179. Thermal Reactions of Guaiazulene and Its 3-Methyl Derivative with Dimethyl Acetylenedicarboxylate

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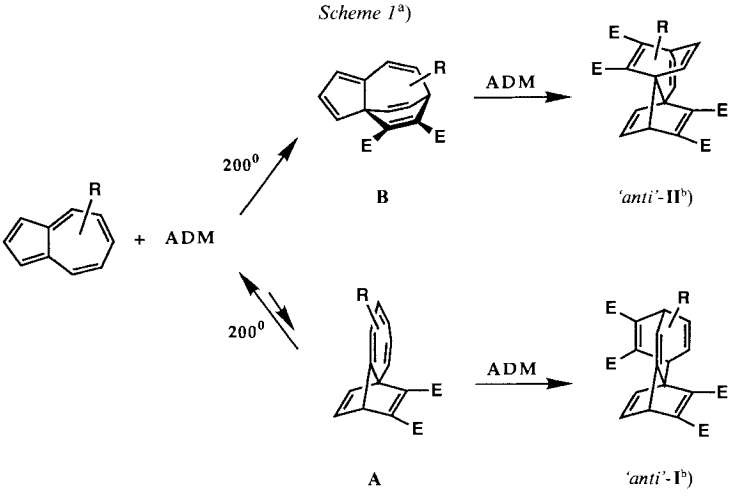
The thermal reaction of 7-isopropyl-1,3,4-trimethylazulene (3-methylguaiazulene; **2**) with excess dimethyl acetylenedicarboxylate (ADM) in decalin at 200° leads to the formation of the corresponding heptalene- (**5a**/**5b** and **6a**/**6b**; *cf. Scheme 3*) and azulene-1,2-dicarboxylates (**7** and **8**, respectively). Together with small amounts of a corresponding tetracyclic compound (*'anti'*-**13**) these compounds are obtained *via* rearrangement (→ **5a**/**5b** and **6a**/**6b**), *retro-Diels-Alder* reaction (→ **7** and **8**), and *Diels-Alder* reaction with ADM (→*'anti'*-**13**) from the two primary tricyclic intermediates (**14** and **15**; *cf. Scheme 5*) which are formed by site-selective addition of ADM to the five-membered ring of **2**. In a competing *Diels-Alder* reaction, ADM is also added to the seven-membered ring of **2**, leading to the formation of the tricyclic compounds **9** and **10** and of the *Diels-Alder* adducts *'anti'*-**11** and *'anti'*-**12**, respectively of **9** and of a third tricyclic intermediate **16** which is at 200° in thermal equilibrium with **9** and **10** (*cf. Scheme 6*). The heptalenedicarboxylates **5a** and **5b** as well as **6a** and **6b** are interconverting slowly already at ambient temperature (*Scheme 4*). The thermal reaction of guaiazulene (**1**) with excess ADM in decalin at 190° leads alongside with the known heptalene- (**3a**) and azulene-1,2-dicarboxylates (**4**; *cf. Schemes 2* and *7*) to the formation of six tetracyclic compounds *'anti'*-**17** to *'anti'*-**21** as well as *'syn'*-**19** and small amounts of a 4:1 mixture of the tricyclic tetracarboxylates **22** and **23**. The structure of the tetracyclic compounds can be traced back by a *retro-Diels-Alder* reaction to the corresponding structures of tricyclic compounds (**24**–**29**; *cf. Scheme 8*) which are thermally interconverting by [1,5]-C shifts at 190°. The tricyclic tetracarboxylates **22** and **23**, which are slowly equilibrating already at ambient temperature, are formed by thermal addition of ADM to the seven-membered ring of dimethyl 5-isopropyl-3,8-dimethylazulene-1,2-dicarboxylate (**7**; *cf. Scheme 10*). Azulene **7** