strongly depend on the number of Me groups in the *peri*-positions of the starting azulenes as long as we regard only alkyl substituted azulenes. If one Me group is missing at the five-membered ring of the azulene moiety the amount of 'anti'-**V** is reduced by a factor of at least 6 (*cf.* the reaction of **15** in comparison to that of **25**). A similar effect is observed when a *peri*-position at the seven-membered ring is not occupied (*cf.* the reaction of **1** in comparison to

Table 1. *Product Composition of the Thermal Reaction of Azulenes with ADM^{a)}*

Starting Azulene	R ¹	R ²	No.	Tetra-cycle 'anti'-V ^{b)}	Tri-cycle E ^{b)}	Tetra-cycle 'syn'/'anti'-VI ^{b)}	Azulene-1,2-dicarboxylates	Heptalene-1,2-dicarboxylates
	H	Me	1	60 (5)	2.7 (4)	— ^{c)}	~ 1 (3)	4.8 (2)
	Me	Me	6	47 (9)	2.1 (8)	— ^{c)}	< 0.5 (3)	12 (7)
	H	Pr	11	38 (14)	— ^{c)}	— ^{c)}	40 (13)	19.5 (12)
	H	<i>t</i> -Bu	15	69 (16) ^{d)}	— ^{c)}	— ^{c)}	— ^{e)}	— ^{e)}
	H	Me	21	— ^{c)}	— ^{c)}	5.0 (24) ^{f)}	(39) (22) ^{g)}	(40) (23) ^{g)}
	Me	Me	38	—	—	5.9 (40) ^{f)}	9.8 (22)	36–58 (39)
							1.7 (3)	
	H	<i>t</i> -Bu	25	8.2 (29) 3.4 (30) ^{h)}	—	—	18 (26)	18 (27)
	—	—	32	9.8 (36) 3.9 (37)	—	< 1 (35) ⁱ⁾	21 (33)	7 (34)
	Me	—	41	2.7 (43)	—	~ 0.1 (44) ^{f)}	7 (22)	61 (42)
	E _{Me}	—	46	50 (48)	—	—	25.5 (22)	19.4 (47)

^{a)} Amounts in %. 3–5 molar excess of ADM in decalin or tetralin at 180–200°. ^{b)} Cf. Scheme 2; in parentheses formula numbers. ^{c)} Not observed⁵⁾. ^{d)} Includes 7% of the pentacyclic compound **17**. ^{e)} Observed but not isolated. ^{f)} 'syn'-structure. ^{g)} Values in parentheses taken from [4]. ^{h)} Includes 0.5% of the pentacyclic compound **31**. ⁱ⁾ 'anti'-structure.

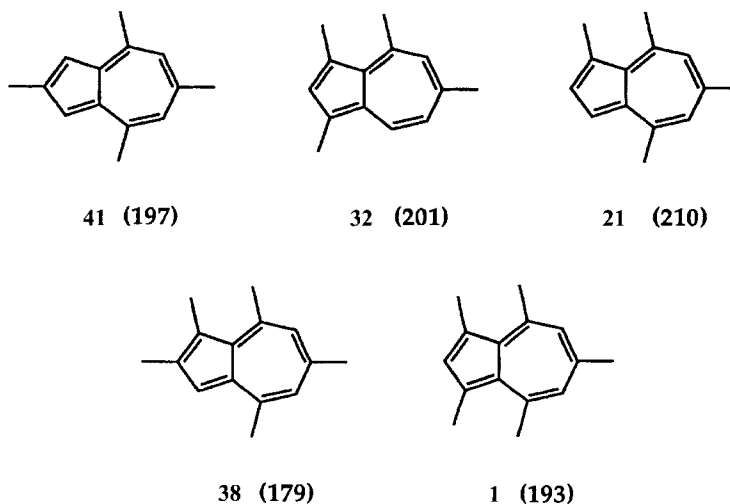
that of **32**). If both *peri*-positions at the five membered ring are not occupied by Me groups the amount of the tetracycle of type 'anti'-V is further reduced (cf. the reaction of **41**)⁸⁾. However, there are exceptions. For example, the thermal reaction of 1,4,6,8-tetramethyl- and 1,2,4,6,8-pentamethylazulene (**21** and **38**, respectively), both with three Me groups in *peri*-position, gave with ADM no detectable tetracyclic compounds of type 'anti'-V at all. On the other hand, the exchange of the Me group at C(2) of **41** by a COOCH₃ group (→**46**) reduces the thermal reactivities of the azulene **46** against ADM but increases the amount of the tetracyclic compound of type 'anti'-V from 2.7% to 50%.

All these observations can be understood, if we regard the expected actual concentration and reactivity of the primary intermediates **A** (cf. Scheme 2) formed reversibly in a concerted *Diels-Alder*-type thermal addition of ADM to the five-membered ring of the azulenes⁹⁾.

⁸⁾ The reaction of 1,4,6- and 1,6,8-trimethylazulene with ADM in decalin at 180–200° yields only the corresponding heptalenedicarboxylates (44% and 12%, respectively) and azulene-1,2-dicarboxylates (8% and 40%, respectively) [19]. (1 + 2) Adducts were not observed.

⁹⁾ The thermolysis of dimethyl 3-isopropyl-6,11-dimethyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate (cf. **62**, Scheme 17) yields guaiazulene and ADM with $\Delta H_{298}^\ddagger = 109.6$ (110.5) kJ mol⁻¹ and $\Delta S_{298}^\ddagger = 10.0$ (–4.6) J grd⁻¹ mol in MeCN (decane) [13] [20], i.e. the transition state of the cleavage reaction which should be, on grounds of microscopic reversibility, the same as for the cycloaddition step show little influence by the solvent as expected for a concerted process.

Scheme 12 shows the calculated ΔH_f° values of the investigated tetra- and penta-methylated azulenes. Obviously, the ground-state energy of the azulenes are raised with the number of Me groups in its *peri*-positions, *i.e.* the thermal preequilibrium between the azulenes, ADM and the tricyclic intermediates **A** (see *Scheme 2*) should be shifted with the number of Me groups in *peri*-positions towards **A**. In the presence of excess ADM, the bimolecular *Diels-Alder* reaction of **A** with ADM can effectively compete with the unimolecular reactions of **A** to yield the corresponding heptalene- and azulene-1,2-dicarboxylates (*cf.* *Scheme 2*). This effect is especially pronounced in all cases where all four *peri*-positions of the azulenes are occupied by Me groups (see *Schemes 3* and *4*). On the

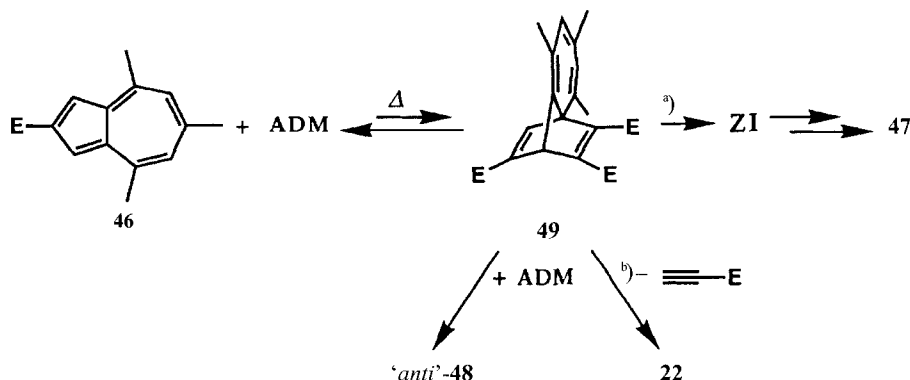
Scheme 12^{a)}

^{a)} In brackets ΔH_f° (kJ mol⁻¹) according to AM1 calculations [21].

other hand, the formation of the tetracyclic compounds of type **V** may also be favored, when the actual concentration of the tricyclic intermediates **A** is low, and the unimolecular reactions of **A** are disfavored for electronic reasons. This seems to be the case in the reaction of the azulene-2-carboxylate **46** with ADM (see *Scheme 11*). The expected tricyclic intermediate **49** should not undergo easily the rearrangement to the corresponding heptalenes **47**, since the heterolytic cleavage of the C(1)–C(10) bond must be retarded by the σ - and π -acceptor effect of the COOCH₃ group at C(12) (*Scheme 13*). Indeed, in the thermal reaction of **46** with ADM the formation of the tetracyclic compound ‘*anti*’-**48** predominates, whereas the corresponding reaction of the sterically comparable azulene **41** is governed by heptalene formation, and the generation of the tetracyclic compound ‘*anti*’-**43** plays only a minor rôle (see *Scheme 11*).

The formation of the tricyclic intermediates **A** seems also be dependent on Me substituents placed at C(6) and/or C(8) in the course of their formation from azulenes and ADM. The structural analysis of the products from the reaction of 1,4,6,8-tetramethyl-

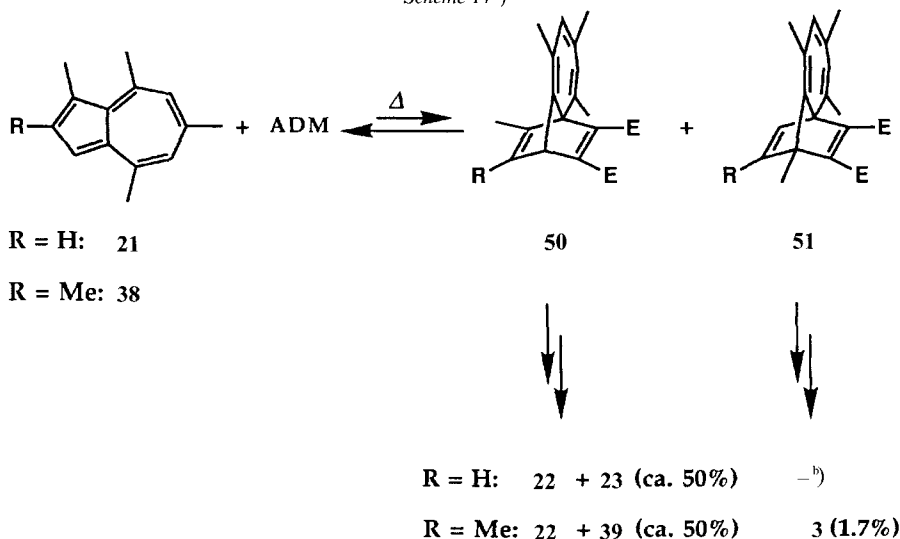
Scheme 13



^{a)} Formation of a corresponding zwitterionic intermediate **ZI** by heterolytic cleavage of the C(1)–C(10) bond.

^{b)} *Retro-Diels-Alder* reaction by concerted cleavage of the C(1)–C(11) and C(8)–C(12) bond.

(**21**) and 1,2,4,6,8-pentamethylazulene (**38**) shows that from the two possible tricyclic intermediates **50** and **51** ($R = \text{H}$ or Me) only one, namely **50**, is exclusively ($R = \text{H}$) or at least predominantly ($R = \text{Me}$) responsible for the formation of the products (*cf.* Scheme 14 as well as Schemes 8 and 10). This is also true for the thermal reaction of 6-(*tert*-butyl)-1,4,8-trimethylazulene (**25**; *cf.* Scheme 8) which gave products, derived from tricyclic intermediates comparable with **50** and **51** ($R = \text{H}, \text{Me}-\text{C}(4) \rightarrow t\text{-Bu}-\text{C}(4)$), to an extent of *ca.* 40% and 8%, respectively¹⁰).

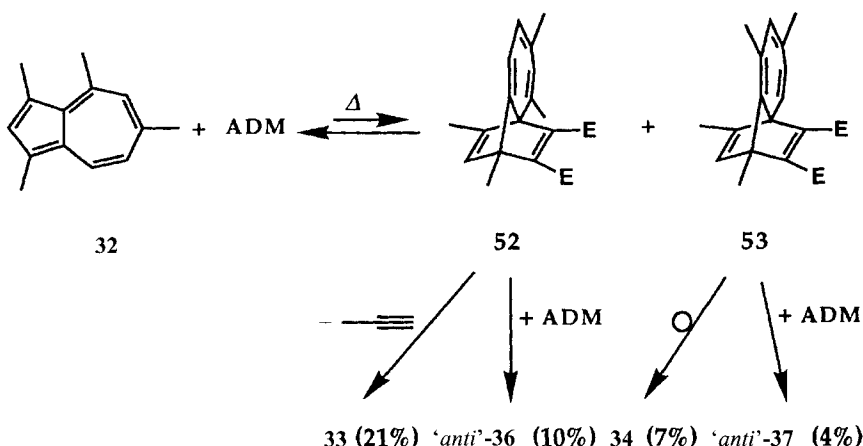
Scheme 14^{a)}

^{a)} *Cf.* also [4]. ^{b)} No products observed⁵⁾.

¹⁰⁾ For further examples showing the discussed tendencies, see [2–5] as well as [15].

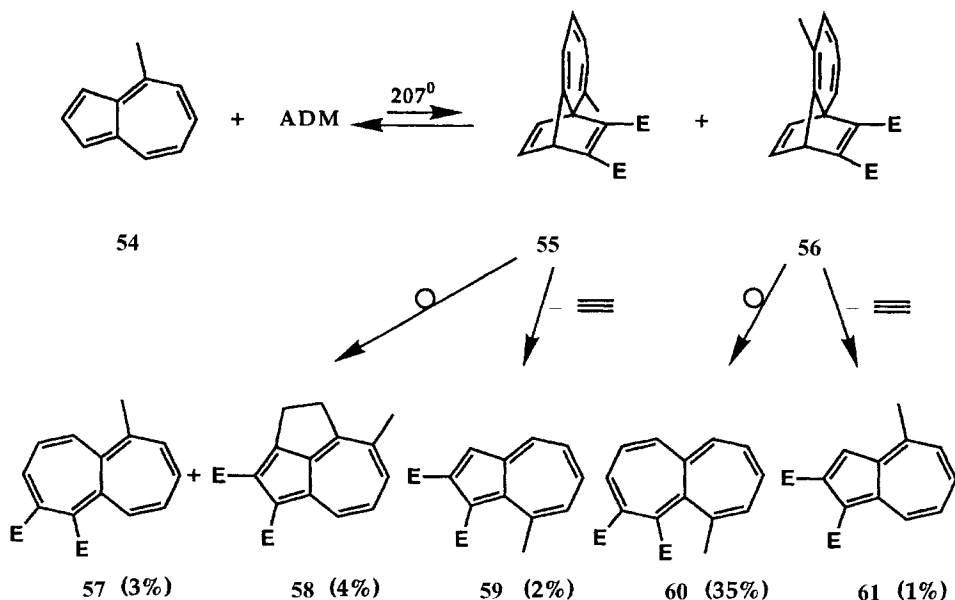
Another interesting case is represented by the thermal reaction of 1,3,4,6-tetramethylazulene (**32**) with ADM (see *Scheme 9*), since both reaction centers at the five-membered ring (C(1) and C(3)) are occupied by Me groups. The structural analysis of the products shows that both possible tricyclic intermediates **52** and **53** are involved in product formation (*Scheme 15*). However, once again the pathway *via* **52** that carries only one Me group in the discussed C-positions 6 and 8, namely at C(8), predominates clearly over the pathway *via* **53** that exhibits Me groups at C(6) and C(8). From these observations, the rule can be derived that product formation in the thermal reaction of unsymmetrically substituted azulenes with ADM will be determined by the tricyclic intermediate having the minimum number of alkyl substituents at C(6) and C(8). This intermediate will be less sterically congested and, therefore, will have the higher concentration in the thermal equilibrium between the corresponding azulene and excess ADM.

Scheme 15



The structural analysis of the products of the last reaction teaches us another rule of thermal heptalene formation from azulenes and ADM in apolar solvents, namely that the generation of the heptalene-1,2-dicarboxylates from the tricyclic intermediates is strongly favored by a Me group at C(6). In the present case, only the tricyclic intermediate **53** gives rise to the formation of the corresponding heptalene-1,2-dicarboxylates **34**, whereas its counterpart **52** undergoes the corresponding *retro-Diels-Alder* reaction to yield the azulene-1,2-dicarboxylate **33**. Another typical example, taken from the work of *Hafner et al.* (*cf.* [2]), is shown in *Scheme 16*. The amount of the heptalene-1,2-dicarboxylate **60**, arising from the tricyclic intermediate **56** with the Me substituent at C(6), exceeds the amount of the heptalene-1,2-dicarboxylate **57**, derived from the alternative tricyclic intermediate **55** with the Me substituent at C(2), by a factor $> 10^{11}$). Responsible for this effect is the σ -donor and hyperconjugative π -donor property of the Me group at C(6) that favors the

¹¹⁾ For further examples in accordance with the formulated 'C(6)–Me rule' for heptalene formation, see [1–5] [13] [20].

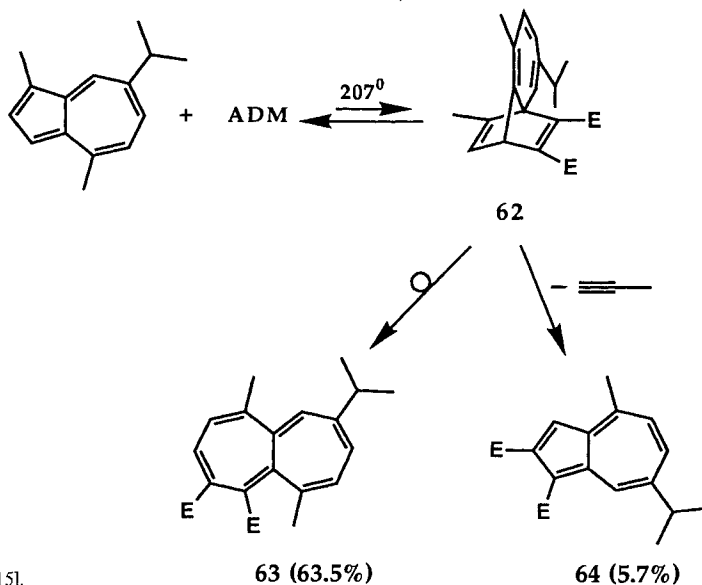
Scheme 16^{a)}

^{a)} The arrows with the attached circles should symbolize rearrangements *via* corresponding zwitterionic intermediates (cf. **ZI** in Scheme 1) and consecutive intermediates of type **B** and **D** (cf. Scheme 1).

heterolytic cleavage of the C(1)–C(10) bond already at an early stage of charge development at C(1). A similar effect should be expected when C(3) in the tricyclic intermediates of type **A** is substituted by Me or alkyl groups. This is indeed the case (cf. [13] [20]). The fact that the thermal reaction of guaiazulene and ADM in tetralin gives the highest yield so far observed of a heptalene-1,2-dicarboxylate (cf. **63**; Scheme 17) may be attributed to the cumulative σ -donor and π -hyperconjugative effect of the *i*-Pr group at C(3) and the Me group at C(6)¹²⁾.

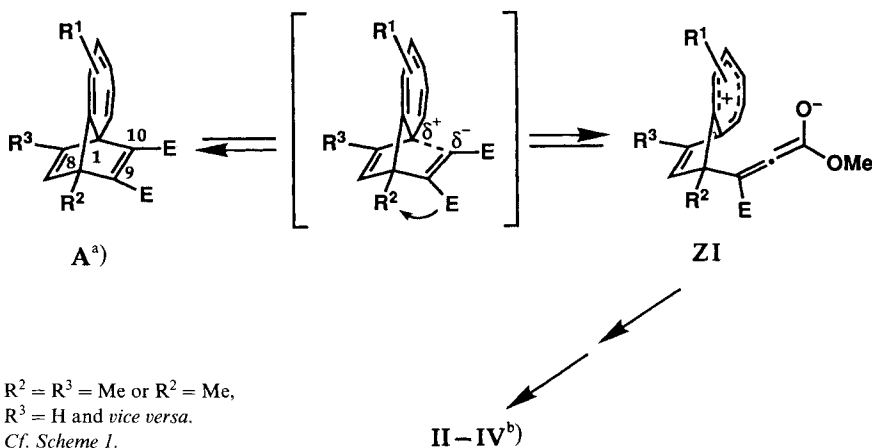
Another general property of reactivity of the tricyclic intermediates of type **A** can be recognized by comparing the amounts of heptalene-1,2-dicarboxylates obtained from the differently substituted azulenes with ADM. The yields of heptalene-1,2-dicarboxylates from 1,3-dimethylazulenes are appreciably smaller in comparison to those from similar 1-methylazulenes. The tricyclic intermediates arising from the 1,3-dimethylazulenes and ADM necessarily bear a Me substituent at the bridgehead position (C(8)), whereas the tricyclic intermediates formed from the 1-methylazulenes normally carry the regarded Me substituent at C(11), *i.e.* the bridgehead position is not occupied. The second possible tricyclic structures from 1-methylazulenes and ADM, in general formed in minor amounts (*vide supra* and, for example, Scheme 8), would, of course, exhibit the Me

¹²⁾ The kinetic data of the thermal reaction of **62** and of analogous tricyclic compounds are in agreement with this view (cf. [13] [15]).

Scheme 17^{a)}

^{a)} See [3] [13] [15].

substituent at C(8). The formation of the zwitterionic intermediates **ZI** (cf. Scheme 18) from the tricyclic structures of type **A** starts with the stretching of the C(1)–C(10) bond in **A**. This means that in the completely rigid tricyclic structure **A** the COOCH₃ substituent at C(9) will move to a certain extent towards the substituent R² at C(8). This movement should be hindered more strongly, when C(8) is substituted by a Me group or another alkyl group, *i.e.* the heptalene formation that occurs necessarily by the described process *via* **ZI** should decrease in cases where R² in **A** represents a Me group or another alkyl substituent. An extreme example is represented by the thermal reaction of 1,3-dimethyl-

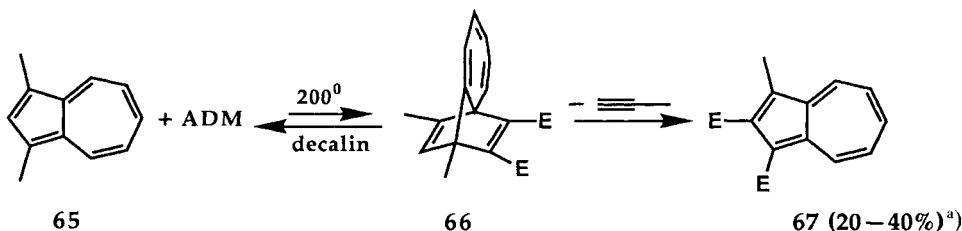
Scheme 18


^{a)} R² = R³ = Me or R² = Me,
 R³ = H and *vice versa*.

^{b)} Cf. Scheme 1.

azulene (**65**) and ADM at 200 or 207° which results in the sole formation of the corresponding azulene-1,2-dicarboxylate **67** (Scheme 19) [16] [2], i.e. the concerted stretching of the C(1)–C(11) and C(8)–C(12) bond which leads to the transition state of the *retro-Diels-Alder* reaction yielding **67** is favored over the formation of the zwitterion that results from stretching of the C(1)–C(10) bond¹³).

Scheme 19



^{a)} In the presence of a seven-fold molar excess of ADM, a 1:1 mixture of **67** (20%) and the corresponding tetracyclic compound 'anti'-**VI** (cf. Scheme 2) is formed [16]. At 207° in tetralin, the formation of 40% of **67** was observed [2].

What has been discussed here for an extreme example is also reflected in other thermal reaction of azulenes with ADM described in this paper. For example, the structural analysis of the products of the thermal reaction of 6-(*tert*-butyl)-1,4,8-trimethylazulene (**25**) with ADM showed that both possible tricyclic intermediates **50** and **51** (R = H, Me–C(4)→*t*-Bu–C(4); cf. Scheme 14) are formed. However, the observed heptalenes are only derived from **50** which carries the Me group at C(11) (cf. also Scheme 8). Also in the thermal reaction of 1,2,4,6,8-pentamethylazulene (**38**) with ADM the tricyclic intermediate **51** (R = Me) which is formed in minor amounts (cf. Scheme 14) and carries a Me group at C(8) shows no heptalene formation but only formation of the corresponding azulene-1,2-dicarboxylate **3** (1.7%)¹⁴.

We have discussed the formation of heptalene- and azulene-1,2-dicarboxylates in apolar solvents such as tetralin or decalin at temperatures > 180° as a result of the highly reversible generation of tricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentane-9,10-dicarboxylates (cf. A, Scheme 2) from azulenes and ADM and the intrinsic reactivity properties of these primary intermediates. However, the system azulene/ADM shows a second reactivity pattern at 200° that is not coupled with the discussed one and leads to the formation of tricyclic compounds of type **E** (see Scheme 2) which may combine with excess ADM in a *Diels-Alder* reaction to yield tetracyclic structures of type 'anti'-**VI** (or 'syn'-**VI**)¹⁵. The

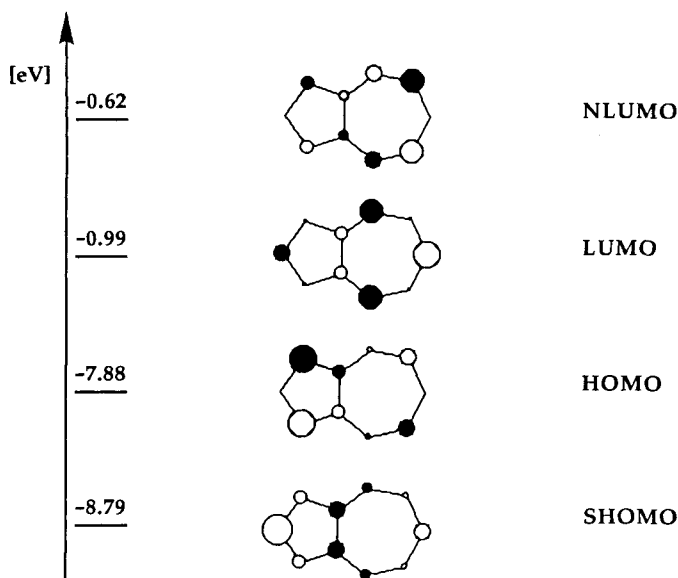
¹³⁾ Of course, the other *retro-Diels-Alder* reaction leading to the starting material should also be favored over the formation of the zwitterion.

¹⁴⁾ I may be that traces of the corresponding heptalene-1,2-dicarboxylate derived from **51** (R = Me) were not detected⁵). However, the general feature of heptalene- and azulene-1,2-dicarboxylate formation from the tricyclic intermediates of type A is that, as a rule, the formation of heptalene-1,2-dicarboxylate predominates.

¹⁵⁾ Formal cleavage of the C(8), C(9) bond in the tricyclic intermediates A would lead to an intermediate diradical (or zwitterion) that could recombine at C(6), C(8) to yield the tricyclic structures of type **E**. Such a process is unprobable on thermochemical grounds. The structural strain in the tricyclic compounds of type A is mainly located in the C(1), C(10) bond which is distinctly longer than its C(8), C(9) counterpart bond according to an X-ray diffraction analysis of **62** (cf. Scheme 17) [13] [20].

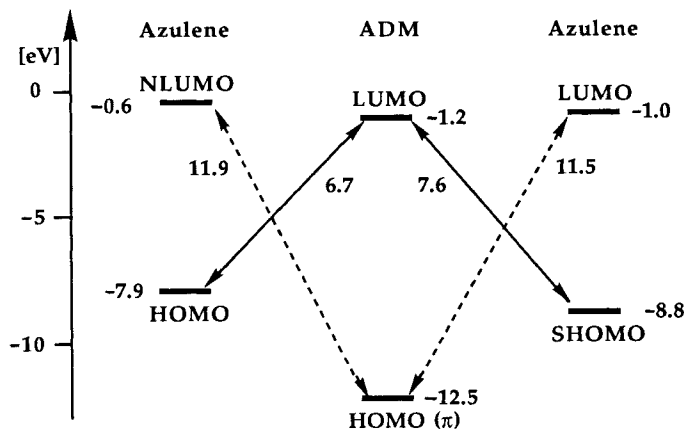
formation of **E** as well as of 'anti'-**VI** occurs irreversibly under the applied conditions. The amount of **E** (cf. **4** and **8**; Table 1) or their *Diels-Alder* adducts with ADM (cf. 'syn'-**24**, 'syn'-**40** or 'syn'-**44** as well as 'anti'-**35**; Table 1) varies in the range of ca. 0.1 to 6%, i.e. the formation of **E** or 'syn'/'anti'-**VI** takes place to a much smaller extent than the formation of products arising *via* the tricyclic intermediates **A** (cf. Scheme 2). On the other hand, the formation of **E** or 'syn'/'anti'-**VI** seems to be much less prone to the substitution pattern of the azulenes. They are constantly present in the reaction mixtures in small percentages except for the cases where the involved azulenes carry alkyl substituents at C(6) which exceed the steric encumbrance of a Me group (cf. **11** and **15** in Scheme 4). We have to assume that the tricyclic compounds of type **E** are formed directly from the azulenes and ADM¹⁵) in a *Diels-Alder*-type cycloaddition competing with the one leading to the formation of the tricyclic compounds of type **A** (Scheme 2). Such type of reaction selectivity of π systems is, in principle, wellknown and called *site selectivity* of cycloaddition reaction (cf. [21]). According to frontier-orbital theory, it is governed by the magnitude of the respective orbital coefficients in the site determining HOMO/LUMO interaction (cf. also [22]). Scheme 20 shows the frontier HMO of azulene [23]. The

Scheme 20



cycloaddition of ADM to the five-membered ring is strongly retarded by π - and σ -acceptor substituents at the five-membered ring. Thus, there is little doubt that the cycloaddition of the electron-deficient ADM to the five-membered ring of azulenes is – as in many other reactions of azulenes (cf. [24]) – determined by the corresponding HOMO(azulene)/LUMO(ADM) interaction in perfect agreement with the symmetry of the involved MO. However, the site-selective cycloaddition of ADM to the seven-membered ring of the azulenes cannot be the result of the same HOMO(azulene)/LUMO(ADM) interaction at

C(3a) and C(6), since one of the nodal planes of the HOMO(azulene) passes through C(2) and C(6). On the other hand, the HOMO(ADM) energy (see *Scheme 21*) is too low that the reverse interaction, namely LUMO(azulene)/HOMO(ADM) should become determining. The accompanying interaction, *i.e.* SHOMO(azulene)/LUMO(ADM), however, is of the right order and symmetry to compete energetically with the HOMO(azulene)/LUMO(ADM) interaction and should give rise for the observed site-selectivity.

Scheme 21^{a)}

^{a)} MO energies of azulene¹⁶⁾ and ADM (as diacid) according to AM1 calculations (*cf.* Table 2).

Scheme 21 shows the MO energies of the involved orbitals¹⁷⁾. The energy difference of 0.9 eV of the two discussed site-determining MO interactions is also found for the methylated azulenes investigated in this work (see Table 2). Responsible for the fact that

Table 2. Frontier-Orbital Energies of Azulene and Some of Its Methyl Derivatives^{a)}

Azulene No.	Position of Me Groups	MO Energies [eV]				ΔE [eV] ^{b)}		
		SHOMO	HOMO	LUMO	NLUMO	Δ_1	Δ_2	$\Delta_1 - \Delta_2$
1	1, 3, 4, 6, 8	-8.39	-7.49	-0.85	-0.46	6.3	7.2	0.9
21	1, 4, 6, 8	-8.45	-7.61	-0.89	-0.46	6.5	7.3	0.8
32	1, 3, 4, 6	-8.47	-7.52	-0.89	-0.51	6.5	7.3	0.8
38	1, 2, 4, 6, 8	-8.23	-7.60	-0.88	-0.43	6.4	7.1	0.7
41	2, 4, 6, 8	-8.26	-7.75	-0.92	-0.43	6.6	7.1	0.5
—	—	-8.79	-7.88	-0.99	-0.62	6.7	7.6	0.9

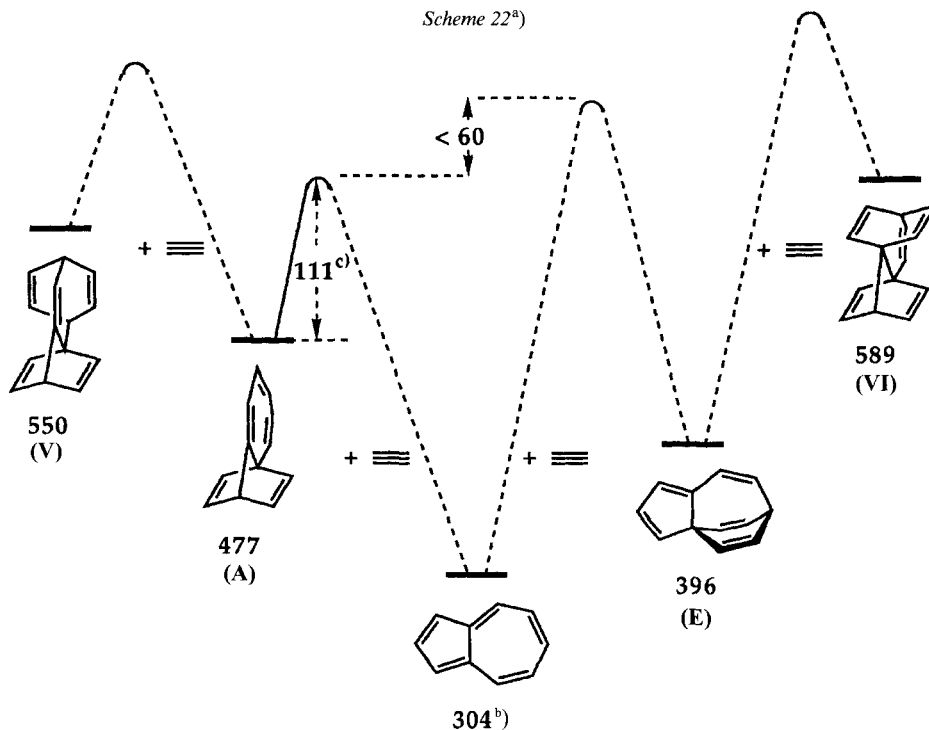
^{a)} Frontier orbital energies according to AM1 calculations with MOPAC V6.0 [27].

^{b)} $\Delta_1 = E(\text{LUMO}_{\text{ADM}} = -1.16 \text{ eV}) - E(\text{HOMO}_{\text{Azulene}})$; $\Delta_2 = E(\text{LUMO}_{\text{ADM}}) - E(\text{SHOMO}_{\text{Azulene}})$.

¹⁶⁾ For *ab initio* calculations of azulenes, *cf.* [25] and literature cited there.

¹⁷⁾ Indeed, we observed the formation of a tetracyclic compound of type *anti*-**VI**, beside the established products [1], also with azulene itself and ADM [16]. Subjacent orbital control in pericyclic reactions has already been discussed, however, in terms that HOMO 'forbidden' reaction may become 'allowed' by intervention of the corresponding SHOMO showing the right orbital symmetry (*cf.* [26] as well as [21]).

the SHOMO-controlled cycloaddition of the azulenes can compete with the HOMO controlled reaction is the high reversibility of the latter one. *Scheme 22* shows the ΔH_f° values of the parent compounds of the two observed tricyclic structures and their consecutive tetracyclic structures arising from the *Diels-Alder* reaction with acetylene. The high



^{a)} ΔH_f° values [kJ mol^{-1}] according to MM3 calculations [28]. ^{b)} ΔH_f° [kJ mol^{-1}] according to AM1 calculations (cf. Table 2). ^{c)} $\Delta H_{298}^\ddagger$ [kJ mol^{-1}] for the *retro-Diels-Alder* reaction of the tricyclic compound **62** from guaiazulene and ADM (cf. Scheme 17) in decane [13].

ΔH_f° value for the tricyclic structure of type **A** explains the high degree of reversibility with the starting materials. On the other hand, the second tricyclic structure of type **E** is by $> 80 \text{ kJ mol}^{-1}$ more stable than **A** which explains its irreversible formation in competition to **A** despite the fact that acetylene (ADM) has to interact on orbital-symmetry grounds with the energetically less favorable SHOMO. The two final tetracyclic structures **V** and **VI** show a difference of 39 kJ mol^{-1} in favor of **V** in their calculated ΔH_f° values¹⁸⁾. Therefore, it is plausible that the tricyclic structures **A** with the appreciably higher energy content will undergo much easier the *Diels-Alder* reaction to yield **V** ($\Delta H_f^\circ(\text{V}) - \Delta H_f^\circ(\text{A}) = 73 \text{ kJ mol}^{-1}$) than the tricyclic structure **E** which leads to the formation of **VI** (ΔH_f°

¹⁸⁾ The third observed tetracyclic skeleton (cf. 'anti'- and 'syn'-**45** in Scheme 11) shows a MM3-calculated ΔH_f° of 585 kJ mol^{-1} , i.e. comparable with those of the fundamental structures of **V** and **VI**.

(VI) – $\Delta H_f^\circ(\text{E}) = 193 \text{ kJ mol}^{-1}$). Indeed, the thermal reaction of 1,3,4,6,8-pentamethyl-(1) as well as of 1,2,3,4,6,8-hexamethylazulene (6; cf. Scheme 3) with ADM demonstrates that steric congestion may prevent the formation of tetracyclic compounds of type ‘anti’- or ‘syn’-VI but not the formation of the corresponding compounds of type ‘anti’-V (cf. Scheme 2).

All thermal ADM additions to the tricyclic intermediates of type A in decalin or tetralin at 200° occur in an ‘anti’ manner (cf. Scheme 2). We never observed tetracyclic compounds having a ‘syn’-relation of the two maleic ester substructures (cf. [15]). We suppose that the ‘syn’-face of the cycloheptatriene moiety of A, especially in the region of C(2), is strongly shielded by the COOCH_3 group at C(10). The shielding effect against an approaching ADM molecule may be attributable to steric as well as to dipol/dipol repulsion effects in the apolar solvents. On the other hand, the thermal ADM addition to the cyclopentadiene moiety of the tricyclic compounds of type E seems to follow a steric selection rule saying that the approach of an ADM molecule is hindered by substituents at C(10) and C(11) in the order $\text{Me} > \text{E}_{\text{Me}} > \text{H}$. This means that ‘syn’-VI will be observed when C(11) is substituted by a Me group and ‘anti’-VI when C(11) carries an H-atom (cf. Scheme 2; for a more detailed discussion, see [15] [16]).

4. Structural Features and Spectroscopic Properties of Some Thermal Products. – 4.1. *X-Ray Diffraction Data.* A stereoscopic projection of the structure of the two dimethyl heptalene-4,5-dicarboxylates **7b** and **12b** are shown in Figs. 1 and 2. Since **7b** and **12b**

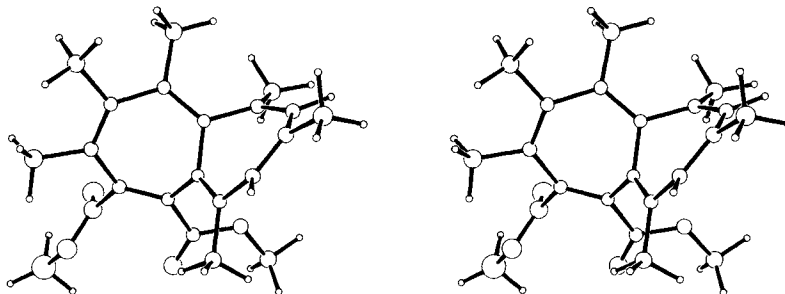


Fig. 1. Stereoscopic projection of the X-ray structure of dimethyl 1,2,3,6,8,10-hexamethylheptalene-4,5-dicarboxylate (**7b**; shown in the (P)-configuration)

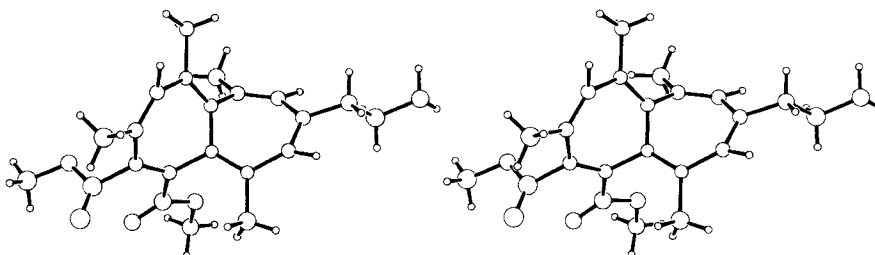


Fig. 2. Stereoscopic projection of the X-ray structure of dimethyl 1,3,6,10-tetramethyl-6-propylheptalene-4,5-dicarboxylate (**12b**; shown in the (P)-configuration)

represent the two heptalene-dicarboxylates with the highest number of alkyl substituents at the heptalene skeleton which have so far been subjected to an X-ray diffraction analysis, it is worthwhile to compare some of their characteristic structural data with those of other, less substituted dimethyl heptalenedicarboxylates (*cf.* Table 3). For all structures, we recognize a clear alternation in the bond lengths. The variation in the average length of the single bonds (ρ_2) is for all structures very small except for dimethyl heptalene-3,8-dicarboxylate (*Entry* 2), where the average single bond length is 3 pm shorter than the mean value of the average single-bond length of the other structures. Dimethyl heptalene-3,8-dicarboxylate possesses no substituent in the *peri*-positions and, therefore, shows the greatest torsion angle of the three sequential single bond vectors (Θ_1) which is a measure of the flatness of the heptalene skeleton. This is also reflected in the average torsion angle around the other four single bonds (*cf.* Θ_3). The smaller average single-bond length in dimethyl heptalene-3,8-dicarboxylate may, therefore, be an expression of the higher degree of conjugation in this molecule. Already one substituent (*e.g.* E_{Me}) in the *peri*-position of the heptalene skeleton is sufficient to strongly fold the skeleton as can be seen from the pronounced decrease in Θ_1 and accompanying increase in Θ_3 in going from *Entry*

Table 3. Characteristic Structural X-Ray Data of Dimethyl Heptalenedicarboxylates

Entry	Heptalene substituents: Position	Torsion angles ^{a)} [°]			Bond angles ^{b)} [°]		Bond lengths ^{c)} [pm]			Ref.
		Θ_1	Θ_2	Θ_3	Φ_1	Φ_2	ρ_1	ρ_2	ρ_3	
1	E _{Me} : 1, 2	120.8	52.5	31.5	125.5	114.9	148.2	145.0	136.0	[29]
2	E _{Me} : 3, 8	143.6	37.9	18.5	127.9	118.7	144.4	142.1	135.1	[30]
3	E _{Me} : 1, 2 i-Pr: 7 Me: 5, 10	112.5	62.7	33.2	124.2	113.3	147.9	144.6	135.2	[10]
4	E _{Me} : 4, 5 t-Bu: 8 Me: 1, 6, 10	113.8	63.6	34.4	123.9	112.1	147.8	145.5	135.0	[5]
5	E _{Me} : 4, 5 Pr: 8 Me: 1, 3, 6, 10 (12b)	117.3	62.2	33.2	123.8	114.1	147.4	146.1	134.4	^{d)}
6	E _{Me} : 4, 5 Me: 1, 2, 3, 6, 8, 10 (7b)	116.5	61.3	32.9	123.7	112.7	147.3	145.5	135.6	^{d)}
7	E _{Me} : 3, 4 Me: 1, 8, 10	119.4	57.9	32.9	124.6	114.1	147.9	145.1	135.0	[19]

^{a)} Θ_1 = Torsion angle of the three sequential σ -bond vectors; Θ_2 = average torsion angle of the two *ac* conformations at the C(5a)–C(10a) bond; Θ_3 = average torsion angle at the four σ -bonds in the two seven-membered rings.

^{b)} Φ_1 = Average bond angle at the seven-membered rings with the exception of $\Phi(5, 5a, 10a)$ and $\Phi(5a, 10a, 10)$; Φ_2 = average of $\Phi(5, 5a, 10)$ and $\Phi(5a, 10a, 10)$.

^{c)} ρ_1 = Average length of the three sequential σ -bonds; ρ_2 = average length of the four residual σ -bond in the perimeter; ρ_3 = average length of the six π -bonds.

^{d)} This work (*cf.* Figs. 1 and 2).

2 to 1. Indeed, further introduction of *peri*-substituents at the heptalene skeleton do only slightly change the said values (*cf.* Entry 7 with two, Entry 3 with three, and the others with 4 substituents in *peri*-position). It seems that the maximum of ‘foldedness’ of the heptalene skeleton is already attained with three substituents in the *peri*-positions, and that further attachment of substituents at the heptalene skeleton induces again a small reduction in the ‘foldedness’ (*cf.* Θ_1 of **7b** and **12b** in comparison with Θ_1 of Entries 3 and 4).

The strain of the heptalenes seems mainly be located around the central single bond (C(5a)–C(10a)). This is indicated by the significantly longer average bond length of the three sequential single bonds (ρ_1) in comparison to the average bond length of the other four single bonds (ρ_2) in the two seven-membered rings. Another strain indicator is the average bond angle at the two ‘intercalated’ heptafulvene substructures (Φ_2) which is in all cases substantially smaller than the average bond angle of the two seven-membered rings of the heptalene skeleton (Φ_1). It is, indeed, also appreciably smaller than the ideal sp^2 bond angle of 120° .

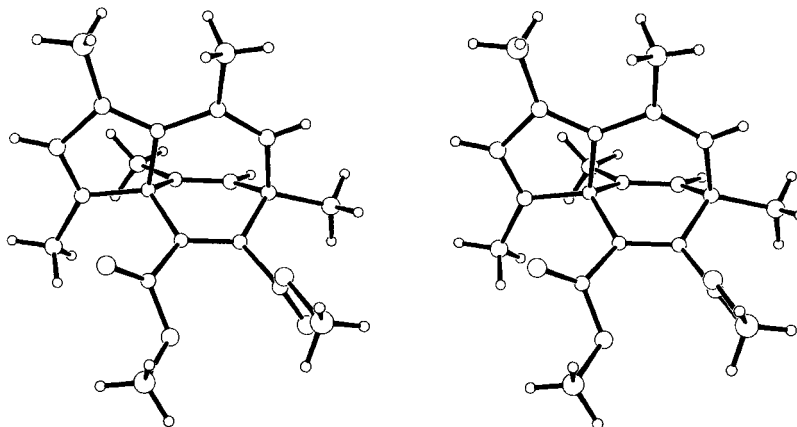


Fig. 3. Stereoscopic projection of the X-ray structure of dimethyl 2,4,6,8,11-pentamethyltricyclo[6.2.2.0^{1,5}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate (**4**)

Fig. 3 shows a stereoscopic projection of the structure of the tricycle **4**. The structure deviates slightly from bisection by a plan passing through C(1) to C(8). The interatomic distance $C(5) \cdots C(11) = 246.6$ pm is slightly shorter than the corresponding distance $C(5) \cdots C(10) = 250.8$ pm. This is also expressed in the bond angles $C(11)–C(1)–C(5) = 105.8^\circ$ and $C(10)–C(1)–C(5) = 109.7^\circ$. The bond length $C(1)–C(11) = 155.0$ pm is the longest $sp^2–sp^3$ bond length in the molecule and well above the average $sp^2–sp^3$ bond length (153.0 pm) in the molecule. On the other hand, the interatomic distance of $C(7) \cdots C(12) = 247.8$ pm is very similar to that of $C(9) \cdots C(12) = 246.5$ pm what is also reflected in the corresponding bond angles $C(7)–C(8)–C(12) = 109.1^\circ$ and $C(9)–C(8)–C(12) = 107.7^\circ$. These structural data of **4** show that in this rigid compound the bridging partial structure $C(11)–C(12)$ is closer to

the transition state of a [1s,5s]-C shift (*cf.* Scheme 6) than the corresponding bridging partial structure C(10)–C(9)¹⁹).

The structure of the tetracyclic compound 'anti'-5 is shown in Fig. 4. It is composed of a 7-methylenenorbornadiene and a cyclohexa-1,4-diene substructure. The rear part of the molecule (see projection in Fig. 4) can also be regarded as a homobarrelene (with C(1) as the 'homo-C atom'). The C–C bond lengths at the two junctions (C(1)–C(2) and C(5)–C(6), respectively) are of interest. The average bond length of 156.0 pm of the four tetrahedral bonds at C(1) is distinctly longer than the average skeletal bond length at C(5) (152.5 pm) and C(8) (154.0 pm), respectively. Thus, most of the steric strain of the molecule seems to be located around the C(1)–C(2) bond which obviously has some impact on the mass-spectrometric behavior of molecules of this type (see Chapt. 4.3).

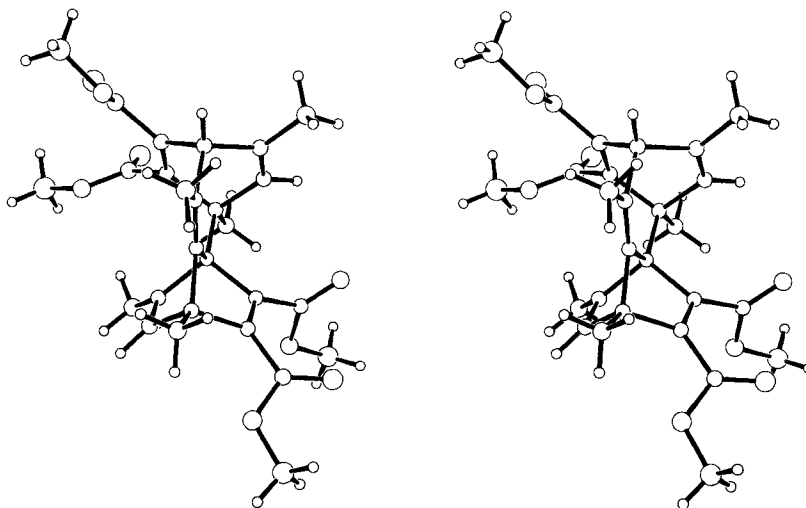


Fig. 4. Stereoscopic projection of the X-ray structure of tetramethyl (1RS,2RS,5RS,8RS)-2,6,8,11,13-pentamethyltetracyclo[6.2.2.2^{2,3,0}^{1,7}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate ('anti'-5)

4.2. ¹H-NMR Spectra of the Tetracyclic Compounds of Type 'anti'-V. The structural assignment of these compounds is well based on the observed chemical shifts, coupling constants, and ¹H-NOE measurement. The spatial relations of the substituents at C(2) and C(11) as well as at C(5) and C(6) is established by strong ¹H-NOE observed between the substituents (Me or H) at this positions. Further support for the elucidation of the

¹⁹) The thermal equilibrium between 4 and 18 as well as between 8 and 19 (*cf.* Scheme 6) shows that, indeed, at least the reactions 18 → 4 and 19 → 8 have to occur *via* [1,5]-C migration of the Me substituted sp²-C-atoms. On the grounds of microscopic reversibility, we have to assume that the corresponding reverse reactions (4 → 18 and 8 → 19) also take place *via* [1,5]-C shifts of C(11)–Me. However, we cannot say at the moment to what extent these migrations are accompanied by [1,5]-C shifts of C(10)–E_{Me}. If we take into account CT contributions to the stabilization of the transition state of sigmatropic rearrangements (*cf.* [31]), we have to assume that C(11)–Me migrates in preference to C(10)–E_{Me}, since CT contributions to the transition state of [1,5] sigmatropic rearrangements in cyclopentadienes will favor a transition state composed of a cyclopentadienide anion and a migrating cation R⁺ (*cf.* [32]). The vinyl cation structure in our case will be destabilized by a COOCH₃ substituent at C(α)⁶).

structures is given by complete sets of 'closed' ^1H -NOE measurements, *i.e.* starting, for example, at $\text{CH}_3\text{--C}(2)$, we can follow the skeletal positions of H and alkyl substituents all around the molecule, until we reach again $\text{CH}_3\text{--C}(11)$ or $\text{H--C}(11)$ which showed a strong ^1H -NOE already when $\text{CH}_3\text{--C}(2)$ was irradiated.

The chemical shifts and coupling constants of the H-atoms at the tetracyclic skeleton are also of importance for the assignments of the skeletal positions. *Table 4* shows the observed typical values for the chemical shifts and coupling constants²⁰⁾.

Table 4. Characteristic Chemical Shifts and Coupling Constants of the Skeletal H-Atoms in Tetracyclic Compounds of Type 'anti'-V^{a)}

Position of H-Atom	δ [ppm] (CDCl_3)	3J [Hz]	4J [Hz] ^{b)}
C(2)	4.33 (1) ^{c)}	6.2 (1)	—
C(5)	3.32–3.45 (5) ^{d)}	—	1.6–1.8 (7)
	3.58 (1) ^{e)}	8.3 (1)	1.8 (1)
C(6)	4.94 (1)	8.3 (1)	1.8 (1)
C(8)	3.92–4.10 (2) ^{f)}	3.3 (1)	1.2 (2)
C(11)	6.54 (1) ^{g)}	—	1.2 (1)
	7.10 (1) ^{h)}	5.4 (1)	—
C(12)	6.15–6.25 (6)	—	1.5–1.7 (6)
	6.49 (1) ^{e)}	3.3 (1)	—
	6.66 (1) ^{h)}	5.4 (1)	—
C(14)	5.60–5.88 (7)	6.2 (1)	1.6–1.8 (7)

^{a)} In parentheses the number of observations.

^{b)} Allylic coupling constants with H-atoms or Me groups at skeletal positions.

^{c)} $\delta(\text{C}_6\text{D}_6) = 4.81$ ppm.

^{d)} δ if C(6) and C(13) are occupied by Me groups.

^{e)} H at C(6).

^{f)} $\delta = 4.61$ ppm if C(12) is occupied by a COOCH_3 group.

^{g)} No Me group at C(8).

^{h)} No Me group at C(11).

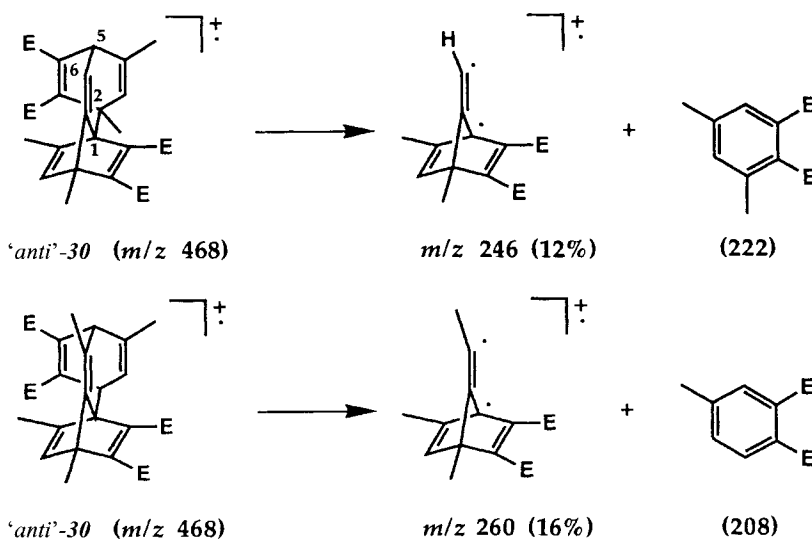
ⁱ⁾ Me group at C(12).

^{j)} H at C(12).

4.3. *Mass Spectra of the Tetracyclic Compounds of Type 'anti'-V.* The mass spectra (EI, 70 eV) of the tetracyclic compounds are mainly determined by fragment ions arising from the degradation of the ester groups, *i.e.* important ions are found at m/z $[M - 31]^+$, $[M - 32]^+$, $[M - 59]^+$ as well as $[M - 32 - 28]^+$ *etc.* However, there is one fragmentation pattern that seems to be quite characteristic for tetracyclic compounds of type 'anti'-V and that is not detectable in the mass spectra of their 'isoskeletal' analogues of type 'anti'- or 'syn'-VI, *i.e.* the fragmentation of the molecular ion (M^+) at C(1), C(2) and C(5), C(6) to yield a corresponding dimethyl phthalate and a residual fragment ion (*cf.* Scheme 23 and Table 5). The charge of M^+ seems to be localized in the 7-methylidene-norbornadiene substructure, since the discussed fragmentation leads to this fragment ion. The corresponding phthalic ion is not detected in the mass spectra. The ion of the 7-methylidenenorbornadiene fragment seems easily to lose MeOH to yield in most of the

²⁰⁾ See also [15] [16].

Scheme 23

Table 5. Loss of Dimethyl Phthalates in the Mass Spectra (70 eV) of Tetracyclic Compounds of Type 'anti'-V^{a)}

Substituent: Position in 'anti'-V	Tetracycle No.	M^+ [m/z]	$[M - \text{Phthalate}]^+$ [m/z]	$[M - \text{Phthalate} - \text{MeOH}]^+$ [m/z]
Me: 2, 6, 8, 11, 13	5	482 (5)	260 (26)	228 (100)
Me: 2, 6, 8, 11, 12, 13	9	496 (43)	274 (26)	242 (31)
Me: 2, 6, 8, 11; Pr: 13	14	510 (13)	260 (42)	228 (100)
Me: 2, 6, 8, 11; <i>t</i> -Bu: 13	16	524 (13)	260 (34)	228 (100)
Me: 2, 8, 11, 13	36	468 (14)	246 (12)	214 (100)
Me: 6, 8, 11, 13	37	468 (10)	260 (16)	228 (100)
Me: 2, 6, 13; E _{Me} : 12	48	512 (31)	290 (14)	258 (72)

^{a)} In parentheses: relative percentages. Masses of the phthalates: dimethyl 4-methylphthalate = 208; dimethyl 3,5-dimethylphthalate = 222; dimethyl 3-methyl-5-propylphthalate = 250.

cases the reference (100%) ion. It is of interest to note that we found a dimethyl phthalate (**28**; cf. Scheme 8) in one of the reaction mixtures of the thermal reaction of a corresponding azulene with ADM. However, we found no thermal fragmentation of the corresponding tetracyclic compound 'anti'-**29** to yield the phthalate, neither in solution nor in the gas phase.

We thank P. Schönholzer, F. Hoffmann-La Roche AG, Basel, and Dr. A. Linden, at our Institute for X-ray diffraction analyses. We also thank Prof. M. Hesse and his coworkers for mass spectra, Prof. W. von Philipsborn and his coworkers for NMR support and a great number of ¹H-NOE measurements, and our microanalytical laboratory under the direction of H. Frohofer for elemental analyses. The financial support of this work by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung and by F. Hoffmann-La Roche AG, Basel, is gratefully acknowledged.

Experimental Part

General. See [4–6] [10] [13]. Anal. and prep. HPCL were performed on a *Hewlett-Packard* instrument (model 1040 A) [13] with the following columns: *Spherisorb CN* (ODS 5 μ m; length 250, diam. 4.5 mm) for anal. runs and *Spherisorb CN* (ODS 5 μ m; length 250, diam. 20 mm) for prep. runs. Column chromatography (CC) if not otherwise stated on Al_2O_3 basic, Act. III or IV.

1. Synthesis of Azulenes. – 1.1. *1,3,4,6-Tetramethylazulene (32)*. 1.1.1. *4,6-Dimethylazulene (68)* (cf. [33]). A 1.1 M soln. of MeLi in hexane (6.8 ml; 9.5 mmol) was added to a soln. of 6-methylazulene (1.14 g; 8.02 mmol; prepared from 1-butyl-4-methylpyridinium bromide and sodium cyclopentadienide in DMF according to [34]) in dry Et_2O (50 ml). The mixture was heated gently until the color had changed (blue $\rightarrow$ grey). The mixture was cooled to -70° and decomposed with MeOH (7 ml). Then, chloranil (2.65 g) in toluene (50 ml) was added and the mixture heated at reflux during 5 h. After cooling, the mixture was extracted with aq. NaOH (4%) and washed with H_2O . The solvent mixture was removed after drying (CaCl_2) and **68** (1.01 g; 80.6%) isolated by CC on Al_2O_3 with petroleum ether (60–90°). $^1\text{H-NMR}$ (300 MHz): 8.199 (*d*, $^3J(\text{H,H-C}(7)) = 9.7$, H–C(8)); 7.714 (*t*, $^3J(\text{H,H-C}(1)) = ^3J(\text{H,H-C}(3)) = 3.8$, H–C(2)); 7.339 (*d*, $^3J(\text{H,H-C}(2)) = 3.8$, H–C(3)); 7.291 (*d*, $^3J(\text{H,H-C}(2)) = 3.8$, H–C(1)); 7.104 (*s*, H–C(5)); 7.003 (*d*, $^3J(\text{H,H-C}(8)) = 9.8$, H–C(7)); 2.878 (*s*, $\text{CH}_3\text{-C}(4)$); 2.635 (*s*, $\text{CH}_3\text{-C}(6)$).

1.1.2. *4,6-Dimethylazulene-1-carbaldehyde (69)* (cf. [35]). PCl_5 (6.25 g, 0.03 mol) was slowly added to DMF (30 ml). A soln. of **68** (4.33 g, 0.028 mol) in DMF (50 ml) was added dropwise under stirring to the cooled *Vilsmeier* soln. A red color appeared immediately. After additional stirring at r.t. during 30 min, the red mixture was poured into ice-water. Usual workup and CC on silica gel (pentane/ Et_2O 3:1) yielded in the first fractions 3.05 g (60%) of **69** and in later fractions 0.27 g (5.2%) of 6,8-dimethylazulene-1-carbaldehyde (**70**).

Data of 69: violet crystals. M.p. 68–70° (hexane). R_f (pentane/ Et_2O 3:1): 0.18. UV (hexane): λ_{max} 382 (3.93), 364 (3.83), 312 (4.57), 303 (sh, 4.49), 244 (4.24), 219 (4.18); λ_{min} 3.72 (3.79), 338 (3.65), 264 (3.70), 232 (4.17). IR (KBr): 2717, 1657, 1567, 1498, 1428, 1412, 1397, 1371, 1290, 1261, 1052, 834, 796, 778, 714. $^1\text{H-NMR}$ (300 MHz): 10.308 (*s*, CHO); 9.477 (*d*, $^3J(\text{H,H-C}(7)) = 10.3$, H–C(8)); 8.102 (*d*, $^3J(\text{H,H-C}(3)) = 4.2$, H–C(2)); 7.469 (*s*, H–C(5)); 7.464 (*d*, $^3J(\text{H,H-C}(8)) \approx 8.9$, H–C(7)); 7.280 (*d*, $^3J(\text{H,H-C}(2)) = 4.3$, H–C(3)); 2.930 (*s*, $\text{CH}_3\text{-C}(4)$); 2.728 (*s*, $\text{CH}_3\text{-C}(6)$). MS: 184 (68, M^+), 183 (100). Anal. calc. for $\text{C}_{13}\text{H}_{12}\text{O}$ (184.24): C 84.75, H 6.57; found: C 85.00, H 6.60.

Data of 70: violet crystals. M.p. 90–91° (hexane). R_f (pentane/ Et_2O 3:1): 0.33. UV (hexane): λ_{max} 387 (3.91), 374 (sh, 3.86), 312 (4.61), 305 (sh, 4.52), 237 (4.30), 222 (4.39); λ_{min} 334 (3.68), 2.60 (3.71), 234 (4.26). IR (KBr): 1625, 1500, 1438, 1363, 1321, 1260, 1045, 827, 769, 750, 725, 700. $^1\text{H-NMR}$ (300 MHz): 10.684 (*s*, CHO); 8.360 (*d*, $^3J(\text{H,H-C}(3)) = 4.3$, H–C(2)); 8.313 (*d*, $^3J(\text{H,H-C}(5)) = 9.9$, H–C(4)); 7.478 (*s*, H–C(7)); 7.351 (*d*, $^3J(\text{H,H-C}(4)) = 9.9$, H–C(5)); 7.227 (*d*, $^3J(\text{H,H-C}(2)) = 4.4$, H–C(3)); 3.197 (*s*, $\text{CH}_3\text{-C}(8)$); 2.711 (*s*, $\text{CH}_3\text{-C}(6)$). MS: 185 (100, $[M + 1]^+$), 184 (10, M^+). Anal. calc. for $\text{C}_{13}\text{H}_{12}\text{O}$ (184.24): C 84.75, H 6.57; found: C 84.68, H 6.78.

1.1.3. *1,4,6-Trimethylazulene (71)*. The reduction of **69** (4.48 g; 0.024 mol) was achieved with $\text{NaBH}_4/\text{BF}_3 \cdot \text{OEt}_2$ in diglyme under the usual conditions (cf. [4] [5] and 1.4) to yield 2.84 g (69%) of **71** as a blue oil after chromatography on silica gel (petroleum ether, 60–90°): 0.36. UV (hexane): λ_{max} 369 (3.25), 352 (3.65), 343 (sh, 3.51), 336 (sh, 3.47), 328 (sh, 3.42), 306 (3.91), 291 (4.73), 285 (4.73), 241 (4.33); λ_{min} 256 (2.93). IR (film): 3059, 1587, 1564, 1511, 1439, 1416, 1384, 1365, 813, 772. $^1\text{H-NMR}$ (300 MHz): 8.081 (*d*, $^3J(\text{H,H-C}(7)) = 9.8$, H–C(8)); 7.532 (*d*, $^3J(\text{H,H-C}(3)) = 3.4$, H–C(2)); 7.241 (*d*, $^3J(\text{H,H-C}(2)) = 3.0$, H–C(3)); 6.977 (*s*, H–C(5)); 6.944 (*d*, $^3J(\text{H,H-C}(8)) = 10.1$, H–C(7)); 2.822 (*s*, $\text{CH}_3\text{-C}(4)$); 2.623 (*s*, $\text{CH}_3\text{-C}(6)$); 2.597 (*s*, $\text{CH}_3\text{-C}(1)$). MS: 171 (100, $[M + 1]^+$), 170 (24, M^+). Anal. calc. for $\text{C}_{13}\text{H}_{14}$ (170.26): C 91.71, H 8.29; found: C 91.63, H 8.05.

1.1.4. *3,6,8-Trimethylazulene-1-carbaldehyde (72)*. The *Vilsmeier* formylation of **71** (2.84 g; 16.7 mmol) was performed as described for **68** (cf. 1.1.2) to yield, after chromatographic workup (CC on silica gel; petroleum ether (60–90°)), 2.80 g (85%) of **72** and, as a by-product, 0.160 g (4.8%) of *3,4,6-trimethylazulene-1-carbaldehyde (73)*.

Data of 72: violet crystals. M.p. 91–93° (hexane). R_f (pentane/ Et_2O 3:1): 0.21. UV (hexane): 399 (4.05), 378 (sh, 3.96), 318 (4.62), 311 (sh, 4.57), 304 (sh, 3.81), 246 (4.39), 220 (4.36); λ_{min} 340 (3.81), 260 (4.06), 230 (4.31). IR (KBr): 1620, 1523, 1433, 1401, 1362, 1288, 1262, 1159, 1088, 877, 818, 775. $^1\text{H-NMR}$ (300 MHz): 10.660 (*s*, CHO); 8.212 (*d*, $^3J(\text{H,H-C}(5)) = 10.0$, H–C(4)); 8.154 (*s*, H–C(2)); 7.398 (*s*, H–C(7)); 7.314 (*d*, $^3J(\text{H,H-C}(4)) = 10.0$, H–C(5)); 3.160 (*s*, $\text{CH}_3\text{-C}(8)$); 2.688 (*s*, $\text{CH}_3\text{-C}(6)$); 2.558 (*s*, $\text{CH}_3\text{-C}(3)$). MS: 198 (100, M^+), 197 (73). Anal. calc. for $\text{C}_{14}\text{H}_{14}\text{O}$ (198.27): C 84.81, H 7.12; found: C 85.07, H 7.35.

Data of 73: violet crystals. M.p. 78–79° (hexane). R_f (pentane/ Et_2O 3:1): 0.20. UV (hexane): λ_{max} 401 (3.89), 380 (sh, 3.87), 317 (4.53), 306 (4.52), 244 (4.28), 224 (4.35); λ_{min} 340 (3.58), 309 (4.58), 260 (3.84), 234 (4.23). $^1\text{H-NMR}$ (300 MHz, D_6 Acetone): 10.132 (*s*, CHO); 9.250 (*d*, $^3J(\text{H,H-C}(7)) = 10.0$, H–C(8)); 7.778 (*s*, H–C(2));

7.291 (s, H–C(5)); 7.240 (d, $^3J(\text{H,H-C}(8)) = 10.1$, H–C(7)); 2.967 (s, CH₃–C(4)); 2.708 (s, CH₃–C(3)); 2.532 (s, CH₃–C(6)). $^1\text{H-NOE}$ (400 MHz, (D₆)Acetone): 2.532 (CH₃–C(6)) → 7.240 (s, H–C(7)), 7.291 (s, H–C(5)); 2.708 (CH₃–C(3)) → 2.967 (s, CH₃–C(4)), 7.778 (s, H–C(2)). MS: 198 (100, M^+), 197 (77). Anal. calc. for C₁₄H₁₄O (198.27): C 84.81, H 7.12; found: C 85.02, H 7.31.

1.1.5. *Reduction of 72 to 32*. The reduction of **72** (2.75 g; 13.9 mmol) with NaBH₄/BF₃·OEt₂ was performed in the usual manner (cf. [4] [5] and 1.4) to yield, after chromatographic workup, 88% (2.25 g) of the azulene **32**. Blue crystals. M.p. 48–49°. R_f (petroleum ether, 60–90°): 0.52. UV (hexane): λ_{max} 373 (3.38), 356 (3.69), 348 (sh, 3.50), 340 (sh, 3.46), 292 (4.68), 287 (4.68), 243 (4.20), 220 (4.02); λ_{min} 368 (3.06); 318 (3.16), 290 (4.66), 260 (4.03), 225 (3.99). IR (KBr): 2919, 1582, 1560, 1526, 1451, 1368, 1344, 1280, 850, 808. $^1\text{H-NMR}$ (300 MHz): 7.902 (d, $^3J(\text{H,H-C}(7)) = 9.9$, H–C(8)); 7.311 (s, H–C(2)); 6.727 (s, H–C(5)); 6.711 (d, $^3J(\text{H,H-C}(8)) = 9.9$, H–C(7)); 2.952 (s, CH₃–C(4)); 2.837 (s, CH₃–C(3)); 2.546 (s, CH₃–C(6)); 2.500 (s, CH₃–C(1)). MS: 185 (100, $[M + 1]^+$), 184 (20). Anal. calc. for C₁₄H₁₆ (184.28): C 91.25, H 8.75; found: C 91.23, H 8.82.

1.2. 2,4,6,8-Tetramethylazulene (**41**). 1.2.1. *Methyl 2-(Hydroxymethyl)-4,6,8-trimethylazulene-1-carboxylate (74)*. Dimethyl 4,6,8-trimethylazulene-1,2-dicarboxylate (**22**; 3.41 g; 11.91 mmol) [4] was dissolved in THF (200 ml). After cooling to –30°, 1M DIBALH soln. in hexane (30 ml) was added dropwise under stirring. After 45 min at –15°, the mixture was carefully hydrolyzed with H₂O and the hydrolysate poured into H₂O (1.5 l). The org. material was extracted (3×) with AcOEt. The AcOEt extract was washed with H₂O, then with sat. NaCl soln., and dried (MgSO₄). Evaporation of AcOEt yielded a first crop of **74**. A further amount of **74** was isolated from the mother liquor by CC on silica gel (AcOEt/hexane 85:15). Recrystallization of the total amount of **74** from Et₂O yielded 1.9 g (62%) of the pure material in red-blue crystals. M.p. 108.5–110.8°. R_f (Et₂O): 0.32. UV (hexane): λ_{max} 372 (sh, 3.43), 354 (3.78), 301 (4.60), 248 (4.34), 228 (4.24); λ_{min} 334 (3.67), 266 (3.70), 233 (4.23), 217 (4.16). IR (CHCl₃): 3474m (OH), 3007s, 2952m, 1675s (COOMe), 1581s, 1557w, 1438s, 1386s, 1374s, 1332m, 1068s, 1008s. $^1\text{H-NMR}$ (300 MHz): 7.26–7.21 (m, H–C(3,5,7)); 4.91 (d, $J = 6.5$, CH₂OH); 3.946 (s, COOCH₃); 3.16 (t-like, OH); 2.865, 2.836 (2s, CH₃–C(4,8)); 2.634 (s, CH₃–C(6)). MS: 258 (100, M^+), 242 (21), 241 (97), 240 (17), 227 (6), 214 (7), 211 (7). Anal. calc. for C₁₆H₁₈O₃ (258.32): C 74.40, H 7.02; found: C 74.15, H 7.14.

1.2.2. *2-(Hydroxymethyl)-4,6,8-trimethylazulene (75)*. The ester **74** (1.8 g; 6.97 mmol) was dissolved in 10% KOH in EtOH/H₂O 1:1 (120 ml) and stirred during 16 h at 70°. The mixture was diluted with 200 ml H₂O and neutralized at 0° with 20% HCl. The org. material was extracted with AcOEt (3×), washed with H₂O, then with sat. NaCl soln., and dried (MgSO₄). Compound **75** was isolated by CC on silica gel (CH₂Cl₂ + 2% MeOH) and crystallized from AcOEt/hexane to yield 1.19 g (85%) of dark blue crystals. M.p. 117.6–118.6°. R_f (Et₂O): 0.40. UV (hexane): λ_{max} 353 (3.77), 337 (3.69), 311 (sh, 3.81), 294 (4.74), 289 (4.72), 247 (4.43); λ_{min} 342 (3.61), 320 (3.51), 291 (4.72), 258 (3.72), 217 (4.12). IR (CHCl₃): 3603w/3468w (OH), 3007s, 2927m, 2873w, 1731s, 1578s, 1480w, 1446m, 1375s, 1333m, 1306m, 1248s, 1088w, 1046s, 1004w. $^1\text{H-NMR}$ (300 MHz): 7.288 (s, H–C(1,3)); 7.073 (s, H–C(5,7)); 5.06 (d, $J = 5.3$, CH₂OH); 2.856 (s, CH₃–C(4,8)); 2.624 (s, CH₃–C(6)); 1.75 (t, $J = 5.7$, OH). MS: 200 (86, M^+), 185 (8), 183 (22), 157 (7), 156 (19), 155 (9). Anal. calc. for C₁₄H₁₆O (200.28): C 83.96, H 8.05; found: C 83.71, H 7.80.

1.2.3. *2-(Chloromethyl)-4,6,8-trimethylazulene (76) and Its Reduction to 41*. Compound **75** (1.343 g; 6.69 mmol) was dissolved in CH₂Cl₂ (135 ml). Ph₃P (2.1 g; 8.03 mmol) was added followed by portionwise addition of *N*-chlorosuccinimide (0.985 g; 7.36 mmol) at 0°. After 1 h additional stirring at 0°, the chloride was isolated by CC filtration on silica gel and elution with Et₂O as a labile blue oil. $^1\text{H-NMR}$ (300 MHz): 7.254 (s, H–C(1,3)); 7.071 (s, H–C(5,7)); 4.944 (s, CH₂Cl); 2.848 (s, CH₃–C(4,8)); 2.618 (s, CH₃–C(6)).

Without further purification the blue oil of **76** was dissolved in DMSO (50 ml) and residues of Et₂O and CH₂Cl₂ were evaporated. Additional DMSO was added (80 ml) and the soln. treated under N₂ with NaBH₄ (1.55 g; 41 mmol) at 20° during 20 h. Workup (addition of H₂O, extraction with Et₂O) and CC on silica gel (hexane/Et₂O 19:1) yielded **41** as a blue oil (0.81 g; 66%). Crystallization from pentane at –20° yielded blue crystals of **41**. M.p. 100–101°. R_f (pentane/Et₂O 7:3): 0.57. UV (hexane): λ_{max} 354 (3.74), 338 (3.61), 313 (3.80), 294 (4.76), 285 (4.71), 246 (4.41); λ_{min} 343 (3.56), 322 (3.46), 310 (3.75), 287 (4.71), 258 (3.65). IR (CHCl₃): 3003m, 2921w, 1578s, 1501s, 1449m, 1374w, 1332s, 1310w, 1088w, 1025w. $^1\text{H-NMR}$ (400 MHz): 7.136 (s, H–C(1,3)); 7.035 (s, H–C(5,7)); 2.835 (s, CH₃–C(4,8)); 2.621/2.612 (2s, CH₃–C(2,6)). MS: 184 (100, M^+), 169 (45), 154 (18), 153 (18), 152 (11), 141 (8). Anal. calc. for C₁₄H₁₆ (184.28): C 91.25, H 8.75; found: C 91.30, H 8.56.

1.3. 1,2,4,6,8-Pentamethylazulene (**38**; cf. also [36]). 1.3.1. *2,4,6,8-Tetramethylazulene-1-carbaldehyde (77)*. Compound **41** (0.385 g; 2.09 mmol) was formylated with DMF/POCl₃ in the usual way (cf. [4] [5] as well as 1.4). Crystallization from AcOEt/hexane yielded **77** (0.40 g; 90%) in wine-red crystals. M.p. 109–110°. R_f (Et₂O/hexane 7:3): 0.20. UV (hexane): λ_{max} 387 (3.79), 367 (3.82), 357 (3.81), 319 (4.65), 309 (sh, 4.57), 246 (4.30), 234 (4.27), 220 (4.24); λ_{min} 379 (3.71), 361 (3.81), 349 (3.79), 277 (3.74), 238 (4.27), 223 (4.23). IR (CHCl₃): 3007m, 1632s, 1584m, 1509m, 1451m, 1427m, 1373m, 1349s, 1330s. $^1\text{H-NMR}$ (300 MHz): 10.80 (s, CHO); 7.363/7.326 (2s, H–C(5,7));

7.068 (s, H–C(3)); 3.104 (s, CH₃–C(8)); 2.856 (s, CH₃–C(4)); 2.796 (s, CH₃–C(2)); 2.653 (s, CH₃–C(6)). CI-MS: 213 (100, [M + 1]⁺), 211 (4), 197 (4), 89 (31). Anal. calc. for C₁₅H₁₆O (212.30): C 84.87, H 7.60; found: C 84.90, H 7.77.

1.3.2. *Reduction of 77*. The reaction was performed with NaBH₄/BF₃·OEt₂ in diglyme in the usual way (cf. [4] [5] as well as 1.4). 0.355 g (1.67 mmol) of **7** yielded, after reduction, by crystallization from pentane at –20°, **38** (0.186 g) in blue crystals. Workup of the mother liquor by CC on Al₂O₃ (hexane/Et₂O 2:3) yielded a further amount of pure **38** (0.138 g; in total 0.324 g; 98%). M.p. 66–69°. R_f (Et₂O/hexane 3:2): 0.62. UV (hexane): λ_{max} 359 (3.67), 344 (3.57), 314 (sh, 3.90), 298 (4.74), 291 (sh, 4.70), 248 (4.35), 202 (4.05); λ_{min} 348 (3.51), 326 (3.36), 262 (3.70), 213 (3.99). IR (CHCl₃): 3002s, 2921m, 2862w, 1577s, 1495m, 1451s, 1373m, 1340w, 1320w, 1263m, 1089m, 1023m. ¹H-NMR (300 MHz): 7.136 (s, H–C(3)); 6.840 (s, H–C(5,7)); 3.000 (s, CH₃–C(8)); 2.766 (s, CH₃–C(4)); 2.718 (s, CH₃–C(1)); 2.521 (s, CH₃–C(6)); 2.492 (s, CH₃–C(2)). MS: 198 (100, M⁺), 184 (11), 183 (79), 167 (14), 165 (16), 153 (10), 152 (10). Anal. calc. for C₁₅H₁₈ (198.31): C 90.85, H 9.15; found: C 90.91, H 9.23.

1.4. 1,3,4,6,8-Pentamethylazulene (**1**). 1.4.1. 3,4,6,8-Tetramethylazulene-1-carbaldehyde (**78**). According to [35], a *Vilsmeier* soln. was prepared by adding POCl₃ (3.2 g; 21.2 mmol) dropwise at 0° to DMF (10 ml). This soln. was added at 15° under stirring and N₂ to 1,4,6,8-tetramethylazulene (3.32 g; 18.0 mmol) [4] in DMF (40 ml). The color of the mixture changed thereby from blue *via* greenish brown to red brown. After 20 min, the mixture was poured onto ice and basified with 4N NaOH. Extraction with Et₂O and CC on Al₂O₃ (Et₂O) yielded **78** in dark wine-red crystals (3.66 g; 96%). M.p. 117–118° (Et₂O). R_f (Et₂O/hexane 1:1): 0.26. UV (cyclohexane): λ_{max} 396 (3.63), 380 (sh, 3.84), 363 (sh, 3.71), 321 (4.56), 313 (sh, 4.50), 280 (sh, 3.86), 250 (4.32), 234 (sh, 4.23), 223 (4.23); λ_{min} 350 (3.65), 274 (3.84), 228 (4.22). IR (KBr): 2960, 2900, 1623s, 1580, 1533, 1508, 1457, 1440, 1429, 1396, 1378, 1347, 1309. ¹H-NMR (250 MHz): 10.572 (s, CHO); 8.049 (br. s, H–C(2)); 7.219/7.192 (2 br. s, H–C(5,7)); 3.081 (s, CH₃–C(8)); 3.027 (s, CH₃–C(4)); 2.773 (s, CH₃–C(3)); 2.600 (s, CH₃–C(6)). MS: 212 (66, M⁺), 197 (100), 195 (45), 184 (3), 183 (6), 180 (12), 165 (17), 153 (15). Anal. calc. for C₁₅H₁₆O (212.29): C 84.87, H 7.60; found: C 84.67, H 7.70.

1.4.2. *Reduction of 78 to 1*. NaBH₄ (2.1 g; 55.5 mmol) was suspended under N₂ and stirring in diglyme (22 ml), and solns. of **78** (3.66 g; 17.24 mmol) in diglyme/Et₂O (1:1; 70 ml) and BF₃·OEt₂ (3.0 ml; 23.5 mmol) in Et₂O (35 ml) were added simultaneously drop by drop under ice cooling. The color of the mixture changed immediately from red to blue. After an additional 1½ h stirring at r.t., the mixture was poured into ice-water. After 30 min, the soln. was extracted with Et₂O (3×) and the azulene **1** isolated by CC on Al₂O₃ (Et₂O/hexane 3:2) and crystallization from MeOH to yield 2.88 g (84%) of the pure material in dark blue plates. M.p. 102–103°. R_f (hexane): 0.26. UV (hexane): λ_{max} 372 (3.23), 360 (3.74), 343 (3.58), 300 (4.69), 295 (4.69), 290 (4.70), 285 (sh, 4.57), 248 (4.35), 217 (4.04); λ_{min} 370 (3.18), 347 (3.56), 322 (3.23), 298 (4.67), 292 (4.69), 265 (3.96), 226 (4.00), 212 (4.03). IR (KBr): 2952, 2920, 2855, 1687, 1622, 1573, 1551, 1457, 1439, 1401, 1364, 1298, 1259, 1181, 1161, 1106, 1031. ¹H-NMR (250 MHz): 7.200 (s, H–C(2)); 6.618 (s, H–C(5,7)); 2.916 (s, CH₃–C(4,8)); 2.795 (s, CH₃–C(1,3)); 2.435 (s, CH₃–C(6)). MS: 198 (100, M⁺), 183 (54), 167 (13), 165 (13), 158 (4), 155 (4), 153 (9), 152 (9). Anal. calc. for C₁₅H₁₈ (198.31): C 90.95, H 9.15; found: C 90.68, H 8.76.

1.5. 1,2,3,4,6,8-Hexamethylazulene (**6**). Azulene **38** (0.14 g; 0.706 mmol) was formylated and subsequently reduced in the usual way (cf. [4] [5] as well as 1.4). Compound **6** was isolated by CC on Al₂O₃ (hexane/Et₂O 3:2) and crystallized from hexane to yield blue crystals of **6** (0.109 g; 73%). M.p. 106.2–107°. R_f (Et₂O/hexane 3:2): 0.53. UV (hexane): λ_{max} 363 (3.70), 348 (3.59), 302 (4.77), 296 (sh, 4.72), 251 (4.34), 197 (4.26); λ_{min} 353 (3.54), 328 (3.37), 267 (3.89), 229 (4.07). IR (CHCl₃): 2999s, 2918s, 1575s, 1508s, 1456s, 1405m, 1373m, 1314w, 1260w, 1170w, 1094m, 1022m. ¹H-NMR (300 MHz): 6.641 (s, H–C(5,7)); 2.937 (s, CH₃–C(4,8)); 2.712 (s, CH₃–C(1,3)); 2.430 (s, CH₃–C(6)); 2.378 (s, CH₃–C(2)). MS: 212 (100, M⁺), 197 (51), 181 (7), 167 (8), 165 (12), 157 (8). Anal. calc. for C₁₆H₂₀ (212.34): C 90.51, H 9.49; found: C 90.33, H 9.27.

1.6. 1,3,4,8-Tetramethyl-6-propylazulene (**11**). 1.6.1. 4,8-Dimethyl-6-propylazulene (**79**). 2,6-Dimethyl-γ-pyrone (7.5 g; 60 mmol; source *Fluka*) in anisole (80 ml) was reacted with PrMgI in Et₂O (prepared from 18.7 g of PrI and 2.7 g of Mg in 40 ml of Et₂O) under cooling (cf. [37]). After additional stirring for 30 min at 0° 2.5 ml of 50% aqueous HBF₄ were added dropwise. The precipitate was separated by decantation and washed several times with hexane/benzene 3:1 by digestion. It was dried at 40° in high vacuum. A third of this material was added to a soln. of Na-cyclopentadienide in THF to yield, after workup, CC on silica gel (hexane/Et₂O 4:1), and distillation (100–110°/0.02), **79** as a blue oil (1.82 g; 46%). R_f (hexane/Et₂O 9:1) 0.52. ¹H-NMR (200 MHz): 7.66 (t, J = 4, H–C(2)); 7.35 (d, J = 4, H–C(1,3)); 7.04 (s, H–C(5,7)); 2.89 (s, CH₃–C(4,8)); 2.75/1.94/0.98 (t/m/t, CH₃CH₂CH₂).

1.6.2. 4,8-Dimethyl-6-propylazulene-1-carbaldehyde (**80**). The azulene **79** (1.82 g; 9.2 mmol) was formylated in the usual way (cf. [4] [5] and 1.4) to yield, after isolation and crystallization from hexane/toluene, **80** in red crystals (1.28 g; 62%). M.p. 90.5–91.1°. R_f (Et₂O/hexane 9:1): 0.40. UV (hexane): 382 (3.98), 364 (sh, 3.85), 353 (sh, 3.83),

316 (4.63), 308 (sh, 4.56), 246 (4.35), 225 (4.30); $\lambda_{\min}$ 340 (3.78), 270 (3.77), 235 (4.27). IR (CHCl₃): 2965w, 2930w, 1625s, 1580m, 1500m, 1380m, 1330s, 1305w, 1109w, 1063w. ¹H-NMR (200 MHz): 10.66 (s, CHO); 8.29 (d, $J = 4.4$, H-C(2)); 7.37/7.35 (2s, H-C(5,7)); 7.31 (d, $J = 4.4$, H-C(3)); 3.19 (s, CH₃-C(8)); 2.93 (s, CH₃-C(4)); 2.81/1.77/1.01 (t/m/t, CH₃CH₂CH₂). CI-MS: 227 (100, $[M + 1]^+$), 209 (5), 199 (3), 183 (5). Anal. calc. for C₁₆H₁₈O (226.32): C 84.91, H 8.02; found: C 84.69, H 8.21.

1.6.3. *1,4,8-Trimethyl-6-propylazulene (81)*. Aldehyde **80** (0.90 g; 3.96 mmol) was reduced with NaBH₄/BF₃·OEt₂ in diglyme/Et₂O in the usual way (cf. [4] [5] and 1.4). Azulene **81** was isolated and purified by CC on Al₂O₃ (hexane/Et₂O 4:1) to yield 0.73 g (87%) of the pure material in dark blue crystals. M.p. 47.6–48.7°. R_f (Et₂O/hexane 9:1): 0.62. UV (hexane): $\lambda_{\max}$ 345 (3.69), 340 (3.57), 298 (sh, 4.64), 294 (4.67), 289 (4.69), 248 (4.41), 201 (4.14); $\lambda_{\min}$ 318 (3.28), 292 (4.67), 262 (3.78), 225 (3.99). IR (CHCl₃): 3008m, 2965s, 2935m, 2875m, 1573s, 1537w, 1513m, 1443m, 1418w, 1373m, 1337w, 1038w. ¹H-NMR (200 MHz): 7.428 (d, $J = 3.5$, H-C(2)); 7.229 (d, $J = 3.5$, H-C(3)); 6.831 (s, H-C(5,7)); 3.017 (s, CH₃-C(8)); 2.868 (s, CH₃-C(1)); 2.807 (s, CH₃-C(4)); 2.665/1.714/0.974 (t/m/t, CH₃CH₂CH₂). CI-MS: 213 (62, $[M + 1]^+$), 212 (100), 197 (5), 183 (3). Anal. calc. for C₁₆H₂₀ (212.34): C 90.50, H 9.49; found: C 90.76, H 9.75.

1.6.4. *3,4,8-Trimethyl-6-propylazulene-1-carbaldehyde (82)*. Azulene **81** (0.713 g; 3.86 mol) was formylated in the usual way (cf. [4] [5] and 1.4) to yield, after extraction of the hydrolyzed mixture with AcOEt and crystallization from AcOEt/hexane, pure **82** (0.776 g; 96%) in red-violet plates. M.p. 110.5–111.3°. R_f (Et₂O/hexane 9:1): 0.41. UV (hexane): $\lambda_{\max}$ 394 (3.93), 380 (sh, 3.84), 322 (4.58), 312 (sh, 4.53), 251 (4.33), 222 (4.27); $\lambda_{\min}$ 349 (3.66), 272 (3.85), 237 (4.25). IR (CHCl₃): 3007m, 2965m, 2935w, 1620s, 1582w, 1533w, 1444w, 1360m, 1170m, 1111w. ¹H-NMR (200 MHz): 10.60 (s, CHO); 8.07 (s, H-C(2)); 7.20/7.17 (2s, H-C(5,7)); 3.11 (s, CH₃-C(8)); 3.05 (s, CH₃-C(4)); 2.79 (s, CH₃-C(3)); 2.73/1.74/1.00 (t/m/t, CH₃CH₂CH₂). CI-MS: 241 (100, $[M + 1]^+$), 240 (46), 225 (5), 223 (5), 197 (13). Anal. calc. for C₁₇H₂₀O (240.35): C 84.96, H 8.39; found: C 84.74, H 8.13.

1.6.5. *Reduction of 82 to 11*. Aldehyde **82** (0.762 g; 3.17 mmol) was reduced with NaBH₄/BF₃·OEt₂ in diglyme/Et₂O in the usual way (cf. [4] [5] and 1.4) to yield, after workup, CC on Al₂O₃ (Et₂O/hexane 7:3), and crystallization from hexane, pure **11** (0.643 g; 90%) in dark blue needles. M.p. 90.4–91.7°. R_f (Et₂O/pentane 7:3): 0.63. UV (hexane): $\lambda_{\max}$ 359 (3.72), 343 (3.58), 302 (4.68), 295 (sh, 4.69), 291 (4.70), 249 (4.36), 219 (4.09), 200 (4.17); $\lambda_{\min}$ 322 (3.26), 299 (4.66), 266 (3.98), 228 (4.05). IR (CHCl₃): 3007m, 2965s, 2930s, 2875m, 1573s, 1547m, 1512m, 1458m, 1443s, 1373w, 1162w, 1107w, 1030w. ¹H-NMR (200 MHz): 7.21 (s, H-C(2)); 6.60 (s, H-C(5,7)); 2.93 (s, CH₃-C(8)); 2.80 (s, CH₃-C(1,3)); 2.57/1.68/0.96 (t/m/t, CH₃CH₂CH₂). MS: 226 (100, M^+), 211 (28), 197 (19), 183 (12), 181 (10), 179 (8), 169 (8), 167 (13), 166 (9), 165 (16). Anal. calc. for C₁₇H₂₂ (226.37): C 90.20, H 9.80; found: C 90.23, H 10.03.

1.7. *6-(tert-Butyl)-1,3,4,8-tetramethylazulene (15)*. 1.7.1. *6-(tert-Butyl)-3,4,8-trimethylazulene-1-carbaldehyde (83)*. 6-(tert-Butyl)-1,3,8-trimethylazulene (2.54 g; 11.22 mmol) [5] was formylated (1.55 g (16.73 mmol) of POCl₃ in 9 ml of DMF) in the usual way (cf. [4] [5] and 1.4) to yield, after CC on silica gel, **83** in blue crystals which were recrystallized from cyclohexane (1.62 g; 56.7%). M.p. 112.2–113.3°. R_f (Et₂O/hexane 7:3): 0.30. UV (hexane): $\lambda_{\max}$ 391 (3.95), 384 (sh, 3.87), 365 (sh, 3.74), 320 (4.58), 313 (sh, 4.53), 251 (4.32), 224 (4.24); $\lambda_{\min}$ 350 (3.67), 274 (3.86), 229 (4.23). IR (CHCl₃): 3006s, 2968s, 1630s, 1578s, 1537m, 1461m, 1443m, 1398s, 1362s, 1318m, 1246m, 1169m, 1143m, 845m. ¹H-NMR (300 MHz): 10.591 (s, CHO); 8.078 (s, H-C(2)); 7.471, 7.434 (2 br. s, H-C(5,7)); 3.148 (s, CH₃-C(8)); 3.090 (s, CH₃-C(4)); 1.453 (s, *t*-Bu). MS: 254 (100, M^+), 239 (34), 237 (75), 197 (25), 183 (6), 181 (8), 165 (9). Anal. calc. for C₁₈H₂₂O (254.38): C 84.99, H 8.72; found: C 84.76, H 8.69.

1.7.2. *Reduction of 83 to 15*. It was performed in the usual way (cf. [4] [5] and 1.4) by reacting **83** (0.50 g; 1.97 mmol) with NaBH₄/BF₃·OEt₂ in diglyme/Et₂O. Workup and CC on Al₂O₃ (Et₂O) followed by crystallization from MeOH yielded **15** in blue needles (0.281 g; 59%). M.p. 118.2–119.1°. R_f (Et₂O/hexane 3:2): 0.59. UV (hexane): $\lambda_{\max}$ 371 (sh, 3.21), 358 (3.73), 342 (3.58), 300 (4.70), 294 (sh, 4.71), 291 (4.72), 249 (4.36), 220 (4.03); $\lambda_{\min}$ 346 (3.55), 323 (3.24), 298 (4.69), 265 (4.00), 228 (3.97). IR (CHCl₃): 3002s, 2966s, 2872m, 1573s, 1533s, 1518m, 1459s, 1442s, 1372m, 1309w, 1274w, 1262w, 1160w, 1102w, 1017m, 979w, 806m. ¹H-NMR (300 MHz): 7.225 (br. s, H-C(2)); 6.853 (br. s, H-C(5,7)); 2.968 (s, CH₃-C(4,8)); 2.800 (s, CH₃-C(1,3)); 1.389 (s, *t*-Bu). CI-MS: 242 (13, $[M + 2]^+$), 241 (100, $M + 1]^+$).

2. Thermal Reactions of the Azulenes with Dimethyl Acetylenedicarboxylate (ADM). – 2.1. *Azulene 32 and ADM*. The azulene (0.360 g, 1.95 mmol) and ADM (1.11 g, 0.96 ml, 7.81 mmol) were dissolved in freshly distilled decalin (4 ml) and heated under N₂ during 3 h at 200°. Decalin and excess ADM were distilled off, and the residue was subjected to CC (silica gel; hexane/Et₂O 3:2). Fractions containing *dimethyl 3,5,8,10-tetramethylheptalene-1,2-dicarboxylate (34a)* and its DBS isomer **34b** (in total 0.044 g, 7.0%), *dimethyl 3,6,8-trimethylazulene-1,2-dicarboxylate (33)*; 0.170 g, 20.9%), *tetramethyl (1RS,2RS,5RS,8RS)-2,8,11,13-(‘anti’-36)*; 0.90 g, 9.8%) and *-6,8,11,13-tetramethyltetracyclo[6.2.2.2^{2,5}0^{1,7}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate (‘anti’-37)*; 0.036 g;

3.9%) as well as traces (< 1%) of *tetramethyl (1RS,2RS,5RS,8RS)-2,6,8,13-tetramethyltetracyclo-[6.2.2.2^{2,5}.0^{1,5}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate ('anti'-35)* in a mixture with 'anti'-37 were eluted.

Data of 34a. Yellow crystals from hexane. M.p. 161–163°. In soln. at r.t. **34a** readily isomerized into its DBS isomer **34b**. The equilibrium concentrations amounted to 61 % of **34a** and 39 % of **34b**. R_f (hexane/Et₂O 3:2, 0°): 0.29. UV (hexane, qual. according to isomerization): $\lambda_{\max}$ 320 (sh, 3.62), 265 (4.30), 209 (4.35); $\lambda_{\min}$ 247 (4.21). IR (KBr): 2948, 1733/1720, 1430, 1280, 1262, 1227, 1200, 1140, 1067, 1007. ¹H-NMR (300 MHz, 233 K): 6.34 (br. *d*, ³*J*(H,H-C(6)) = 6.5, H-C(7)); 6.14 (br. *s*, H-C(9)); 6.04 (br. *s*, H-C(4)); 5.97 (*d*, ³*J*(H,H-C(7)) = 6.2, H-C(6)); 3.73 (*s*, C(1)-COOCH₃); 3.67 (*s*, C(2)-COOCH₃); 2.28 (*s*, CH₃-C(3)); 2.11 (br. *s*, CH₃-C(8)); 2.06 (br. *s*, CH₃-C(10)); 2.03 (br. *s*, CH₃-C(5)). ¹H-NOE (400 MHz, 30°): 2.03 (CH₃-C(5))→6.04 (*s*, H-C(4)), 5.97 (*s*, H-C(6)); 2.11 (CH₃-C(8))→6.34 (*s*, H-C(7)), 6.14 (*s*, H-C(9)); 2.28 (CH₃-C(3))→6.04 (*s*, H-C(4)); 6.04 (H-C(4))→2.28 (*s*, CH₃-C(3)), 2.03 (*s*, CH₃-C(5)); 6.14 (H-C(9))→2.11 (*s*, CH₃-C(8)), 2.06 (*s*, CH₃-C(10)). CI-MS: 327 (84, [*M* + 1]⁺), 326 (7, *M*⁺), 296 (20), 295 (100). Anal. calc. for C₂₀H₂₂O₄ (326.40): C 73.60, H 6.79; found: C 73.49, H 6.86.

Data of 34b. The heptalene could be separated from its DBS isomer by TLC at 0°. R_f (hexane/Et₂O 3:2, 0°): 0.37. It isomerized rapidly at 20° to yield the equilibrium mixture of **34b** and **34a**. ¹H-NMR (300 MHz, 233 K; mixture of 27 % of **34b** and 73 % of **34a**): 6.51 (br. *s*, H-C(2)); 6.29 (br. *s*, H-C(7)); 6.15 (*d*, partly covered by signals of **34a**, H-C(9)); 5.93 (*d*, ³*J*(H,H-C(9)) = 10.5, H-C(10)); 3.95 (*s*, C(5)-COOCH₃); 3.71 (*s*, C(4)-COOCH₃); 2.04 (br. *s*, CH₃-C(3)); 2.03 (br. *s*, CH₃-C(8)); 1.78 (*s*, CH₃-C(1)); 1.66 (*s*, CH₃-C(6)). ¹H-NOE (400 MHz, mixture as above): 1.66 (CH₃-C(6))→6.29 (*s*, H-C(7)); 6.51 (H-C(2))→2.04 (*s*, CH₃-C(3)), 1.78 (*s*, CH₃-C(1)).

Data of 33. Violet crystals. M.p. 94–95° (hexane/Et₂O). R_f (hexane/Et₂O 3:2): 0.23. UV (hexane): $\lambda_{\max}$ 359 (3.73), 343 (sh, 3.62), 307 (4.65), 297 (4.63), 246 (4.31), 220 (4.07); $\lambda_{\min}$ 328 (3.47), 300 (4.61), 267 (3.99), 227 (4.03). IR (KBr): 2948, 1712, 1590, 1445, 1409, 1370, 1250, 1205, 1171, 998. ¹H-NMR (300 MHz): 8.285 (*d*, ³*J*(H,H-C(5)) = 9.7, H-C(4)); 7.085 (*s*, H-C(7)); 7.069 (*d*, ³*J*(H,H-C(4)) = 10.0, H-C(5)); 3.963, 3.928 (2*s*, 2 COOCH₃); 2.823 (*s*, CH₃-C(8)); 2.742 (*s*, CH₃-C(3)); 2.613 (*s*, CH₃-C(6)). MS: 286 (90, *M*⁺), 255 (69), 254 (68), 220 (100). Anal. calc. for C₁₇H₁₈O₄ (286.33): C 71.31, H 6.34; found: C 71.40, H 6.58.

Data of anti-36. Colorless crystals. M.p. 186–187° (hexane/Et₂O). R_f (hexane/Et₂O 3:2): 0.17. UV (hexane): $\lambda_{\max}$ 280 (sh, 3.41), 224 (sh, 4.09). IR (KBr): 2951, 1710 (H₃COOOC), 1620, 1587, 1438, 1383, 1249, 1134, 1106, 1082, 1055, 1028.5, 1003, 785. ¹H-NMR (300 MHz, CDCl₃/C₆D₆): 6.252/6.302 (*q*, ⁴*J*(H,CH₃-C(11)) = 1.6/1.6, H-C(12)); 5.677/5.966 (*quint.*, ⁴*J*(H,CH₃-C(13)) = 1.6/1.6, H-C(14)); 4.939/4.882 (*d*, ³*J*(H,H-C(5)) = 8.3/8.3, H-C(6)); 3.843, 3.798, 3.729, 3.689/3.511, 3.469, 3.211, 3.155 (4*s*, 4 COOCH₃); 3.581/3.631 (*dd*, ³*J*(H,H-C(6)) = 8.3/8.3, ⁴*J*(H,H-C(14)) = 1.7/1.7, H-C(5)); 2.079/2.225 (*d*, ⁴*J*(CH₃,H-C(12)) = 1.6/1.6, CH₃-C(11)); 1.822/1.600 (*d*, ⁴*J*(CH₃,H-C(14)) = 1.5/1.5, CH₃-C(13)); 1.542/1.804 (*s*, CH₃-C(2)); 1.480/1.494 (*s*, CH₃-C(8)). ¹H-NOE (400 MHz, CDCl₃): 1.480 (CH₃-C(8))→6.252 (*s*, H-C(12)), 4.939 (*s*, H-C(6)), 3.689 (*w*, C(9)-COOCH₃); 1.542 (CH₃-C(2))→5.677 (*s*, H-C(14)), 3.843 (*m*, C(3)-COOCH₃), 3.798 (*m*, C(10)-COOCH₃), 2.079 (*s*, CH₃-C(11)); 2.079 (CH₃-C(11))→6.252 (*s*, H-C(12)), 3.843 (*m*, C(3)-COOCH₃), 3.798 (*w*, C(10)-COOCH₃), 1.542 (*s*, CH₃-C(2)); 3.689 (C(9)-COOCH₃)→1.480 (*m*, CH₃-C(8)). MS: 468 (14, *M*⁺), 436 (30), 421 (32), 409 (21), 377 (100), 349 (37), 345 (30), 317 (26), 246 (12), 235 (68), 228 (70), 214 (96), 203 (43). Anal. calc. for C₂₆H₂₈O₈ (468.51): C 66.66, H 6.02; found: C 66.86, H 6.08.

Data of anti-37. Colorless crystals from hexane. M.p. 160–162°. R_f (hexane/Et₂O 2:3): 0.40. UV (hexane): $\lambda_{\max}$ 276 (sh, 3.23), 216 (sh, 4.08). IR (KBr): 2952, 1717 (COOCH₃), 1637, 1607, 1435.5, 1356, 1268, 1139, 1080.5, 1047, 924, 873.5, 776. ¹H-NMR (300 MHz, CDCl₃/C₆D₆; CHCl₃ at 7.263/C₆D₃H at 7.158): 6.143/5.908 (*q*, ⁴*J*(H,H-C(11)) = 1.68/1.72, H-C(12)); 5.877/6.083 (*d* *quint.*, ³*J*(H,H-C(2)) = 6.21/6.20, ⁴*J*(H,H-C(5)) ≈ ⁴*J*(H,CH₃-C(13)) = 1.67/1.72, H-C(14)); 4.329/4.808 (*d*, ³*J*(H,H-C(14)) = 6.23/6.24, H-C(2)); 3.789, 3.780, 3.776, 3.771/3.384, 3.371, 3.357, 3.337 (4*s*, 4 COOCH₃); 3.063/3.074 (*d*, ⁴*J*(H,H-C(14)) = 1.80/1.78, H-C(5)); 1.826/1.792 (*s*, CH₃-C(6)); 1.807/1.462 (*d*, ⁴*J*(CH₃,H-C(14)) = 1.55/1.56, CH₃-C(13)); 1.772/1.887 (*d*, ⁴*J*(CH₃,H-C(12)) = 1.76/1.73, CH₃-C(11)); 1.614/1.603 (*s*, CH₃-C(8)). ¹H-NOE (400 MHz, C₆D₆): 1.462 (CH₃-C(13))→6.083 (*s*, H-C(14)), 3.074 (*s*, H-C(5)); 1.603 (CH₃-C(8))→5.908 (*s*, H-C(12)), 1.792 (*m*, CH₃-C(6)); 1.792 (CH₃-C(6))→3.074 (*s*, H-C(5)), 1.603 (*m*, CH₃-C(8)); 1.887 (CH₃-C(11))→5.908 (*s*, H-C(12)), 4.808 (*s*, H-C(2)). CI-MS: 469 (100, [*M* + 1]⁺), 437 (5). MS: 468 (10, *M*⁺), 436 (12), 421 (14), 409 (6), 408 (8), 377 (18), 349 (9), 317 (7), 260 (16), 228 (100). Anal. calc. for C₂₆H₂₈O₈ (468.51): C 66.66, H 6.02; found: C 66.73, H 6.23.

Data of anti-35. The tetracycle was only obtained in a mixture with *anti*-37 containing ca. 47 % of the latter. ¹H-NMR (400 MHz, CDCl₃/C₆D₆; CHCl₃ at 7.263/C₆D₃H at 7.158): 6.143/6.088 (*q*, ⁴*J*(H,CH₃-C(12)) = 1.79/1.64, H-C(14)); 6.131/6.195 (*d*, ³*J*(H,H-C(12)) = 8.40/8.39, H-C(11)); 6.121/5.942 (*d*, ³*J*(H,H-C(11)) = 8.40/

8.40, H-C(12)); 5.853/5.860 (q , $^4J(\text{H}, \text{CH}_3\text{-C}(6)) = 1.45/1.44$, H-C(7)); 3.766, 3.727, 3.698, 3.642/3.374, 3.371, 3.366, 3.283 (4s, 4 COOCH₃); 1.812/1.668 (d , $^4J(\text{CH}_3, \text{H-C}(14)) = 1.88/1.74$, CH₃-C(13)); 1.791/2.109 (s , CH₃-C(2)); 1.689/1.689 (d , $^4J(\text{CH}_3, \text{H-C}(7)) = 1.41/1.41$, CH₃-C(6)); 1.371/1.275 (s , CH₃-C(8)). ¹H-NOE (400 MHz, CDCl₃): 1.689 (CH₃-C(6))→5.853 (s , H-C(7)), 3.727 (m , C(4)-COOCH₃), 1.812 (m , CH₃-C(13)). ¹H-NOE (400 MHz, C₆D₆): 1.668/1.689 (CH₃-C(13), CH₃-C(6))→6.088 (s , H-C(14)), 5.860 (s , H-C(7)); 2.109 (CH₃-C(2))→6.195 (s , H-C(11)), 6.088 (s , H-C(14)); 5.942 (H-C(12))→6.195 (s , H-C(11)), 1.275 (m , CH₃-C(8)); 6.195 (H-C(11))→5.942 (s , H-C(12)), 2.109 (m , CH₃-C(2)); no effect on H-C(14) at 6.088.

2.2. **Azulene 21 and ADM** (cf. [4]). The azulene (0.491 g, 2.66 mmol) and ADM (1.85 g, 13.0 mmol) were heated in decalin (10 ml) at 200° during 2 h. Chromatographic workup (Alox B, III, hexane/Et₂O 2:3) gave, after yellow fractions containing the known heptalenes **23a**, **23b** [4] and violet fractions containing the azulene-1,2-dicarboxylate **22** [4], colorless fractions which comprised *syn*-**24** (0.063 g, 5.0%).

Tetramethyl (1RS,2SR,5SR,8SR)-6,8,11,13-Tetramethyltetracyclo[6.2.2.2.5⁰.1.5]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate (syn-24). Colorless oil which was further purified by prep. TLC. *R_f* (Alox; hexane/Et₂O 2:3): 0.42. UV (qual., CH₂Cl₂): λ_{max} 284 (sh), 240 (sh), 225. IR (CHCl₃): 3030, 2952, 2928, 2856, 1726 (COOCH₃), 1618, 1436, 1381. ¹H-NMR (300 MHz): 6.503 (*sext.*-like, $^4J(\text{H}, \text{CH}_3\text{-C}(13)) \approx \frac{1}{2} \cdot ^3J(\text{H}, \text{H-C}(2)) \approx 1.7$, H-C(14)); 5.789 (q , $^4J(\text{H}, \text{CH}_3\text{-C}(6)) = 1.4$, H-C(7)); 5.761 (q , $^4J(\text{H}, \text{CH}_3\text{-C}(11)) = 1.6$, H-C(12)); 4.377 (d , $^3J(\text{H}, \text{H-C}(14)) = 3.5$, H-C(2)); 3.757 (s , C(4)-COOCH₃); 3.742 (s , C(9)-COOCH₃); 3.725 (s , C(10)-COOCH₃); 3.577 (s , C(3)-COOCH₃); 1.847 (d , $^4J(\text{CH}_3, \text{H-C}(14)) = 1.8$, CH₃-C(13)); 1.821 (d , $^4J(\text{CH}_3, \text{H-C}(12)) = 1.6$, CH₃-C(11)); 1.696 (d , $^4J(\text{CH}_3, \text{H-C}(7)) = 1.4$, CH₃-C(6)); 1.262 (s , CH₃-C(8)). ¹H-NOE (400 MHz): 1.262 (CH₃-C(8))→5.789 (s , H-C(7)), 5.761 (s , H-C(12)); and 3.742 (w , C(9)-COOCH₃); 1.696 (CH₃-C(6))→5.789 (s , H-C(7)), 3.757 (m , C(4)-COOCH₃), 1.847 (m , CH₃-C(13)); 1.821 (CH₃-C(11))→6.503 (s , H-C(14)), 5.761 (s , H-C(12)), 4.377 (s , H-C(2)); 1.847 (CH₃-C(13))→6.503 (s , H-C(14)), 1.696 (s , CH₃-C(6)); 4.377 (H-C(2))→6.503 (s , H-C(14)), 3.577 (w , C(3)-COOCH₃), 1.821 (s , CH₃-C(11)). CI-MS: 469 (70, [*M* + 1]⁺), 437 (64), 409 (3), 405 (9), 187 (100), 163 (62), 137 (23).

2.2.1. *Control Experiment with syn-24*. The tetracycle, when heated in decalin at 200° during 14 h, did not decompose.

2.3. **Azulene 41 and ADM**. The azulene (0.0058 g; 0.314 mmol) and ADM (0.14 g; 0.98 mmol) were heated in decalin (3 ml) under Ar at 180° during 6.5 h. Decalin and excess ADM were distilled off (high vacuum; 50°) and the residue separated by prep. TLC on silica gel (hexane/Et₂O 7:3) to yield a mixture (0.086 g; 83.9%) of *dimethyl 2,6,8,10-tetramethylheptalene-4,5-dicarboxylate (42b)* and *dimethyl 4,6,8,10-tetramethylheptalene-1,2-dicarboxylate (42a)*, and pure *dimethyl 4,6,8-trimethylazulene-1,2-dicarboxylate (22)* (0.0093 g; 10.3%). Crystallization of the heptalene mixture from hexane/Et₂O at -20° yielded orange-red crystals of **42b** (0.073 g; 71.5%). From the mother liquor, a small amount of yellow crystals of the isomeric heptalene **42a** could be obtained. Compound **22** was crystallized from hexane/Et₂O at 5° to yield dark blue crystals (0.0046 g; 5.1%). M.p. 141.4–141.7° (cf. [4]; m.p. 141–142°).

Data of 42b. Orange-red crystals. M.p. 129.8–130.8°. *R_f* (pentane/Et₂O 3:2): 0.20. The heptalene isomerized in soln. already at 0° partially into its DBS isomer **42a** (ca. 27%; see 2.3.1). UV (hexane, 20°; qual. with regard to its partial isomerization): λ_{max} 319 (sh), 267, 210; λ_{min} 246. IR (KBr): 2989, 2946, 2911, 2852, 1733/1714 (COOMe), 1646, 1592, 1569, 1528, 1433, 1374, 1357, 1297, 1260, 1209, 1189, 1162, 1125, 1088, 1057, 1014, 1032, 880, 868, 837, 790. ¹H-NMR (300 MHz, 263 K): 6.230 (*quint.*-like, $^4J(\text{H}, \text{CH}_3\text{-C}(2)) \approx 1.3$, H-C(3)); 6.107 (br. s , H-C(7)); 5.923 (*quint.*-like, $^4J(\text{H}, \text{CH}_3\text{-C}(10)) \approx ^4J(\text{H}, \text{H-C}(7)) \approx 1.3$, H-C(9)); 5.714 (d , $^4J(\text{H}, \text{H-C}(3)) = 1.3$, H-C(1)); 3.840, 3.702 (2s, 2 COOCH₃); 2.095 (d -like, $^4J(\text{CH}_3, \text{H-C}(10)) \approx 1.1$, CH₃-C(10)); 2.020 (d -like, $^4J(\text{CH}_3, \text{H-C}(3)) \approx 1.2$, CH₃-C(2)); 1.963 (d -like, $^4J(\text{CH}_3, \text{H-C}(7)) \approx 1.2$, CH₃-C(8)); 1.613 (s , CH₃-C(6)). ¹H-NOE (400 MHz): 2.095 (CH₃-C(10))→5.923 (s , H-C(9)), 5.714 (s , H-C(1)); 1.963 (CH₃-C(8))→6.107 (s , H-C(7)), 5.923 (s , H-C(9)); 1.613 (CH₃-C(6))→6.107 (s , H-C(7)). MS: 326 (63, *M*⁺), 295 (14), 279 (16), 267 (17), 235 (11), 207 (21), 193 (16), 192 (12), 185 (15), 178 (11), 169 (12), 165 (11). Anal. calc. for C₂₀H₂₂O₄ (326.39): C 73.60, H 6.79; found: C 73.57, H 6.86.

Data of 42a. Yellow crystals. M.p. ca. 80–90°; after melting, **42a** crystallized again > 90° and melted anew at ca. 132° (isomerization!). *R_f* (pentane/Et₂O 3:2): 0.20. ¹H-NMR (300 MHz, 25°; mixture of ca. 27% of **42b** and ca. 73% of **42a**; only the signals of the latter compound are reported): 7.46 (s , H-C(3)); 6.12 (br. s , H-C(7)); 5.93 (*quint.*-like, H-C(9)); 5.80 (br. s , H-C(5)); 3.71, 3.69 (2s, 2 COOCH₃); 2.035 (d -like, $^4J(\text{CH}_3, \text{H-C}(5)) \approx 1.4$, CH₃-C(4)); 2.01 (br. s , CH₃-C(8)); 1.98 (d -like, $^4J(\text{CH}_3, \text{H-C}(9)) \approx 1.2$, CH₃-C(10)); 1.73 (s , CH₃-C(6)). ¹H-DR (400 MHz): 7.648 (s , H-C(3))→2.035 (*sd*, CH₃-C(4)); 2.035 (d , CH₃-C(4))→5.806 (*ss*, H-C(5)); 2.017 (br. s , CH₃-C(8))→6.129 (*ss*, H-C(7)), 5.942 (*t*-like, $J \approx 0.9$, H-C(9)); 1.985 (d , CH₃-C(10))→5.942 (*ss*, H-C(9)).

In a second addition experiment, **41** (0.122 g, 0.662 mmol) and ADM (0.380 g, 3.267 mmol) in decalin (6 ml) were heated under Ar at 190° during 3 h. Workup yielded the mixture **42b/42a** (after crystallization from Et₂O/hexane: 0.131 g, 61%), **22** (after crystallization from Et₂O/hexane: 0.0062 g, 3.3%) and *trimethyl 5-methoxyfuran-2,3,4-tricarboxylate* (**10**; after crystallization from Et₂O/hexane: 0.011 g, m.p. 121.1–121.9° [17]). The mother liquor of the crystallization of **22** (0.034 g) contained a further compound, namely *anti*-**43**, which was isolated and purified by prep. HPLC (eluant: hexane/(CH₂Cl₂ + 0.5% MeOH) 4:1) to yield 0.0083 g (2.7%) in addition to **22** (0.0068 g, 3.6%). The mother liquor of **10** consisted of two further compounds, namely '*syn*'- and '*anti*'-**45**²¹), which were isolated by prep. HPLC (*vide supra*) to yield 0.0051 g (1.6%).

Tetramethyl (1RS,2RS,5RS,8RS)-2,6,12,13-Tetramethyltetracyclo[6.2.2.2^{2.5}0^{1.7}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate ('anti'-43). *R*_f (hexane/Et₂O 2:3): 0.35. ¹H-NMR (300 MHz): 6.540 (*quint.*-like, ⁴*J*(H,CH₃–C(12)) ≈ 1.7, ⁴*J*(H,H–C(8)) ≈ 1.1, H–C(11)); 5.604 (*quint.*-like, ⁴*J*(H,CH₃–C(13)) ≈ ⁴*J*(H,H–C(5)) ≈ 1.6, H–C(14)); 3.921 (*d*, ⁴*J*(H,H–C(11)) ≈ 1.2, H–C(8)); 3.833, 3.821, 3.732, 3.717 (4s, 4 COOCH₃); 3.413 (*d*, ⁴*J*(H,H–C(14)) = 1.6, H–C(5)); 1.918 (*d*, ⁴*J*(CH₃,H–C(11)) = 1.6, CH₃–C(12)); 1.848 (*d*, ⁴*J*(CH₃,H–C(14)) = 1.5, CH₃–C(13)); 1.631 (*s*, CH₃–C(6)); 1.368 (*s*, CH₃–C(2)). ¹H-NOE (400 MHz): 1.368 (CH₃–C(2))→6.540 (*s*, H–C(11)), 5.604 (*s*, H–C(14)), 3.833, 3.821 (*m*, C(3,10)–COOCH₃); 1.631 (CH₃–C(6))→3.921 (*s*, H–C(8)), 3.413 (*s*, H–C(5)); 1.848 (CH₃–C(13))→5.604 (*s*, H–C(14)), 3.413 (*s*, H–C(5)); 1.918 (CH₃–C(12))→6.540 (*s*, H–C(11)), 3.921 (*s*, H–C(8)); 6.540 (H–C(11))→1.918 (*s*, CH₃–C(11)), 1.368 (*s*, CH₃–C(2)).

Tetramethyl (1RS,2RS,7RS,8SR)-1,4,7,12-Tetramethyltetracyclo[6.2.2.2^{2.7}0^{2.6}]tetradeca-3,5,9,11,13-pentaene-9,10,13,14-tetracarboxylate ('anti'-45). Only obtained as a 3:1 mixture with its '*syn*'-isomer. *R*_f (hexane/Et₂O 2:3): 0.30. ¹H-NMR (600 MHz, C₆D₆/300 MHz, CDCl₃): 6.277/6.11 (*quint.*, ⁴*J*(H,CH₃–C(4)) ≈ ⁴*J*(H,H–C(5)) = 1.36, H–C(3)); 6.161/6.14 (*d*, ⁴*J*(H,H–C(3)) = 1.24, H–C(5)); 5.185/5.27 (*quint.*, ⁴*J*(H,CH₃–C(12)) ≈ ⁴*J*(H,H–C(8)) = 1.70, H–C(11)); 3.841/3.83 (*d*, ⁴*J*(H,H–C(11)) = 1.86, H–C(8)); 3.537, 3.495, 3.321, 3.138 (4s, 4 COOCH₃); 1.783/1.78 (*s*, CH₃–C(7)); 1.765/2.04 (*d*, ⁴*J*(CH₃,H–C(3)) = 1.36, (CH₃–C(4)); 1.747/2.01 (*d*, ⁴*J*(CH₃,H–C(11)) = 1.64, CH₃–C(12)); 1.499/1.59 (*s*, CH₃–C(1)). ¹H-NOE (400 MHz, C₆D₆): 1.747 (CH₃–C(12))→5.185 (*s*, H–C(11)), 3.841 (*s*, H–C(8)), 3.321 (*m*, C(13)–COOCH₃), 1.783 (*s*, CH₃–C(7)); 1.765 (CH₃–C(4))→6.277 (*s*, H–C(3)), 6.161 (*s*, H–C(5)); 1.783 (CH₃–C(7))→6.277 (*vw*, H–C(3)), 3.841 (*s*, H–C(8)), 3.321 (*m*, C(13)–COOCH₃). ¹H-NOE (400 MHz, CDCl₃): 1.59 (CH₃–C(1))→6.11 (*s*, H–C(3)), 5.27 (*m*, H–C(11)); 1.78 (CH₃–C(7))→3.83 (*s*, H–C(8)), 3.67 (*w*, C(13)–COOCH₃), 2.01 (*w*, CH₃–C(12)); 2.01 (CH₃–C(12))→5.27 (*s*, H–C(11)), 3.83 (*s*, H–C(8)), 3.67 (*m*, C(13)–COOCH₃); 2.04 (CH₃–C(4))→6.14 (*s*, H–C(5)), 6.11 (*s*, H–C(3)); 5.27 (H–C(12))→2.01 (*s*, CH₃–C(12)), 1.59 (*s*, CH₃–C(1)).

Tetramethyl (1SR,2RS,7SR,8RS)-1,4,7,12-Tetramethyltetracyclo[6.2.2.2^{2.7}0^{2.6}]tetradeca-3,5,9,11,13-pentaene-9,10,13,14-tetracarboxylate ('syn'-45). Only obtained as a 1:3 mixture with its '*anti*'-isomer. *R*_f: see *anti*-**45**. ¹H-NMR (600 MHz, C₆D₆/300 MHz, CDCl₃): 6.249/6.11 (*quint.*, ⁴*J*(H,CH₃–C(4)) = 1.32, H–C(3)); 5.839/6.01 (*quint.*, ⁴*J*(H,H–C(3)) = 1.27, H–C(5)); 5.272/5.50 (*quint.*, ⁴*J*(H,CH₃–C(12)) = 1.62, H–C(11)); 3.752/3.80 (*d*, ⁴*J*(H,H–C(11)) = 1.67, H–C(8)); 3.565, 3.481, 3.448, 3.297 (4s, 4 COOCH₃); 1.757/1.75 (*s*, CH₃–C(7)); 1.596/2.03 (*d*, ⁴*J*(CH₃,H–C(3)) = 1.32, CH₃–C(4)); 1.419/1.79 (*d*, ⁴*J*(CH₃,H–C(11)) = 1.59, CH₃–C(12)); 1.503/1.57 (*s*, CH₃–C(1)). ¹H-NOE (400 MHz, C₆D₆): 1.419 (CH₃–C(12))→5.272 (*s*, H–C(11)), 3.752 (*s*, H–C(8)); 1.596 (CH₃–C(4))→6.249 (*s*, H–C(3)), 5.839 (*s*, H–C(5)); 1.757 (CH₃–C(7))→3.752 (*s*, H–C(8)), 3.448 (*m*, C(13)–COOCH₃). ¹H-NOE (400 MHz, CDCl₃): 1.75 (CH₃–C(7))→3.80 (*m*, H–C(8)), 3.53 (*w*, C(13)–COOCH₃); 5.50 (H–C(11))→1.79 (*s*, CH₃–C(12)), 1.57 (*s*, CH₃–C(1)).

2.3.1. *Control Experiments with 42b and 42a*. 2.3.1.1. *Thermal Isomerizations*. Crystalline **42b** (m.p. 130–131°) was dissolved in CDCl₃ at –10°. ¹H-NMR (300 MHz) at 0° indicated after 30 min the presence of already 30%, and after 90 min of 40% of the DBS isomer **42a**. The equilibrium mixture at 25° consisted of 27.5% of **42b** and 72.5% of **42a**. The same result was obtained, when **42a** (1 mg) was heated in decalin (0.5 ml) at 100° during 15 min and the ratio **42b/42a** determined at 25° by ¹H-NMR.

2.4. *Azulene 25 and ADM* (*cf.* [15]). The azulene (0.403 g; 1.78 mmol) and ADM (1.27 g; 8.96 mmol) were heated in decalin (8 ml) during 100 min at 200°. Decalin was distilled off and the residue subjected to

²¹) In the ¹H-NMR of this mixture weak signals of an additional (1 + 2)-adduct which had to be assigned to *tetramethyl (1RS,2RS,5RS,8RS)-6,8,11,14-tetramethyltetracyclo[6.2.2.2^{2.5}0^{1.5}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate* (*syn*-**44**) were detected. ¹H-NMR (C₆D₆, 600 MHz): 5.841 (*quint.*-like, H–C(13)); 5.629 (*q*, ⁴*J*(H,CH₃–C(6)) = 1.55, H–C(7)); 5.582 (*q*, ⁴*J*(H,CH₃–C(11)) = 1.70, H–C(12)); 4.482 (*d*, ⁴*J*(H,H–C(13)) = 1.52, H–C(2)); 1.798 (*d*, ⁴*J*(CH₃,H–C(13)) = 1.81, CH₃–C(14)); 1.636 (*d*, ⁴*J*(CH₃,H–C(12)) = 1.60, CH₃–C(11)); 1.591 (*d*, ⁴*J*(CH₃,H–C(7)) = 1.52, CH₃–C(6)); 1.30 (*s*, CH₃–C(8)). The signals of the COOCH₃ groups could not be identified due to the presence of the great excess '*anti*'- and '*syn*'-**45**.

CC (Al₂O₃, Act. III; Et₂O/hexane 4:1) to yield 4 fractions (A–D). Fraction A (0.204 g) contained mainly *dimethyl 8-(tert-butyl)-5,6,10-trimethylheptalene-1,2-dicarboxylate* (**27a**) [5], its DBS isomer **27b** [5], and *dimethyl 5-(tert-butyl)-3-methylphthalate* (**28**); fraction B (0.209 g) consisted mainly of *dimethyl 6-(tert-butyl)-4,8-dimethylazulene-1,2-dicarboxylate* (**26**) [5] and small amounts of the isomeric tetracyclic compounds 'anti'-**29** and 'anti'-**30** as well as **27a**; fraction C (0.077 g) represented nearly pure tetracyclic compound 'anti'-**29** which was further purified by crystallization from hexane. Fraction D contained beside polymeric material the pentacyclic compound **31** which was further purified by HPLC (0.010 g) and crystallization from hexane/Et₂O. Fractions A and B were further separated by fractionated crystallization from hexane and HPLC of the mother liquors. The total yields of the pure and crystallized compounds were the following: **27a** (17.1%), **26** (18.0%), 'anti'-**29** (8.2%), 'anti'-**30** (2.9%), and **31** (0.5%). The heptalene **27b** (0.8%) and phthalate **28** (2.4%) were only obtained as a *ca.* 1:3 mixture.

Compound 27a [5]. M.p. 136.0–136.6° [5].

Dimethyl 8-(tert-Butyl)-1,6,10-trimethylheptalene-4,5-dicarboxylate (27b) [5]. Identified by its ¹H-NMR (300 MHz, CDCl₃).

Compound 26 [5]. M.p. 121.5–123.5°.

Data of 28. Obtained as a 3:1 mixture with **27b**. ¹H-NMR (300 MHz): 7.829 (*d*, ⁴*J*(H,H–C(4)) = 1.9, H–C(6)); 7.406 (*d*, ⁴*J*(H,H–C(6)) = 1.7, H–C(4)); 3.930, 3.890 (2s, 2 COOCH₃); 2.351 (*s*, CH₃–C(3)); 1.323 (*s*, *t*-Bu). ¹H-NOE (400 MHz): 1.323→7.829 (*s*, H–C(6)), 7.406 (*s*, H–C(4)), 2.351 (*w*, CH₃–C(3)); 2.351→7.406 (*s*, H–C(4)).

Tetramethyl (1RS,2RS,5RS,8RS)-13-(tert-Butyl)-2,6,8-trimethyltetracyclo[6.2.2.2^{5,0}.1⁷]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate ('anti'-29). Colorless crystals. M.p. 124.8–125.7°. *R*_f (hexane/Et₂O 3:2): 0.18. UV (EtOH): λ_{max} 290 (sh, 3.05), 218 (sh, 4.08). IR (CHCl₃): 3030m, 2953m, 1716s, 1662w, 1628w, 1566w, 1459w, 1435m, 1388w, 1364w, 1268m, 1145m, 1129m, 1046m. ¹H-NMR (300 MHz; CDCl₃/C₆D₆): 7.104/7.534 (*d*, ³*J*(H,H–C(12)) = 5.4/5.4, H–C(11)); 6.656/6.508 (*d*, ³*J*(H,H–C(11)) = 5.4/5.2, H–C(12)); 5.720/6.117 (*d*, ⁴*J*(H,H–C(5)) = 1.9/1.9, H–C(14)); 3.724/4.007 (*d*, ⁴*J*(H,H–C(14)) = 1.9/1.9, H–C(5)); 3.826/3.506, 3.799/3.460, 3.741/3.206, 3.689/3.191 (4s, 4 COOCH₃); 1.773/1.855 (*s*, CH₃–C(6)); 1.755/1.782 (br. *s*, CH₃–C(8)); 1.448/1.746 (*s*, CH₃–C(2)); 1.066/1.093 (*s*, *t*-Bu). ¹H-NOE (400 MHz, C₆D₆): 1.855→4.007 (*s*, H–C(5)), 1.782 (*m*, CH₃–C(8)), 1.093 (*w*, *t*-Bu); 1.782→6.508 (*s*, H–C(12)), 1.855 (*m*, CH₃–C(6)); 1.746→7.534 (*s*, H–C(11)), 6.117 (*s*, H–C(14)). CI-MS ([NH₃]): 529 (31, [M + 2 + NH₃]⁺), 528 (100, [M + 1 + NH₃]⁺), 511 (69, [M + 1]⁺), 496 (30), 479 (23), 452 (5). Anal. calc. for C₂₉H₃₄O₈ (510.59): C 68.22, H 6.71; found: C 67.96, H 6.97.

Tetramethyl (1RS,2RS,5RS,8RS)-13-(tert-Butyl)-2,6,11-trimethyltetracyclo[6.2.2.2^{5,0}.1⁷]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate ('anti'-30). In a 2:3 mixture with 'anti'-**29**. *R*_f: identical with that of 'anti'-**29**. ¹H-NMR (300 MHz, CDCl₃/C₆D₆): 6.490/6.299 (*sext.*-like, ½·³*J*(H,H–C(8)) ≈ ⁴*J*(H,CH₃–C(11)) = 1.8/1.8, H–C(12)); 5.683/6.030 (*s*, ⁴*J*(H,H–C(5)) = 2.1/2.0, H–C(14)); 4.096/4.252 (*d*, ³*J*(H,H–C(12)) = 3.4/3.3, H–C(8)); ²²/3.894 (*d*, ⁴*J*(H,H–C(14)) = 2.1, H–C(5)); 3.861/3.551, 3.790/3.489, 3.740/3.228, 3.698/3.192 (4s, 4 COOCH₃); 2.065/2.238 (*d*, ⁴*J*(CH₃, H–C(12)) = 1.7/1.6, CH₃–C(11)); 1.717/1.877 (*s*, CH₃–C(2)); 1.576/1.723 (*s*, CH₃–C(6)); 1.030/1.015 (*s*, *t*-Bu). ¹H-NOE (400 MHz, C₆D₆): 1.877→6.030 (*s*, H–C(14)), 2.238 (*m*, CH₃–C(11)).

Hexamethyl (1RS,2RS,5RS,8RS,9RS,11RS)-13-(tert-Butyl)-2,6,11-trimethylpentacyclo[6.2.2.2^{5,0}.1^{2,0}.1⁷.0^{10,11}]hexadeca-3,6,13,15-tetraene-3,4,9,10,15,16-hexacarboxylate (31). Colorless crystals. M.p. *ca.* 95–115° → recryst. → 175–178° (hexane). UV (EtOH): λ_{max} 288 (sh, 3.58), 218 (sh, 4.13), 199 (4.26). IR (CHCl₃): 3028m, 2954s, 1730s, 1664w, 1616m, 1436s, 1263s, 1159m, 1138m, 1094m, 1046w. ¹H-NMR (300 MHz, CDCl₃/C₆D₆): 5.710/6.084 (*d*, ⁴*J*(H,H–C(5)) = 1.8/1.8, H–C(14)); 3.841/4.095 (*d*, ⁴*J*(H,H–C(14)) = 1.8/1.8, H–C(5)); 3.824/3.504, 3.790/3.439, 3.777/3.433, 3.757/3.421, 3.645/3.354, 3.289 (5s (1:1:1:1:2)/6s, 6 COOCH₃); 3.182/2.951 (*d*, ³*J*(H,H–C(8)) = 2.4/2.4, H–C(12)); 2.947/2.804 (*d*, ³*J*(H,H–C(12)) = 2.4/2.4, H–C(8)); 1.792/1.812 (*s*, CH₃–C(6)); 1.530/1.878 (*s*, CH₃–C(11)); 1.440/1.802 (br. *s*, CH₃–C(2)); 1.061/1.087 (*s*, *t*-Bu). ¹H-NOE (400 MHz, CDCl₃): 1.440→5.710 (*s*, H–C(14)); 1.530→3.182 (*m*, H–C(12)); 1.792→3.841 (*s*, H–C(5)), 2.947 (*s*, H–C(8)). ¹H-DR (400 MHz, C₆D₆): 6.084→4.095 (*s*, H–C(5)); 2.951→2.804 (*s*, H–C(8)). CI-MS ([NH₃]): 670 (66, [M + 1 + NH₃]⁺), 653 (90, [M + 1]⁺), 639 (37), 638 (100), 621 (15).

2.4.1. *Control Experiment with 'anti'-29.* The tetracycle 'anti'-**29** (5.3 mg) was heated in decalin (0.2 ml) at 200° for 5.5 h. Decalin was distilled off. ¹H-NMR (300 MHz, CDCl₃) of the residue showed only the signals of 'anti'-**29**. The signals of **28** could not be detected.

2.5. *Azulene 38 and ADM.* The azulene (0.075 g; 0.378 mmol) and ADM (0.215 g; 1.513 mmol) were heated in degassed decalin (3 ml) under Ar at 180° during 3.25 h. The usual chromatographic workup yielded a

²²⁾ Covered by H₃COOC-signals.

yellow heptalene fraction (0.075 g; 58.5%) from which by crystallization from hexane/Et₂O pure *dimethyl 4,5,6,8,10-pentamethylheptalene-1,2-dicarboxylate* (**39a**; 0.061 g; 47.5%) could be separated. The mother liquor contained the DBS isomer **39b** (see 2.5.1). The second chromatographic fraction consisted of *dimethyl 4,6,8-trimethylazulene-1,2-dicarboxylate* (**22**) which yielded dark blue crystals (0.008 g; 7.3%; m.p. 141–142° (cf. [4] and 2.6).

Data of 39a. Yellow crystals. M.p. 141–142°. *R_f* (Et₂O/hexane 3:2): 0.37. UV (hexane): $\lambda_{\max}$ 283 (sh, 4.16), 262 (4.23), 198 (4.76); $\lambda_{\min}$ 247 (4.21). IR (CHCl₃): 3003m, 2950m, 2916m, 2856w, 1713s, 1643w, 1601w, 1567w, 1436s, 1375m, 1157m, 1109w, 1094m, 1057m, 1008m. ¹H-NMR (300 MHz): 7.520 (*d*-like, ⁵*J*(H,CH₃–C(5)) < 0.5, H–C(3)); 6.142 (br. s, H–C(7)); 6.009 (*quint.*-like, ⁴*J*(H,CH₃–C(10)) ≈ ⁴*J*(H,H–C(7)), H–C(9)); 3.701, 3.694 (2s, 2 COOCH₃); 2.038 (*d*, ⁴*J*(CH₃,H–C(9)) ≈ 1.0, CH₃–C(10)); 1.979 (*d*-like, ⁵*J*(CH₃,CH₃–C(5)) ≈ 0.7, CH₃–C(4)); 1.965 (*d*, ⁴*J*(CH₃,H–C(7)) ≈ 1.1, CH₃–C(8)); 1.892 (*quint.*-like, ⁵*J*(CH₃,H–C(3)) ≈ ⁴*J*(CH₃,CH₃–C(4)) ≈ 1, CH₃–C(5)); 1.698 (s, CH₃–C(6)). MS: 340 (100, *M*⁺), 325 (19), 309 (12), 293 (23), 281 (14), 266 (12), 254 (12), 242 (13), 221 (11), 199 (15), 198 (93, [*M* – ADM]⁺), 183 (13). Anal. calc. for C₂₁H₂₄O₄ (340.42): C 74.09, H 7.11; found: C 73.86, H 7.10.

In a second run, 0.069 g (0.349 mmol) of **38** and 0.200 g (1.41 mmol) of ADM in 3 ml of decalin at 190° were reacted during 2.5 h. The chromatographic workup yielded, beside the heptalene mixture **39a/39b** (0.0432 g, 36.4%), also a mixture of **22** (0.0115 g, 9.8%) and **3** (0.0056 g, 1.7%; cf. 2.1) and as a further compound the tetracycle 'syn'-**40** (0.022 g, 13%) which was additionally purified by prep. HPLC to yield 0.010 g (5.9%) of the pure compound.

Tetramethyl (1RS,2RS,5SR,8RS)-6,8,11,13,14-pentamethyltetracyclo[6.2.2.2^{2,5}.0^{1,5}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate ('syn'-40**).** Colorless oil, *R_f* (Et₂O/hexane 3:2): 0.13. ¹H-NMR (300 MHz, CDCl₃/C₆D₆): 5.763/5.795 (*q*, ⁴*J*(H,CH₃–C(6)) = 1.4, H–C(7)); 5.721/5.598 (*q*, ⁴*J*(H,CH₃–C(11)) = 1.6, H–C(12)); 4.181/4.490 (*s*, H–C(2)); 3.744, 3.729, 3.717, and 3.561/3.481, 3.423, and 3.413 (4s/3s (1:2:1), 4 COOCH₃); 1.894/1.720 (*q*-like, ⁵*J*(CH₃,CH₃–C(13)) ≈ 1.2, CH₃–C(14)); 1.731/1.591 (*d*, ⁴*J*(CH₃,H–C(12)) = 1.5, CH₃–C(11)); 1.687/1.550 (*q*-like, ⁵*J*(CH₃,CH₃–C(14)) ≈ 1.2, CH₃–C(13)); 1.677/1.699 (*d*, ⁴*J*(CH₃,H–C(7)) = 1.4/1.3, CH₃–C(6)); 1.250/1.285 (*s*, CH₃–C(8)). ¹H-NOE (400 MHz, C₆D₆): 1.550 (CH₃–C(13)) → 1.720 (*m*, CH₃–C(14)), 1.699 (*s*, CH₃–C(6)); 1.591 (CH₃–C(11)) → 5.598 (*s*, H–C(12)), 4.490 (*s*, H–C(2)), 1.720 (*m*, CH₃–C(14)); 1.699 (CH₃–C(6)) → 5.795 (*s*, H–C(7)), 3.481 (*m*, C(4)–COOCH₃), 1.550 (*s*, CH₃–C(13)); 1.720 (CH₃–C(14)) → 4.490 (*s*, H–C(2)), 1.591 (*m*, CH₃–C(11)), 1.550 (*m*, CH₃–C(13)).

2.5.1. Control Experiments with 39a. 2.5.1.1. **Photochemical Isomerization into Dimethyl 1,2,6,8,10-pentamethylheptalene-4,5-dicarboxylate (39b).** Compound **39a** (4.4 mg) was dissolved in hexane/(CH₂Cl₂ + 0.5% MeOH) 9:1 and irradiated with 366-nm light during 76 h. According to HPLC, a new compound (69%), namely **39b**, had been formed beside **39a** (31%). Crystallization of the mixture from hexane at –20° yielded a small amount of **39b**. M.p. 114.3–115.7°. UV (hexane): $\lambda_{\max}$ 370 (2.93), 268 (4.33), 246 (sh, 4.18), 208 (sh, 4.36); $\lambda_{\min}$ 347 (2.90), 232 (4.17). ¹H-NMR (300 MHz; taken from the photo-mixture of 69% of **39b** and 31% of **39a**): 6.474 (*d*, ⁴*J*(H,CH₃–C(2)) = 1.2, H–C(3)); 6.066 (br. s, H–C(7)); 5.985 (*quint.*-like, ⁴*J*(H,CH₃–C(10)) ≈ ⁴*J*(H,H–C(7)),H–C(9)); 3.827 (*s*, C(4)–COOCH₃); 3.704 (*s*, C(5)–COOCH₃); 2.048 (*d*, ⁴*J*(CH₃,H–C(3)) = 1.3, CH₃–C(2)); 2.035 (*d*, ⁴*J*(CH₃,H–C(9)) = 1.3, CH₃–C(10)); 1.999 (*d*, ⁴*J*(CH₃,H–C(7)) = 1.1, CH₃–C(8)); 1.756 (*s*, CH₃–C(1)); 1.663 (*s*, CH₃–C(6)). ¹H-DR (400 MHz): 6.474 (*q*, H–C(3)) → 2.048 (*s*, CH₃–C(2)); 6.066 (br. s, H–C(7)) → 5.985 (*q*-like, H–C(9)), 1.999 (*s*, CH₃–C(8)); 5.985 (*quint.*-like, H–C(9)) → 2.035 (*s*, CH₃–C(10)). ¹H-NOE (400 MHz): 1.999 (CH₃–C(8)) → 6.066 (*s*, H–C(7)), 5.985 (*s*, H–C(9)); 1.756 (CH₃–C(1)) → 2.048 (*s*, CH₃–C(2)), 2.035 (*s*, CH₃–C(10)); 1.663 (CH₃–C(6)) → 6.066 (*s*, H–C(7)), 3.704 (*m*, C(5)).

2.5.1.2. Thermal Isomerization. The soln. of **39a** (11.9 mg) in decalin (1 ml) was not changed when heated at 60 to 150°. However, the equilibrium mixture of 77% of **39a** and of 23% of **39b** (HPLC) was attained after heating at 180° during 6 h. Prolonged heating at 180° led to partial decomposition of **39a/39b**.

2.6. Azulene 1 and ADM. The azulene (0.815 g; 4.11 mmol) and ADM (2.0 g; 14.07 mmol) were heated in freshly under Ar distilled decalin (15 ml) during 55 min at 220°. Decalin and excess ADM were distilled off (high vacuum) and the residue chromatographed (CC; Et₂O/hexane 3:2) on silica gel to yield 1.2 g of a fraction mainly consisting of the bisadduct '*anti*'-**5** (total yield *ca.* 60%) and traces of *dimethyl 3,4,6,8-tetramethylazulene-1,2-dicarboxylate* (**3**; total yield *ca.* 1%) and three additional fractions (in total 0.154 g; 11%²³).

²³) A second run was performed with 1.3 g (6.6 mmol) of **1** and 1.6 g of ADM (11.3 mmol) in 15 ml of tetralin at 150° for 4 h. Chromatographic workup yielded 0.35 g of **1** (27%), 0.254 g (11.3%) of a mixture **2a/2b/4**, as well as a fraction (containing > 10% of '*anti*'-**5** and **3**) from which after crystallization from Et₂O 0.115 g (5%) '*anti*'-**5** and after prep. TLC of the mother liquor *ca.* 0.015 g (*ca.* 1%) **3** were obtained.

containing nearly pure *dimethyl 1,3,6,8,10-pentamethylheptalene-4,5-dicarboxylate* (**2b**; 0.065 g), a mixture (0.058 g) of *dimethyl 3,5,6,8,10-pentamethylheptalene-1,2-dicarboxylate* (**2a**), and *dimethyl 2,4,6,8,11-pentamethyltricyclo[6.2.2.0^{1,5}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**4**), and finally pure **2a** (0.031 g). Fractionated crystallization of the first fraction from AcOEt/hexane yielded pure '*anti*'-**5** (0.74 g; 37%) and **3** (5 mg; 0.4%). Fractions **3** and **4** yielded by crystallization from hexane a first crop of pure **4** and **2a**. The mother liquors and the second fraction were subjected to prep. HPLC with hexane/(CH₂Cl₂ + 0.5% MeOH) 9:1 to yield in total (after recrystallization) 32 mg (2.3%; from Et₂O/hexane) of **2b**, 35 mg (2.5%; from hexane/Et₂O at –20°) of **2a**, and 38 mg (2.7%; from hexane) of **4**.

Tetramethyl (1RS,2RS,5RS,8RS)-2,6,8,11,13-pentamethyltetracyclo[6.2.2.2^{2,5}.0^{1,7}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate ('*anti*'-**5**). Colorless crystals. M.p. 159–160°. *R*_f (hexane/Et₂O 3:2 [1:2]): 0.18 [0.43]. UV (hexane): $\lambda_{\max}$ 290 (sh, 2.99), 220 (4.10); $\lambda_{\min}$ 216 (4.09). IR (KBr): 2988, 2951, 2910, 2856, 1718s (COOMe), 1631, 1598, 1434, 1388, 1342, 1310, 1258, 1229, 1143, 1114, 1085, 1051, 1033, 955, 926, 877, 813, 795, 775, 757, 737. ¹H-NMR (400 MHz): 6.226 (*q*-like, ⁴*J*(H,CH₃–C(11)) = 1.7, H–C(12)); 5.668 (*quint*-like, ⁴*J*(H,CH₃–C(13)) ≈ ⁴*J*(H,H–C(5)) ≈ 1.6, H–C(14)), 3.828, 3.797, 3.742, 3.690 (4s, 4 COOCH₃); 3.331 (*d*-like, ⁴*J*(H,H–C(14)) = 1.6, H–C(5)); 2.050 (*d*-like, ⁴*J* = 1.6, CH₃–C(11)); 1.863 (*s*, CH₃–C(6)); 1.841 (*d*-like, ⁴*J* ≈ 1.4, CH₃–C(13)); 1.733 (*s*, CH₃–C(8)); 1.542 (*s*, CH₃–C(2)). MS: 482 (4, *M*⁺), 467 (1), 451 (7), 450 (10), 435 (10), 423 (7), 407 (6), 403 (5), 391 (16), 375 (5), 363 (10), 359 (7), 331 (8), 303 (6), 299 (5), 260 (22), 249 (9), 245 (6), 241 (8), 228 (100). Anal. calc. for C₂₇H₃₀O₈ (482.53): C 67.21, H 6.27; found: C 67.23, H 6.31.

The structure of '*anti*'-**5** was confirmed by an X-ray structure analysis. *Crystal data*: space group and cell dimensions: triclinic *P*1 with *a* = 1187.2, *b* = 1402.1, *c* = 1612.9 pm and α = 110.39°, β = 104.06°, γ = 91.21°; *D*_{calc.} 1.32 Mg m^{–3}, *Z* = 4, μ (MoK α) = 0.06 mm^{–1}; measured data: 8853, observed data: 5888; *R* = 0.0498. Bond lengths [pm]: C(1)–C(2), 155.6; C(1)–C(7), 155.1; C(1)–C(10), 156.9; C(1)–C(12), 156.7; C(2)–C(3), 153.7; C(2)–C(14), 152.8; C(3)–C(4), 133.7; C(4)–C(5), 151.3; C(5)–C(6), 154.1; C(5)–C(13), 152.0; C(6)–C(7), 132.0; C(7)–C(8), 154.5; C(8)–C(9), 154.9; C(8)–C(11), 152.6; C(9)–C(10), 133.7; C(11)–C(12), 132.0; C(13)–C(14), 132.2. Valence angles [°]: C(1)–C(2)–C(3), 108.7; C(1)–C(2)–C(14), 106.2; C(1)–C(7)–C(6), 129.5; C(3)–C(2)–C(14), 107.0; C(2)–C(1)–C(7), 117.8; C(2)–C(1)–C(10), 117.0; C(10)–C(1)–C(12), 104.6; C(2)–C(3)–C(4), 118.1; C(3)–C(4)–C(5), 118.1; C(4)–C(5)–C(6), 110.3; C(4)–C(5)–C(13), 108.9; C(6)–C(5)–C(13), 109.4; C(5)–C(6)–C(7), 119.2; C(6)–C(7)–C(8), 134.0; C(7)–C(8)–C(9), 96.2; C(7)–C(8)–C(11), 97.0; C(8)–C(9)–C(10), 108.5; C(8)–C(11)–C(12), 110.6; C(1)–C(10)–C(9), 107.6; C(1)–C(12)–C(11), 106.5; C(5)–C(13)–C(14), 116.6; C(2)–C(14)–C(13), 120.4. Torsion angles [°]: C(2)–C(3)–C(4)–C(5), 0.3; C(2)–C(1)–C(6)–C(5), 179.1; C(5)–C(6)–C(7)–C(1), –3.6; C(1)–C(7)–C(6)–CH₃, 173.6; C(8)–C(7)–C(6)–CH₃, 0.8; C(5)–C(6)–C(7)–C(8), –176.4; C(5)–C(13)–C(14)–C(2), –0.8; C(8)–C(11)–C(12)–C(1), 2.0; C(8)–C(9)–C(10)–C(1), 1.4.

Data of 3. Dark blue crystals. M.p. 152–153°. *R*_f (hexane/Et₂O 3:2 [1:2]): 0.16 [0.23]. UV (hexane): $\lambda_{\max}$ 372 (sh, 3.51), 359 (3.79), 347 (sh, 3.73), 309 (4.70), 300 (sh, 4.65), 253 (4.44), 224 (4.13); $\lambda_{\min}$ 334 (3.64), 272 (3.89), 230 (4.12). IR (KBr): 2991, 2951, 2920, 1725s/1712s (COOMe), 1584, 1553, 1506. ¹H-NMR (250 MHz): 6.982 (br. *s*, H–C(5,7)); 3.915, 3.910 (2s, 2 COOCH₃); 3.015, 2.882 (2s, CH₃–C(4,8)); 2.780 (*s*, CH₃–C(3)); 2.540 (*s*, CH₃–C(6)). MS: 300 (95, *M*⁺), 285 (4), 269 (86), 268 (87), 253 (23), 240 (21), 237 (42), 236 (100), 225 (11), 209 (28), 208 (80). Anal. calc. for C₁₈H₂₀O₄ (300.35): C 71.98, H 6.71; found: C 71.54, H 6.58.

Data of 2b. Orange crystals. M.p. 121–122°. *R*_f (hexane/Et₂O 3:2 [7:3]): 0.29 [0.24]. UV (hexane): $\lambda_{\max}$ 382 (2.86), 310 (sh, 3.60), 269 (4.25), 234 (sh, 4.22), 207 (4.36); $\lambda_{\min}$ 362 (2.82), 252 (4.16). IR (KBr): 2949, 2914, 2856, 1734/1713 (COOMe), 1606, 1556, 1515, 1429, 1373, 1322, 1261, 1222, 1186, 1157, 1121, 1066, 1048, 1033, 1002, 959, 905, 870, 843, 829, 791, 773, 745, 717, 630, 585. ¹H-NMR (400 MHz): 6.439 (*q*-like, ⁴*J*(H,CH₃–C(3)) = 1.4, H–C(2)); 6.115 (br. *s*, H–C(7)); 6.009 (*t*-like, ⁴*J* ≈ 1.3, H–C(7)); 3.885, 3.666 (2s, 2 COOCH₃); 2.024 (*d*-like, ⁴*J*(CH₃,H–C(2)) = 1.4, CH₃–C(3)); 1.995 (*d*-like, ⁴*J*(CH₃,H–C(7)) = 1.2, CH₃–C(8)); 1.973 (*d*-like, ⁴*J*(CH₃,H–C(9)) = 1.3, CH₃–C(10)); 1.766 (*s*, CH₃–C(1)); 1.644 (*s*, CH₃–C(6)). ¹H-DR (400 MHz): 2.024 (CH₃–C(3)) → 6.439 (*s*, H–C(2)); 1.995 (CH₃–C(8)) → 6.115 (*ss*, H–C(7)), 6.009 (*ss*, H–C(9)); 1.973 (CH₃–C(10)) → 6.009 (*d*, ⁴*J*(H,H–C(7)) ≈ 1, H–C(9)); 1.644 (CH₃–C(6)) → 6.115 (*ss*, H–C(7)). ¹H-NOE (400 MHz): 2.024 (CH₃–C(3)) → 6.439 (H–C(2), 10.7%), 1.995 (CH₃–C(8)) → 6.115 (H–C(7), 9.4%), 6.009 (H–C(9), 9.0%), 1.766 (CH₃–C(1)) → 6.439 (H–C(2), 8.5%), 1.644 (CH₃–C(6)) → 6.115 (H–C(7), 9.4%). MS: 340 (90, *M*⁺), 325 (71), 309 (17), 300 (3, [*M* – CH₃–C≡CH]⁺), 293 (17), 286 (2), 281 (22), 266 (31), 254 (5), 249 (19), 242 (100, [*M* – CH₃–C≡C–COOCH₃]⁺), 227 (8), 221 (23), 211 (34), 207 (26), 198 (24, [*M* – ADM]⁺), 191 (16), 183 (12), 165 (15). Anal. calc. for C₂₁H₂₄O₄ (340.42): C 74.09, H 7.11; found: C 73.82, H 7.11.

Data of 2a. Yellow crystals. M.p. 143.7–145.6°. *R*_f (hexane/Et₂O 3:2): 0.24. UV (hexane): $\lambda_{\max}$ 319 (3.58), 261 (4.24), 213 (4.39), 201 (sh, 4.33); $\lambda_{\min}$ 309 (3.57), 246 (4.21). IR (KBr): 2985, 2950, 2910, 1728 (COOMe), 1435, 1373, 1280, 1230, 1195, 1144, 1110, 1066, 1011, 943, 878, 790, 747. ¹H-NMR (400 MHz): 6.159 (br. *s*, H–C(7));

6.068 (*d*, $^4J(\text{H}, \text{CH}_3-\text{C}(5)) = 1.2$, $\text{H}-\text{C}(4)$); 6.000 (*t*-like, $\text{H}-\text{C}(9)$); 3.671, 3.637 (2*s*, 2 COOCH_3); 2.269 (*s*, $\text{CH}_3-\text{C}(3)$); 2.056 (*d*, $^4J(\text{CH}_3, \text{H}-\text{C}(9)) = 1.1$, $\text{CH}_3-\text{C}(10)$); 1.984 (*d*, $^4J(\text{CH}_3, \text{H}-\text{C}(7)) = 1.2$, $\text{CH}_3-\text{C}(8)$), 1.941 (*d*, $^4J(\text{CH}_3, \text{H}-\text{C}(4)) = 1.2$, $\text{CH}_3-\text{C}(5)$); 1.774 (*s*, $\text{CH}_3-\text{C}(6)$). MS: 340 (100, M^+), 235 (50), 309 (15), 293 (13), 281 (16), 266 (16), 242 (59, $[\text{M} - \text{CH}_3 - \text{C} \equiv \text{C} - \text{COOCH}_3]^+$), 222 (13), 221 (16), 211 (61), 207 (19), 206 (12), 198 (13, $[\text{M} - \text{ADM}]^+$), 192 (13), 191 (17), 165 (14). Anal. calc. for $\text{C}_{21}\text{H}_{24}\text{O}_4$ (340.42): C 74.09, H 7.11; found: C 73.80, H 7.30.

Data of 4. Dark yellow crystals. M.p. 87.2–88.4°. R_f (hexane/Et₂O 3:2): 0.24. UV (hexane): λ_{max} 330 (3.68), 296 (3.72), 221 (3.96); λ_{min} 317 (3.66), 272 (3.68). IR (KBr): 3030, 2970, 2915, 1733/1723 (COOMe), 1614, 1450, 1435, 1381, 1302, 1258, 1232, 1209, 1182, 1153, 1139, 1084, 1050, 1008, 945, 914, 876, 825, 806, 790, 770, 739, 698, 641. $^1\text{H-NMR}$ (200 MHz): 6.206 (*q*-like, $^4J(\text{H}, \text{CH}_3-\text{C}(2)) = 1.5$, $\text{H}-\text{C}(3)$); 5.670 (*q*, $^4J(\text{H}, \text{CH}_3-\text{C}(11)) = 1.6$, $\text{H}-\text{C}(12)$); 5.240 (br. *s*, $\text{H}-\text{C}(7)$); 3.769 (*s*, $\text{C}(9)-\text{COOCH}_3$); 3.611 (*s*, $\text{C}(10)-\text{COOCH}_3$); 2.199 (*s*, $\text{CH}_3-\text{C}(4)$); 2.016 (*d*, $^4J(\text{CH}_3, \text{H}-\text{C}(7)) = 1.6$, $\text{CH}_3-\text{C}(6)$); 1.999 (*d*, $^4J(\text{CH}_3, \text{H}-\text{C}(3)) = 1.4$, $\text{CH}_3-\text{C}(2)$); 1.487 (*d*, $^4J(\text{CH}_3, \text{H}-\text{C}(12)) = 1.6$, $\text{CH}_3-\text{C}(11)$); 1.423 (*s*, $\text{CH}_3-\text{C}(8)$). $^1\text{H-DR}$ (400 MHz): 1.487 (*d*, $\text{CH}_3-\text{C}(11) \rightarrow 5.670$ (*s*, $\text{H}-\text{C}(12)$); 1.999 (*d*, $\text{CH}_3-\text{C}(2) \rightarrow 6.206$ (*s*, $\text{H}-\text{C}(3)$); 2.016 (*d*, $\text{CH}_3-\text{C}(6) \rightarrow 5.240$ (*ss*, $\text{H}-\text{C}(7)$); 2.199 (*s*, $\text{CH}_3-\text{C}(4) \rightarrow 6.206$ (*sq*, $J = 1.6$, $\text{H}-\text{C}(3)$); 5.240 (*q*-like, $J = 1.5$, $\text{H}-\text{C}(7)$). $^1\text{H-NOE}$ (400 MHz): 1.423 ($\text{CH}_3-\text{C}(8) \rightarrow 5.670$ (*s*, $\text{H}-\text{C}(12)$), 5.240 (*s*, $\text{H}-\text{C}(7)$), 3.769 (*w*, $\text{C}(9)-\text{COOCH}_3$); 1.999 ($\text{CH}_3-\text{C}(2) \rightarrow 6.206$ (*s*, $\text{H}-\text{C}(3)$), 1.487 (*m*, $\text{CH}_3-\text{C}(11)$), 3.611 (*w*, $\text{C}(10)-\text{COOCH}_3$); 2.016 ($\text{CH}_3-\text{C}(6) \rightarrow 5.240$ (*s*, $\text{H}-\text{C}(7)$), 2.199 (*s*, $\text{CH}_3-\text{C}(4)$); 2.199 ($\text{CH}_3-\text{C}(4) \rightarrow 6.206$ (*s*, $\text{H}-\text{C}(3)$), 2.016 (*s*, $\text{CH}_3-\text{C}(6)$). CI-MS: 341 (100, $[\text{M} + 1]^+$), 310 (45), 309 (22), 281 (5), 266 (5), 208 (4).

The structure of **4** was confirmed by an X-ray structure analysis. *Crystal data*: space group and cell dimensions: monoclinic $P2_1/c$ with $a = 1293.2$, $b = 1475.8$, $c = 1030.2$ pm, and $\beta = 111.28^\circ$; D_{calc} : 1.234 Mg m^{-3} , $Z = 4$; $\mu(\text{MoK}\alpha) = 0.788 \text{ cm}^{-1}$; measured reflexions (at -60°): 4296, observed 2307; $R = 0.044$. Bond lengths [pm]: $\text{C}(1)-\text{C}(2)$, 150.3; $\text{C}(1)-\text{C}(5)$, 154.1; $\text{C}(2)-\text{C}(3)$, 133.2; $\text{C}(3)-\text{C}(4)$, 145.9; $\text{C}(4)-\text{C}(5)$, 136.0; $\text{C}(5)-\text{C}(6)$, 146.2; $\text{C}(6)-\text{C}(7)$, 134.6; $\text{C}(7)-\text{C}(8)$, 152.4; $\text{C}(8)-\text{C}(9)$, 153.5; $\text{C}(8)-\text{C}(11)$, 151.8; $\text{C}(9)-\text{C}(10)$, 133.5; $\text{C}(10)-\text{C}(1)$, 152.6; $\text{C}(11)-\text{C}(12)$, 131.0; $\text{C}(12)-\text{C}(1)$, 155.0. Valence angles [$^\circ$]: $\text{C}(1)-\text{C}(2)-\text{C}(3)$, 108.5; $\text{C}(1)-\text{C}(5)-\text{C}(6)$, 121.1; $\text{C}(2)-\text{C}(3)-\text{C}(4)$, 111.3; $\text{C}(3)-\text{C}(4)-\text{C}(5)$, 108.9; $\text{C}(4)-\text{C}(5)-\text{C}(1)$, 107.7; $\text{C}(4)-\text{C}(5)-\text{C}(6)$, 131.2; $\text{C}(5)-\text{C}(1)-\text{C}(2)$, 103.2; $\text{C}(5)-\text{C}(6)-\text{C}(7)$, 122.8; $\text{C}(6)-\text{C}(7)-\text{C}(8)$, 127.0; $\text{C}(7)-\text{C}(8)-\text{C}(9)$, 104.7; $\text{C}(7)-\text{C}(8)-\text{C}(11)$, 109.1; $\text{C}(8)-\text{C}(9)-\text{C}(10)$, 117.9; $\text{C}(9)-\text{C}(8)-\text{C}(11)$, 107.7; $\text{C}(9)-\text{C}(10)-\text{C}(1)$, 117.7; $\text{C}(10)-\text{C}(1)-\text{C}(2)$, 115.5; $\text{C}(10)-\text{C}(1)-\text{C}(5)$, 109.7; $\text{C}(10)-\text{C}(1)-\text{C}(12)$, 109.4; $\text{C}(8)-\text{C}(11)-\text{C}(12)$, 120.6; $\text{C}(11)-\text{C}(12)-\text{C}(1)$, 116.0; $\text{C}(12)-\text{C}(1)-\text{C}(2)$, 112.6; $\text{C}(12)-\text{C}(1)-\text{C}(5)$, 105.8. Torsion angles [$^\circ$]: $\text{C}(1)-\text{C}(2)-\text{C}(3)-\text{C}(4)$, 3.2; $\text{C}(2)-\text{C}(3)-\text{C}(4)-\text{C}(5)$, -0.3 ; $\text{C}(3)-\text{C}(4)-\text{C}(5)-\text{C}(1)$, -2.7 ; $\text{C}(3)-\text{C}(4)-\text{C}(5)-\text{C}(6)$, 177.7; $\text{C}(4)-\text{C}(5)-\text{C}(6)-\text{C}(7)$, 173.1; $\text{C}(5)-\text{C}(6)-\text{C}(7)-\text{C}(8)$, -0.2 ; $\text{C}(6)-\text{C}(7)-\text{C}(8)-\text{C}(9)$, 62.0; $\text{C}(6)-\text{C}(7)-\text{C}(8)-\text{C}(11)$, -53.1 ; $\text{C}(7)-\text{C}(8)-\text{C}(9)-\text{C}(10)$, -73.2 ; $\text{C}(7)-\text{C}(8)-\text{C}(11)-\text{C}(12)$, 70.1; $\text{C}(8)-\text{C}(9)-\text{C}(10)-\text{C}(1)$, -1.4 ; $\text{C}(8)-\text{C}(11)-\text{C}(12)-\text{C}(1)$, 0.9; $\text{C}(9)-\text{C}(10)-\text{C}(1)-\text{C}(5)$, 74.4; $\text{C}(11)-\text{C}(12)-\text{C}(1)-\text{C}(5)$, -76.4 ; $\text{C}(10)-\text{C}(1)-\text{C}(2)-\text{C}(3)$, -124.2 ; $\text{C}(10)-\text{C}(1)-\text{C}(5)-\text{C}(6)$, -52.3 ; $\text{C}(12)-\text{C}(1)-\text{C}(2)-\text{C}(3)$, 109.1; $\text{C}(12)-\text{C}(1)-\text{C}(5)-\text{C}(6)$, 65.6; $\text{CH}_3\text{C}(2)-\text{C}(1)-\text{C}(10)$, 56.4; $\text{CH}_3-\text{C}(2)-\text{C}(1)-\text{C}(12)$, -70.3 ; $\text{CH}_3-\text{C}(2)-\text{C}(3)-\text{C}(4)$, -177.4 ; $\text{CH}_3-\text{C}(4)-\text{C}(3)-\text{C}(2)$, -179.3 ; $\text{CH}_3-\text{C}(4)-\text{C}(5)-\text{C}(6)$, -3.4 ; $\text{CH}_3-\text{C}(6)-\text{C}(5)-\text{C}(4)$, -9.4 ; $\text{CH}_3-\text{C}(6)-\text{C}(7)-\text{C}(8)$, -177.7 ; $\text{CH}_3-\text{C}(8)-\text{C}(7)-\text{C}(6)$, -175.5 ; $\text{CH}_3-\text{C}(12)-\text{C}(11)-\text{C}(8)$, -173.5 ; $\text{CH}_3-\text{C}(12)-\text{C}(1)-\text{C}(2)$, -13.8 ; $\text{O}=\text{C}-\text{C}(9)-\text{C}(10)$, -112.9 ; $\text{O}-\text{C}-\text{C}(9)-\text{C}(10)$, 69.6; $\text{O}=\text{C}-\text{C}(10)-\text{C}(9)$, -136.2 ; $\text{O}-\text{C}-\text{C}(10)-\text{C}(9)$, 42.6.

2.6.1. Control Experiments with 2a and 2b. 2.6.1.1. *Photochemical Isomerizations.* Anal. probes of both pure heptalenes were dissolved in hexane/ CH_2Cl_2 (9:1; $c \approx 5 \cdot 10^{-3} \text{ M}$) and irradiated with 366-nm light under stirring. After 18 h, the percentage of **2a** (87%) and **2b** (13%) remained constant in both runs (HPLC).

2.6.1.2. *Thermal Isomerizations.* The two heptalenes (*ca.* 1 mg) were each dissolved in decane (0.2 ml) and heated at 100° under exclusion of light. After 45 h, the percentage of **2a** (73%) and **2b** (27%) remained constant in both runs (HPLC).

2.6.2. Control Experiments with 4. 2.6.2.1. *Thermal Isomerization into Dimethyl 2,4,6,8,10,11-Pentamethyltricyclo[6.2.2.0^{1,5}]dodeca-2,4,6,9,11-pentaene-6,7-dicarboxylate (18).* It turned out that **4** already during $^1\text{H-NMR}$ measurements in CDCl_3 soln. rearranged into a new product, namely **18**. To obtain **18** in a pure state, **4** (4.8 mg) was dissolved in hexane/ CHCl_3 and heated at 40° during 64 h. The new tricycle **18** was formed in *ca.* 30% yield and isolated by prep. HPLC. UV (qual.; hexane/ $(\text{CH}_2\text{Cl}_2 + 0.5\% \text{ MeOH}) = 9:1$): λ_{max} 335 and 217; λ_{min} 252. IR (CHCl_3): 3024*m*, 2928*s*, 2856*m*, 1725*s*, 1616*m*, 1436*s*, 1381*m*, 1263*s*, 1087*m*, 1011*m*, 863*w*, 800*w*. $^1\text{H-NMR}$ (400 MHz): 6.299 (*q*, $^4J(\text{H}, \text{CH}_3-\text{C}(2)) = 1.5$, $\text{H}-\text{C}(3)$); 5.685 (*q*-like, $^4J(\text{H}, \text{CH}_3-\text{C}(10)) = ^4J(\text{H}, \text{CH}_3-\text{C}(11)) = 1.4$, $\text{H}-\text{C}(9,12)$); 3.746 (*s*, $\text{C}(7)-\text{COOCH}_3$); 3.733 (*s*, $\text{C}(6)-\text{COOCH}_3$); 2.175 (*d*, $^4J(\text{CH}_3, \text{H}-\text{C}(3)) = 1.2$, $\text{CH}_3-\text{C}(2)$); 1.877 (*s*, $\text{CH}_3-\text{C}(4)$); 1.522 (*d*, $^4J(\text{CH}_3, \text{H}-\text{C}(9)) = ^4J(\text{CH}_3, \text{H}-\text{C}(12)) = 1.4$, $\text{CH}_3-\text{C}(10,11)$); 1.428 (*s*, $\text{CH}_3-\text{C}(8)$). $^1\text{H-DR}$ (400 MHz): 6.299 (*q*, $\text{H}-\text{C}(3) \rightarrow 2.175$ (*s*, $\text{CH}_3-\text{C}(2)$); 5.685 (*q*-like, $\text{H}-\text{C}(9,12) \rightarrow 1.522$ (*s*,

CH₃–C(10,11)). ¹H-NOE (400 MHz): 2.175 (CH₃–C(2))→6.299 (s, H–C(3)), 1.522 (s, CH₃–C(10,11)); 1.877 (CH₃–C(4))→6.299 (s, H–C(3)), 3.733 (m, C(6)–COOCH₃); 1.428 (CH₃–C(8))→5.685 (s, H–C(9,12)), 3.746 (m, C(7)–COOCH₃). The equilibrium of **4** and **18** in decalin at 100° after 1 h amounted to 73% of **4** and 27% of **18** (determined – after removal of decalin – by ¹H-NMR in CDCl₃ by integration of the signals of the ester groups).

2.6.2.2. *Photochemical Isomerization into Dimethyl 2,4,6,9,11-Pentamethyltetracyclo[7.2.1.0^{1,5}.0^{8,12}]dodeca-2,4,6,10-tetraene-8,12-dicarboxylate (20)*. Compound **4** (4.8 mg) was dissolved in hexane/CH₂Cl₂ 9:1 (2 ml) and irradiated at 366 nm during 18 h. After this time, **4** had been completely consumed, and a new product, namely **20**, had been formed in over 90% yield. Prep. TLC on silica gel (Et₂O/hexane 3:2) yielded pure **20** (3.2 mg; 67%) as a dark yellow oil. UV (qual.; hexane/(CH₂Cl₂ + 0.5% MeOH) 9:1): λ_{max} 409, 318, 257, 223; λ_{min} 376, 285, 244. IR (CHCl₃): 3030m, 2954m, 2856m, 1732s, 1437s, 1379m, 1262s, 1094m, 1015m, 806w. ¹H-NMR (300 MHz): 6.064 (q-like, ⁴J(H,CH₃–C(2)) ≈ 1.6, H–C(3)); 5.601 (br. s, H–C(7)); 5.491 (q-like, ⁴J(H,CH₃–C(11)) = 1.5, H–C(10)); 3.675 (s, C(12)–COOCH₃); 3.606 (s, C(8)–COOCH₃); 2.083 (s, CH₃–C(4)); 2.044 (d, ⁴J(CH₃,H–C(7)) = 1.4, CH₃–C(6)); 1.782 (d, ⁴J(CH₃,H–C(3)) = 1.3, CH₃–C(2)); 1.596 (s, CH₃–C(9)); 1.071 (d, ⁴J(CH₃,H–C(10)) = 1.4, CH₃–C(11)). ¹H-DR (400 MHz): 6.064 (q-like, H–C(3))→1.782 (s, CH₃–C(2)); 5.601 (br. s, H–C(7))→2.044 (s, CH₃–C(6)); 5.491 (q-like, H–C(10))→1.071 (s, CH₃–C(11)); 2.044 (d, CH₃–C(6))→5.601 (ss, H–C(7)); 1.782 (d, CH₃–C(2))→6.064 (s, H–C(3)); 1.071 (d, CH₃–C(11))→5.491 (s, H–C(10)). ¹H-NOE (400 MHz): 2.083 (CH₃–C(4))→6.064 (s, H–C(3)), 2.044 (m, CH₃–C(6)); 2.044 (CH₃–C(6))→5.601 (s, H–C(7)), 2.083 (m, CH₃–C(4)); 1.782 (CH₃–C(2))→6.064 (s, H–C(3)), 3.606 (w, C(12)–COOCH₃), 1.071 (w, CH₃–C(11)); 1.596 (CH₃–C(9))→5.491 (s, H–C(10)), 3.675 (w, C(8)–COOCH₃), 3.606 (w, C(12)–COOCH₃); 1.071 (CH₃–C(11))→5.491 (s, H–C(10)), 1.782 (m, CH₃–C(2)).

2.7. *Azulene 11 and ADM*. The azulene (0.200 g; 0.883 mmol) and ADM (0.600 g; 4.22 mmol) were dissolved in tetralin (4.0 ml) and the soln. distributed over 4 Pyrex ampoules (inner diameter 7 mm). The ampoules were degassed and sealed under high vacuum, preheated at 100° and then dipped for 30 min in an oil bath at 220°. Tetralin and excess ADM were distilled off (high vacuum; 50°) and the residue separated two times on two prep. TLC plates on silica gel (hexane/Et₂O 3:2) to yield three fractions. The first fraction (0.0634 g; 19.5%) contained mainly dimethyl 1,3,6,10-tetramethyl-8-propylheptalene-4,5-dicarboxylate (**12b**) and dimethyl 3,5,6,10-tetramethyl-8-propylheptalene-1,2-dicarboxylate (**12a**), the second (0.116 g; 40%) mainly dimethyl 3,4,8-trimethyl-6-propylazulene-1,2-dicarboxylate (**13**), and the third (0.173 g; 38%) nearly pure bisadduct 'anti'-**14**. The heptalenes **12b** and **12a** were separated by prep. HPLC (hexane/(CH₂Cl₂ + 0.1% MeOH) 88:12) and crystallized from hexane at –20°. The azulene **13** crystallized from Et₂O/hexane at 5° in a small amount. The bisadduct 'anti'-**14** was further purified by prep. TLC on silica gel (toluene/AcOEt 9:1) and obtained as a viscous, slightly greenish oil.

Tetramethyl (1RS,2RS,5RS,8RS)-2,6,8,11-Tetramethyl-13-propyltetracyclo[6.2.2.2^{0,5}.0^{1,7}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate ('anti'-14). Viscous oil. R_f (hexane/Et₂O 3:2): 0.18. UV (Et₂O; qual.): λ_{max} 307 (sh), 296, 221; λ_{min} 282. IR (CHCl₃): 3020m, 2955s, 2872w, 1711s, 1628m, 1595m, 1456m, 1434s, 1385w, 1374w, 1258w, 1145m, 1113w, 1092w, 1050s. ¹H-NMR (400 MHz): 6.219 (q-like, ⁴J(H,CH₃–C(3)) = 1.5, H–C(12)); 5.649 (q-like, ⁴J(H,EtCH₂–C(13)) ≈ ⁴J(H,H–C(5)) ≈ 1.5, H–C(14)); 3.815, 3.791, 3.735, 3.679 (4s, 4 COOCH₃); 3.342 (d-like, ⁴J(H,H–C(14)) ≈ 2.0, H–C(5)); 2.15–2.05 (m, CH₃CH₂CH₂); 2.044 (d-like, ⁴J ≈ 2.0, CH₃–C(11)); 1.850 (s, CH₃–C(6)); 1.720 (s, CH₃–C(8)); 1.559 (s, CH₃–C(2)); 1.53–1.37 (m, CH₃CH₂CH₂); 0.864 (t, CH₃CH₂CH₂). MS: 510 (13, M⁺), 479 (15), 478 (24), 451 (12), 436 (10), 435 (28), 419 (23), 391 (12), 260 (42), 229 (21), 228 (100).

Data of 13. Dark blue crystals. M.p. 131.8–133.1°. R_f (hexane/Et₂O 3:2): 0.23. UV (hexane): λ_{max} 371 (sh, 3.53), 357 (3.79), 346 (sh, 3.73), 310 (4.70), 302 (sh, 4.64), 253 (4.44), 224 (sh, 4.17), 199 (4.65); λ_{min} 335 (3.66), 272 (3.90), 231 (4.14). IR (CHCl₃): 3020w, 2950m, 2872w, 1712s, 1580m, 1550w, 1436s, 1406m, 1373w, 1233s, 1191m, 1113m, 1070w, 1059w, 1038w, 998w. ¹H-NMR (400 MHz): 6.977, 6.971 (2s, H–C(5,7)); 3.921, 3.916 (2s, 2 COOCH₃); 3.039, 2.893 (2s, CH₃–C(4,8)); 2.800 (s, CH₃–C(3)); 2.672, 1.716, 0.984 (t,m,t, CH₃CH₂CH₂). MS: 328 (100, M⁺), 298 (15), 297 (76), 296 (68), 281 (27), 265 (34), 264 (88), 238 (16), 236 (50), 228 (21), 210 (27), 179 (17), 178 (12), 165 (33). Anal. calc. for C₂₀H₂₄O₄ (328.41): C 73.15, H 7.37; found: C 73.37, H 7.29.

Data of 12b. Orange crystals. M.p. 108.1–109.4°. R_f (hexane/Et₂O 3:2): 0.35. UV (hexane): λ_{max} 269 (4.20), 233 (sh, 4.18), 209 (4.32); λ_{min} 253 (4.11). IR (CHCl₃): 3005m, 2952s, 2932s, 2870m, 1725s, 1640w, 1435s, 1372w, 1265w, 1171m, 1156m, 1089w. ¹H-NMR (400 MHz): 6.443 (q-like, ⁴J(H,CH₃–C(3)) = 1.1, H–C(2)); 6.087 (br. s, H–C(7)); 6.010 (quint.-like, ⁴J(H,CH₃–C(10)) ≈ ⁴J(H,H–C(7)) ≈ 1.3, H–C(9)); 3.888, 3.674 (2s, 2 COOCH₃); 2.333, 2.116 (2m, CH₃CH₂CH₂); 2.031 (d-like, ⁴J = 1.3, CH₃–C(3)); 1.975 (d-like, ⁴J(CH₃,H–C(9)) ≈ 1.0, CH₃–C(10)); 1.752 (s, CH₃–C(1)); 1.649 (s, CH₃–C(6)); 1.480 (m, CH₃CH₂CH₂); 0.852 (t, CH₃CH₂CH₂). MS: 368 (100, M⁺), 353 (85), 337 (17), 321 (11), 309 (21), 294 (22), 271 (18), 270 (97), 239 (21), 226 (17), 211 (11), 207 (12), 206 (13), 205 (12). Anal. calc. for C₂₅H₂₈O₄ (368.48): C 74.97, H 7.66; found: C 75.01, H 7.82.

The structure of **12b** was confirmed by an X-ray structure analysis. Crystal data: space group and cell dimensions: monoclinic $P2_1/n$ with $a = 933.3$, $b = 1521.4$, $c = 1525.9$ pm and $\beta = 90.87^\circ$; $D_{\text{calc.}}: 1.129 \text{ Mg m}^{-3}$, $Z = 4$; $\mu(\text{MoK}\alpha) = 0.71 \text{ cm}^{-1}$; measured reflexions (at 21°): 3402, observed reflexions: 1486; $R = 0.066$. Bond lengths [pm]: C(1)–C(2), 147.1; C(2)–C(3), 134.2; C(3)–C(4), 146.1; C(4)–C(5), 132.6; C(5)–C(5a), 148.7; C(5a)–C(6), 134.9; C(6)–C(7), 144.8; C(7)–C(8), 136.2; C(8)–C(9), 146.5; C(9)–C(10), 132.6; C(10)–C(10a), 146.4; C(10a)–C(1), 135.8. Valence angles $^\circ$: C(10a)–C(1)–C(2), 122.5; C(1)–C(2)–C(3), 129.8; C(2)–C(3)–C(4), 122.2; C(3)–C(4)–C(5), 124.7; C(4)–C(5)–C(5a), 121.0; C(5)–C(5a)–C(10a), 112.6; C(5a)–C(10a)–C(1), 120.2; C(5)–C(5a)–C(6), 124.3; C(10a)–C(5a)–C(6), 123.1; C(5a)–C(6)–C(7), 122.0; C(6)–C(7)–C(8), 128.8; C(7)–C(8)–C(9), 124.2; C(8)–C(9)–C(10), 126.7; C(9)–C(10)–C(10a), 119.9; C(10)–C(10a)–C(5a), 115.6. Torsion angles $^\circ$: C(10a)–C(1)–C(2)–C(3), 33.4; C(1)–C(2)–C(3)–C(4), 4.2; C(2)–C(3)–C(4)–C(5), –36.1; C(3)–C(4)–C(5)–C(5a), –5.4; C(4)–C(5)–C(5a)–C(10a), 68.5; C(4)–C(5)–C(5a)–C(6), 112.2; C(5)–C(5a)–C(10a)–C(1), –62.3; C(5)–C(5a)–C(10a)–C(10), 117.3; C(5)–C(5a)–C(6)–C(7), –176.3; C(5a)–C(10a)–C(1)–C(2), 0.3; C(5a)–C(6)–C(7)–C(8), 31.7; C(6)–C(7)–C(8)–C(9), –0.5; C(6)–C(5a)–C(10a)–C(1), 118.4; C(7)–C(8)–C(9)–C(10), –31.7; C(8)–C(9)–C(10)–C(10a), –3.7; C(9)–C(10)–C(10a)–C(1), –118.2; C(10)–C(10a)–C(5a)–C(6), –62.0; C(10)–C(10a)–C(11)–C(2), –179.2; CH_3 –C(3)–C(4)–C(O), –32.0; C(O)–C(4)–C(5)–C(O), –4.5; C(O)–C(5)–C(5a)–C(6), 70.5; C(5)–C(5a)–C(6)– CH_3 , 3.0; CH_3 –C(10)–C(10a)–C(1), 65.0; CH_3 –C(1)–C(10a)–C(10), 5.9; C(3)–C(4)–C=O, 88.0; C(3)–C(4)–C–O, –85.5; C(4)–C(5)–C=O, 8.8; C(4)–C(5)–C–O, –169.9; C(5)–C(4)–C=O, –95.2; C(5)–C(4)–C–O, 91.3; C(5a)–C(5)–C=O, –173.8; C(5a)–C(5)–C–O, 7.4.

Data of 12a. Yellow crystals. M.p. 100.5–101.6°. R_f (hexane/Et₂O 3:2): 0.33. UV (hexane): λ_{max} 325 (3.55), 260 (4.22), 227 (sh, 4.32), 215 (4.36); λ_{min} 308 (3.53), 246 (4.19). IR (KBr): 2940, 2875, 1730/1705 (COOCH₃), 1465, 1434, 1374, 1319, 1285, 1250, 1231, 1141, 1066, 1038, 999, 864, 853, 792. ¹H-NMR (400 MHz): 6.121 (br. s, H–C(7)); 6.061 (*quint*-like, ⁴ J (H,CH₃–C(5)) = 1.5, H–C(4)); 5.970 (*t*-like, ⁴ J (H,CH₃–C(10)) $\approx$ ⁴ J (H,H–C(7)) $\approx$ 1.1, H–C(9)); 3.657, 3.610 (2s, 2 COOCH₃); 2.370, 2.147 (2m, CH₃CH₂CH₂); 2.264 (s, CH₃–C(3)); 1.987 (*d*-like, ⁴ J (CH₃–C(9)) = 1.3, CH₃–C(10)); 1.961 (*d*-like, ⁴ J (CH₃,H–C(4)) = 1.5, CH₃–C(5)); 1.772 (s, CH₃–C(6)); 1.526 (m, CH₃CH₂CH₂); 0.857 (t, CH₃CH₂CH₂). MS: 368 (100, M^+), 354 (19), 353 (76), 337 (18), 321 (12), 309 (22), 294 (24), 293 (12), 277 (10), 271 (18), 270 (95), 239 (21), 226 (17), 207 (10), 206 (10). Anal. calc. for C₂₃H₂₈O₄ (368.48): C 74.97, H 7.66; found: C 75.18, H 7.91.

2.7.1. Control Experiments with 12b and 12a. **2.7.1.1. Photochemical Isomerizations.** Anal. probes of both pure heptalenes were dissolved in hexane/CH₂Cl₂ (9:1; $c \approx 5 \cdot 10^{-3} \text{ M}$) and irradiated with 366-nm light under stirring. After 29 h, the percentage of **12b** (81 %) and of **12a** (19 %) remained constant in both probes (HPLC).

2.7.1.2. Thermal Isomerizations. Both heptalenes (1 mg) were each dissolved in decalin (0.2 ml) and heated at 100° under protection of light. After 45 h, a constant equilibrium ratio of 52 % of **12b** and 48 % of **12a** was attained (HPLC).

2.8. Azulene 15 and ADM. The azulene (0.165 g; 0.686 mmol) and ADM (0.490 g; 3.46 mmol) were heated in decalin (3 ml) during 90 min at 200°. Decalin was removed and the residue chromatographed on Al₂O₃ (Act. III; Et₂O/hexane 4:1). A first slightly yellow fraction (0.015 g) contained three compounds (presumably heptalenes) which were not further investigated. A second slightly blue fraction (0.224 g; 62 %) contained the tetracyclic compound '*anti*'-**16** which was obtained in colorless crystals (0.179 g; 50 %) after recrystallization from AcOEt/hexane. The original faint blue color was presumably caused by the corresponding azulene-1,2-dicarboxylate which was not further investigated. A slow moving third fraction (0.032 g, 7 %) consisted of the pentacyclic compound **17**. Recrystallization from Et₂O/hexane yielded the pure compound (0.018 g; 4 %).

Tetramethyl (1RS,2RS,5RS,8RS)-13-(tert-Butyl)-2,6,8,11-tetramethyltetracyclo[6.2.2.2^{2,5}.0^{1,7}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate ('anti'-16**).** M.p. 122.0–123.5°. R_f (Et₂O/hexane 4:1): 0.38. UV (EtOH): λ_{max} 294 (br. sh, 3.02), 218 (br. sh, 4.08), 198 (4.31). IR (CHCl₃): 3028m, 2953s, 1716s, 1626w, 1594w, 1461w, 1435s, 1389w, 1364w, 1337w, 1261m, 1100s, 1050s, 1030s, 804w. ¹H-NMR (300 MHz): 6.214 (*q*, ⁴ J (H,CH₃–C(11)) = 1.7, H–C(12)); 5.709 (*d*, ⁴ J (H,H–C(5)) = 2.1, H–C(14)); 3.822, 3.796, 3.749, 3.679 (4s, 4 COOCH₃); 3.660 (*d*, ⁴ J (H,H–C(14)) = 2.1, H–C(5)); 2.044 (*d*, ⁴ J (CH₃,H–C(12)) = 1.7, CH₃–C(11)); 1.870 (s, CH₃–C(6)); 1.715 (br. s, CH₃–C(8)); 1.592 (s, CH₃–C(2)); 1.043 (s, *t*-Bu). ¹H-NOE (400 MHz): 1.592 $\rightarrow$ 5.703 (s, H–C(14)), 3.822 (*m*, C(3)–COOCH₃), 3.796 (*m*, C(10)–COOCH₃), 2.044 (s, CH₃–C(11)); 1.715 $\rightarrow$ 6.214 (s, H–C(12)), 3.679 (*w*, C(9)–COOCH₃), 1.870 (*m*, CH₃–C(6)); 1.870 $\rightarrow$ 3.749 (*w*, C(4)–COOCH₃), 3.660 (s, H–C(5)), 1.715 (*m*, CH₃–C(8)), 1.043 (*m*, *t*-Bu). ¹³C-NMR (50 MHz, CDCl₃): 169.22, 168.62 (C(9,10)–COOCH₃); 165.16, 163.97 (C(3,4)–COOCH₃); 159.13, 156.80 (C(9,10)); 153.59, 153.02 (C(3,4)); 150.39 (C(11)); 147.05 (C(13)); 145.01 (C(12)); 141.15 (C(7)); 127.93 (C(14)); 105.90 (C(6)); 65.68 (C(1)); 57.95 (C(8)); 52.30, 52.10, 51.99, 51.61 (4 COOCH₃); 44.21 (C(5)); 42.79 (C(2)); 34.57 ((CH₃)₃C); 28.59 ((CH₃)₃C); 20.88

(CH₃–C(6)); 18.13 (CH₃–C(11)); 17.54 (CH₃–C(2)); 16.37 (CH₃–C(8)). CI-MS ([C₄H₁₀]⁺): 525 (49, *M* + 1⁺), 493 (100), 465 (21), 461 (14), 260 (18). EI-MS: 524 (13, *M*⁺), 493 (6), 435 (27), 260 (34), 228 (100). Anal. calc. for C₃₀H₃₆O₈ (524.62): C 68.68, H 6.92; found: C 68.66, H 7.13.

Hexamethyl (1RS,2RS,5RS,8RS,9RS,12RS)-13-(tert-Butyl)-2,6,8,11-tetramethylpentacyclo[6.2.2.2^{2,5}.2^{9,12}.0^{1,70}.10¹¹]hexadeca-3,6,13,15-tetraene-3,4,9,10,15,16-hexacarboxylate (17). M.p. 151.1–153.9°. *R*_f (Et₂O/hexane 4:1): 0.20. UV (EtOH): λ_{max} 288 (br. sh, 3.58), 220 (br. sh, 4.15), 198 (4.34). IR (CHCl₃): 3030*m*, 2953*s*, 1728*s*, 1670*w*, 1618*w*, 1436*s*, 1388*w*, 1364*w*, 1262*m*, 1164*w*, 1121*w*, 1103*w*, 1058*w*. ¹H-NMR (300 MHz, CDCl₃/C₆D₆): 5.541/5.838 (*d*, ⁴*J*(H,H–C(5)) = 1.9/1.9, H–C(14)); 3.849/4.109 (*d*, ⁴*J*(H,H–C(14)) = 1.9/1.9, H–C(5)); 3.822/3.566, 3.800/3.500, 3.795/3.492, 3.762/3.408, 3.692/3.318, 3.672/3.273 (6*s*, 6 COOCH₃); 3.031/2.910 (*s*, H–C(12)); 2.019/2.016 (*s*, CH₃–C(6)); 1.557/1.953 (*s*, CH₃–C(11)); 1.313/1.621 (br. *s*, CH₃–C(2)); 1.112/1.115 (*s*, *t*-Bu); 1.093/1.065 (br. *s*, CH₃–C(8)). ¹H-NOE (400 MHz, C₆D₆): 2.016→4.109 (*s*, H–C(5)), 1.065 (*m*, CH₃–C(8)); 1.953→2.910 (*s*, H–C(12)), 1.621 (*s*, CH₃–C(2)); 1.621→5.838 (*s*, H–C(14)), 1.953 (*s*, CH₃–C(11)); 1.065→2.910 (*s*, H–C(12)), 2.016 (*s*, CH₃–C(6)). CI-MS ([C₄H₁₀]⁺): 667 (9, [*M* + 1]⁺), 635 (100), 607 (8), 579 (26), 547 (28), 519 (7). Anal. calc. for C₃₆H₄₂O₁₂ (666.73): C 64.85, H 6.35; found: C 64.64, H 6.32.

2.8.1. *Control Experiments*. 2.8.1.1. *Thermal Reaction of 'anti'-16 with ADM*. Tetracycle 'anti'-**16** (0.055 g; 0.105 mmol) and ADM (0.067 g, 0.47 mmol) were heated in decalin (1.5 ml) during 8 h at 200°. Workup with prep. TLC (Et₂O/hexane 9:1) yielded starting material 'anti'-**16** (0.032 g; 58%) and **17** (2.1 mg [4%]; after recryst. from AcOEt/hexane). It was identical with the compound isolated from the reaction mixture of **15** with ADM.

2.8.2. *Thermolysis of 'anti'-16*. Compound 'anti'-**16** was heated at 200° in decalin (3.5 h) as well as at 400° in the gas phase in a stream of N₂. A fragmentation into **28** could not be observed (¹H-NMR evidence).

2.9. *Azulene 6 and ADM*. The azulene (0.597 g; 2.81 mmol) and ADM (1.16 g; 8.14 mmol) were heated in decalin (12 ml) at 180° during 4.5 h. The solvent and excess ADM were distilled off (high vacuum; 50°) and the residue chromatographed on Al₂O₃ (hexane/Et₂O 3:2) to yield after a forerun of unreacted **6** (0.015 g; 2.5%) three heptalene fractions containing *dimethyl 1,2,3,6,8,10-hexamethylheptalene-4,5-dicarboxylate* (**7b**; 0.019 g; 1.9%), pure *dimethyl 3,4,5,6,8,10-hexamethylheptalene-1,2-dicarboxylate* (**7a**; 0.102 g, 10.2%), and in the middle fraction a mixture of **7b**, **7a**, and *dimethyl 2,3,4,6,8,11-hexamethyltricyclo[6.2.2.0^{1,5}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**8**; in total 0.054 g; 5.4%). A further fraction yielded 'anti'-**9** (0.652 g; 46.7%) contaminated with traces of **3**. Heptalene **7b** could be crystallized from pentane at –20°. The tricycle **8** was obtained in pure form (2.1%) from the heptalene mixture by prep. HPLC (hexane/(CH₂Cl₂ + 0.5% MeOH) 9:1). The bisadduct 'anti'-**9** was purified and freed from **3** by two crystallizations from hexane/AcOEt.

Tetramethyl (1RS,2RS,5RS,8RS)-2,6,8,11,12,13-hexamethyltetracyclo[6.2.2.2^{2,5}.0^{1,7}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate ('anti'-9). Colorless crystals. M.p. 121.2–126.6°. *R*_f (Et₂O/hexane 3:2): 0.25. UV (hexane): λ_{max} 221 (sh, 4.24). IR (CHCl₃): 3030*m*, 2952*m*, 1715*s*, 1630*w*, 1600*w*, 1435*s*, 1388*w*, 1342*w*, 1261*s*, 1144*w*, 1118*w*, 1096*w*, 1065*w*. ¹H-NMR (300 MHz): 5.66 (*quint.*-like, ⁴*J*(H,CH₃–C(13)) ≈ ⁴*J*(H,H–C(5)) ≈ 1.6, H–C(14)); 3.81, 3.79, 3.73, 3.67 (4*s*, 4 COOCH₃); 3.32 (*d*-like, ⁴*J*(H,H–C(14)) = 1.8, H–C(5)); 1.90 (*q*-like, ⁵*J*(CH₃,CH₃–C(12)) = 1.5, CH₃–C(11)); 1.85 (*s*, CH₃–C(6)); 1.84 (*d*-like, ⁴*J*(CH₃,H–C(14)) = 1.5, CH₃–C(13)); 1.68 (br. *s*, CH₃–C(8,12)); 1.55 (*s*, CH₃–C(2)). MS: 496 (43, *M*⁺), 465 (100), 437 (33), 405 (24), 377 (12), 274 (26), 242 (31), 191 (13). Anal. calc. for C₂₈H₃₂O₈ (496.56): C 67.73, H 6.50; found: C 67.59, H 6.50.

Data of 7b. Orange crystals. M.p. 132.8–135.6°. *R*_f (Et₂O/hexane 3:2): 0.56 (Al₂O₃). UV (hexane): λ_{max} 362 (sh, 3.05), 266 (4.28), 248 (4.22), 212 (sh, 4.36), 202 (4.37); λ_{min} 252 (4.22), 236 (4.21). IR (KBr): 2955, 2920, 1734/1717 (COOCH₃), 1588, 1446, 1430, 1376, 1295, 1270, 1254, 1222, 1193, 1167, 1138, 1056, 1028, 870, 846, 823, 722. ¹H-NMR (400 MHz): 6.075 (br. *s*, H–C(7)); 5.994 (*quint.*-like, H–C(9)); 3.865, 3.660 (2*s*, 2 COOCH₃); 1.994 (*d*-like, ⁴*J*(CH₃,H–C(7)) ≈ 1.1, CH₃–C(8)); 1.984 (*d*-like, ⁴*J*(CH₃,H–C(9)) ≈ 1.3, CH₃–C(10)); 1.960 (*d*-like, ⁵*J*(CH₃,CH₃–C(2)) < 1, CH₃–C(3)); 1.948 (*d*-like, ⁵*J*(CH₃,CH₃–C(3)) < 1, CH₃–C(2)); 1.784 (*s*, CH₃–C(1)); 1.677 (*s*, CH₃–C(6)). ¹H-NOE (400 MHz): 1.667 (CH₃–C(6))→6.075 (*s*, H–C(7)); 1.784 (CH₃–C(1))→1.984 (*s*, CH₃–C(10)), 1.948 (*s*, CH₃–C(2)). MS: 354 (100, *M*⁺), 339 (72), 323 (24), 307 (17), 295 (40), 280 (56), 235 (46), 221 (45), 206 (36), 191 (23), 165 (25). Anal. calc. for C₂₂H₂₆O₄ (354.45): C 74.55, H 7.39; found: C 74.32, H 7.53.

The structure of **7b** was confirmed by an X-ray structure analysis. Crystal data: space group and cell dimensions: triclinic *P*1 with *a* = 817.9, *b* = 1046.7, *c* = 1305.2 pm and α = 66.74°, β = 99.77°, γ = 104.98°; *D*_{calc}: 1.191 Mg m^{–3}, *Z* = 2; μ(MoK_α) = 0.754 cm^{–1}; measured reflexions (at 24°): 4294, observed reflexions: 2201; *R* = 0.0649. Bond lengths [pm]: C(1)–C(2), 147.7; C(2)–C(3), 136.6; C(3)–C(4), 144.6; C(4)–C(5), 135.9; C(5)–C(5a), 147.4; C(5a)–C(10a), 145.9; C(5a)–C(6), 135.3; C(6)–C(7), 145.4; C(7)–C(8), 135.4; C(8)–C(9), 144.4; C(9)–C(10), 134.5; C(10)–C(10a), 148.7; C(10a)–C(1), 136.1. Valence angles [°]: C(10a)–C(1)–C(2), 122.0; C(1)–C(2)–C(3), 125.6; C(2)–C(3)–C(4), 124.7; C(3)–C(4)–C(5), 125.0; C(4)–C(5)–C(5a), 120.5; C(5)–C(5a)–C(10a), 112.5; C(5a)–C(10a)–C(1), 123.0; C(5)–C(5a)–C(6), 124.4; C(10a)–C(5a)–C(6), 123.0; C(5a)–C(6)–C(7), 122.7; C(6)–C(7)–C(8), 127.8; C(7)–C(8)–C(9), 123.5; C(8)–C(9)–C(10), 127.2;

C(9)–C(10)–C(10a), 119.2; C(10)–C(10a)–C(5a), 112.9. Torsion angles [°]: C(10a)–C(1)–C(2)–C(3), –38.3; C(1)–C(2)–C(3)–C(4), –0.1; C(2)–C(3)–C(4)–C(5), 36.4; C(3)–C(4)–C(5)–C(5a), 2.3; C(4)–C(5)–C(5a)–C(10a), –64.6; C(4)–C(5)–C(5a)–C(6), 117.8; C(5)–C(5a)–C(10a)–C(1), 61.5; C(5)–C(5a)–C(10a)–C(10), –116.5; C(5)–C(5a)–C(6)–C(7), 177.8; C(5a)–C(10a)–C(1)–C(2), 2.5; C(5a)–C(6)–C(7)–C(8), –34.5; C(6)–C(5a)–C(10a)–C(1), –120.9; C(6)–C(7)–C(8)–C(9), –1.2; C(7)–C(8)–C(9)–C(10), 33.3; C(8)–C(9)–C(10)–C(10a), 5.8; C(9)–C(10)–C(10a)–C(5a), –65.2; C(9)–C(10)–C(10a)–C(1), 116.8; C(10)–C(10a)–C(5a)–C(6), 61.1; C(10)–C(10a)–C(1)–C(2), –179.7; CH₃–C(3)–C(4)–C(O), 36.2; C(O)–C(4)–C(5)–C(O), –0.6; C(O)–C(5)–C(5a)–C(6), –64.1; C(5)–C(5a)–C(6)–CH₃, –1.4; CH₃–C(10)–C(10a)–C(1), –69.1; CH₃–C(1)–C(10a)–C(10), –3.1; CH₃–C(1)–C(2)–CH₃, –31.7; CH₃–C(2)–C(3)–CH₃, 1.5; C(3)–C(4)–C=O, 87.4; C(3)–C(4)–C–O, –89.0; C(4)–C(5)–C=O, –26.4; C(4)–C(5)–C–O, 152.7; C(5)–C(4)–C=O, –88.2; C(5)–C(4)–C–O, 95.4; C(5a)–C(5)–C=O, 155.5; C(5a)–C(5)–C–O, –25.4.

Data of 7a. Pale yellow oil. *R_f* (Et₂O/hexane 3:1): 0.37. UV (hexane): λ_{max} 324 (3.55), 255 (sh, 4.15), 225 (4.28), 215 (sh, 4.27); λ_{min} 307 (3.53), 208 (4.26). IR (CHCl₃): 3003*m*, 2950*s*, 2918*m*, 2856*w*, 1721*s*, 1644*w*, 1602*w*, 1435*s*, 1375*w*, 1396*w*, 1289*m*, 1265*s*, 1166*m*, 1125*m*, 1107*w*, 1079*w*, 1056*m*, 1015*w*. ¹H-NMR (400 MHz): 6.167 (br. *s*, H–C(7)); 6.014 (*quint.*-like, ⁴*J*(H,CH₃–C(10)) ≈ ⁴*J*(H,H–C(7)) ≈ 1.1, H–C(9)); 3.663, 3.624 (2*s*, 2 COOCH₃); 2.214 (*s*, CH₃–C(3)); 2.054 (*d*-like, ⁴*J*(CH₃,H–C(7)) = 1.2, CH₃–C(8)); 2.024 (*d*-like, ⁴*J*(CH₃,H–C(9)) = 1.2, CH₃–C(10)); 1.908 (*d*-like, ⁵*J*(CH₃,CH₃–C(4)) ≈ 0.9, CH₃–C(5)); 1.805 (*d*-like, ⁵*J*(CH₃,CH₃–C(5)) ≈ 1.0, CH₃–C(4)); 1.736 (*s*, CH₃–C(6)). MS: 354 (100, *M*⁺), 339 (60), 324 (10), 295 (32), 280 (38), 256 (39), 235 (22), 221 (19), 205 (12), 165 (10).

Data of 8. Pale yellow oil. *R_f* (Et₂O/hexane 3:2): 0.37. UV (hexane): λ_{max} 335 (3.70), 296 (3.72), 257 (sh, 3.81), 200 (4.46); λ_{min} 318 (3.67), 281 (3.70). IR (CHCl₃): 3030*w*, 2952*m*, 1722*s*, 1613*w*, 1434*m*, 1384*w*, 1264*s*, 1122*w*, 909*m*. ¹H-NMR (400 MHz): 5.665 (*q*-like, ⁴*J*(H,CH₃–C(11)) ≈ 1.3, H–C(12)); 5.248 (br. *s*, H–C(7)); 3.762 (*s*, C(9)–COOCH₃); 3.585 (*s*, C(10)–COOCH₃); 2.168 (*s*, CH₃–C(4)); 2.052 (*d*, ⁴*J*(CH₃,H–C(7)) = 1.4, CH₃–C(6)); 1.898 (br. *s*, CH₃–C(2,3)); 1.429 (*s*, CH₃–C(8)); 1.418 (*d*, ⁴*J*(CH₃,H–C(12)) = 1.6, CH₃–C(11)). MS: 354 (47, *M*⁺), 322 (73), 307 (100), 295 (69), 279 (43), 263 (36), 249 (21), 236 (85), 221 (62), 206 (31), 191 (64).

2.9.1. Control Experiments with 7b. 2.9.1.1. *Thermal Isomerization.* Heating of the heptalene in a soln. of decalin (0.1%) at 100° during 2.5 h led to no change. Prolonged heating at 120° (4 h), however, led to a ratio of **7b/7a** of ca. 55%/45%. Continuation of heating over a period of 15 h yielded a new product (UV (from HPLC with hexane)/(CH₂Cl₂ + 0.5% MeOH) 9:1): λ_{max} 295, 285, 245; λ_{min} 280, 265, and 210) which was not further characterized (*cf.* [11]).

2.9.2. Control Experiments with 8. 2.9.2.1. *Thermal Isomerization into Dimethyl 2,3,4,8,10,11-Hexamethyltricyclo[6.2.2.0^{1,5}]dodeca-2,4,6,9,11-pentaene-6,7-dicarboxylate (19).* Similar as in the case of **4**, the tricycle isomerized partially already during ¹H-NMR measurement in CDCl₃ soln. into a new compound, namely **19**. Thermal isomerization of **8** (27 mg) in decalin at 100° during 4 h yielded ca. 30% of **19** which was isolated (4.4 mg; 16%) in a pure state by prep. HPLC. The yellow oil crystallized from hexane at –20° in pale yellow crystals. M.p. 95.2–96.2°. *R_f* (Et₂O/hexane 3:2): 0.37. UV (hexane): λ_{max} 339 (4.08), 208 (4.20); λ_{min} 267 (3.14), 202 (4.19). IR (CHCl₃): 3028*w*, 2951*m*, 1722*s*, 1434*m*, 1382*w*, 1270*m*, 1246*m*, 1258*w*. ¹H-NMR (300 MHz): 5.666 (*q*-like, ⁴*J*(H,CH₃–C(10)) = ⁴*J*(H,CH₃–C(11)) ≈ 1.1, H–C(9,12)); 3.739 (*s*, C(7)–COOCH₃); 3.727 (*s*, C(6)–COOCH₃); 2.064 (*q*-like, ⁵*J*(CH₃,CH₃–C(3)) ≈ 0.8, CH₃–C(2)); 1.909 (*q*-like, ⁵*J*(CH₃–C(2)) ≈ 1.0, CH₃–C(3)); 1.819 (*s*, CH₃–C(4)); 1.448 (*d*, ⁴*J*(CH₃,H–C(9,12)) = 1.4, CH₃–C(10, 11)); 1.417 (*s*, CH₃–C(8)). ¹H-NOE (400 MHz): 1.819 (CH₃–C(4))→3.727 (*s*, C(6)–COOCH₃), 1.909 (*s*, CH₃–C(3)); 1.448 (CH₃–C(10,11))→5.666 (*s*, H–C(9,12)), 2.064 (*s*, CH₃–C(2)); 1.417 (CH₃–C(8))→5.666 (*s*, H–C(9,12)), 3.739 (*w*, C(7)–COOCH₃). MS: 354 (16, *M*⁺), 322 (100), 307 (88), 295 (42), 279 (36), 263 (37), 249 (24), 235 (98), 221 (69), 205 (54), 191 (39), 165 (19).

The equilibrium ratio of **8** and **19** in decalin at 100° was established after 20 min. After 1 h, the ratio amounted to 67% of **8** and 33% of **19** (determined by ¹H-NMR in CDCl₃ by integration of the signals of the ester groups after removal of decalin).

2.9.2.2. Heating of 8 with ADM at 200°. Compound **8** (4.7 mg; 0.013 mmol) and 25 mg (0.18 mmol) of ADM were heated in decalin (0.5 ml) during 2.5 h. No tetracyclic compound could be detected by ¹H-NMR.

2.10. Methyl 4,6,8-Trimethylazulene-2-carboxylate (46) and ADM. The azulene 46²⁴ (0.258 g; 1.13 mmol) and ADM (0.659 g; 4.64 mmol) were heated in decalin (9 ml) during 7.5 h at 200°. After removal of decalin, the residue

²⁴) Azulene **46** was synthesized by Corey oxidation [38] of **75** (*cf.* 1.2.2) in 85% yield. M.p. 183.5–184.5° (AcOEt/hexane).

was filtered through Al_2O_3 (basic, Act. III) with CH_2Cl_2 + 0.5% MeOH and then separated by prep. TLC on silica gel (CH_2Cl_2 + 0.5% MeOH) to yield unreacted **46** (0.123 g; 48%) in addition to a mixture of the heptalenetricarboxylates **47a** and **47b** and the azulenedicarboxylate **22** and a second mixture (0.258 g) of the tetracycle 'anti'-**48** and trimethyl 5-methoxyfuran-2,3,4-tricarboxylate (**10**; cf. [17]). A second TLC separation on silica gel (hexane/AcOEt 1:1) of the first mixture yielded a pure fraction (0.066 g) of **47a/47b** (19.4%) and **22** (25.5%). HPLC (hexane/(CH_2Cl_2 + 0.5% MeOH) 85:15) yielded pure **47a** which was recrystallized from hexane to give crystalline **47a** (0.011 g). The second mixture was crystallized from hexane/AcOEt to yield the pure furan derivative (0.069 g) and in the mother liquor a mixture (0.189 g) of 'anti'-**48** (0.151 g; 49.9%) and the furan derivative (0.038 g). Prep. HPLC (hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1) yielded pure 'anti'-**48** (0.081 g; 37%) which was recrystallized from hexane/AcOEt.

Trimethyl 6,8,10-Trimethylheptalene-1,2,4-tricarboxylate (47a). M.p. 153–155° (hexane). R_f (CH_2Cl_2 + 0.5% MeOH): 0.47. UV (hexane): λ_{max} 404 (sh, 2.89), 332 (sh, 3.52), 280 (4.19), 209 (4.43); λ_{min} 250 (4.09). IR (CHCl_3): 3026m, 2953m, 1719s, 1648w, 1615w, 1473s, 1134m, 1097m, 1059m, 1003m. $^1\text{H-NMR}$ (300 MHz; CHCl_3 at 7.260): 7.954 (d, $^4J(\text{H,H-C}(5)) \approx 0.6$, H-C(3)); 7.077 (br. s, H-C(5)); 6.143 (q-like, H-C(7)); 5.924 (quint.-like, H-C(9)); 3.846, 3.744, 3.679 (3s, 3 COOCH_3); 2.017 (br. s, $\text{CH}_3\text{-C}(8)$); 1.970 (d, $^4J(\text{CH}_3\text{,H-C}(7)) = 1.3$, $\text{CH}_3\text{-C}(10)$); 1.763 (s, $\text{CH}_3\text{-C}(6)$). EI-MS: 370 (87, M^+), 339 (27), 323 (21), 311 (28), 279 (25), 251 (31), 228 (100, $[M - \text{ADM}]^+$), 199 (98), 184 (62), 156 (31), 128 (19). Anal. calc. for $\text{C}_{21}\text{H}_{22}\text{O}_6$ (370.41): C 68.10, H 5.99; found: C 68.10, H 6.20.

In CDCl_3 at r.t., **47a** rapidly isomerized to its DBS isomer **47b**, the content of which was 18% at equilibrium.

Trimethyl 6,8,10-Trimethylheptalene-2,4,5-tricarboxylate (47b). It was only characterized by its $^1\text{H-NMR}$ (300 MHz; in the presence of 82% of **47a**): 7.629 (d, $^4J(\text{H,H-C}(5)) = 1.1$, H-C(3)); 6.341 (d, $^4J(\text{H,H-C}(3)) = 1.1$, H-C(3)); 6.094 (br. s, H-C(7)); 5.941 (quint.-like, H-C(9)); 3.833, 3.742, 3.702 (3s, 3 COOCH_3); 2.150 (d, $^4J(\text{CH}_3\text{,H-C}(9)) \approx 1.2$, $\text{CH}_3\text{-C}(10)$); 1.958 (d, $^4J(\text{CH}_3\text{,H-C}(7)) \approx 1.3$, $\text{CH}_3\text{-C}(8)$); 1.678 (s, $\text{CH}_3\text{-C}(6)$).

Pentamethyl (1RS,2RS,5RS,8RS)-2,6,13-Trimethyltetracyclo[6.2.2.2⁰.7]tetradeca-3,6,9,11,13-pentacene-3,4,9,10,12-pentacarboxylate ('anti'-48). M.p. 159.5–160.0° (hexane/AcOEt). R_f (CH_2Cl_2 + 0.5% MeOH): 0.35. UV (EtOH): λ_{max} 199 (4.35). IR (KBr): 2981w, 2953m, 1732s, 1676m, 1627m, 1588m, 1435s, 1341s, 1313s, 1268s, 1208s, 1145m, 1057s, 1014m. $^1\text{H-NMR}$ (300 MHz, $\text{CDCl}_3/\text{C}_6\text{D}_6$; CHCl_3 at 7.260/ $\text{C}_6\text{D}_5\text{H}$ at 7.160): 7.963/8.478 (d, $^4J(\text{H,H-C}(8)) = 1.19/1.1$, H-C(11)); 5.635/5.863 (quint.-like, $^4J(\text{H,H-C}(5)) \approx ^4J(\text{H,CH}_3\text{-C}(13)) \approx 1.6/1.6$, H-C(14)); 4.609/5.095 (d, $^4J(\text{H,H-C}(11)) = 1.18/1.1$, H-C(8)); 3.845, 3.842, 3.745, 3.743, 3.736/3.531, 3.508, 3.202, 3.172, 3.120 (5s, 2 as sh/5s, 5 COOCH_3); 3.454/3.473 (d, $^4J(\text{H,H-C}(14)) = 1.61/1.6$, H-C(5)); 1.864/1.579 (d, $^4J(\text{CH}_3\text{,H-C}(14)) = 1.53/1.6$, $\text{CH}_3\text{-C}(13)$); 1.690/1.608 (s, $\text{CH}_3\text{-C}(6)$); 1.430/1.558 (s, $\text{CH}_3\text{-C}(2)$). $^1\text{H-NOE}$ (400 MHz, CDCl_3): 7.963 (H-C(11)) → 1.430 (s, $\text{CH}_3\text{-C}(2)$); 1.690 ($\text{CH}_3\text{-C}(6)$) → 4.609 (s, H-C(8)), 3.454 (s, H-C(5)), 1.864 (vw, $\text{CH}_3\text{-C}(13)$). EI-MS: 512 (31, M^+), 480 (30), 465 (22), 453 (15), 420 (63), 393 (29), 361 (25), 290 (14), 258 (72), 241 (45), 59 (100). Anal. calc. for $\text{C}_{27}\text{H}_{28}\text{O}_{10}$ (512.52): C 63.27, H 5.51; found: C 62.99, H 5.48.

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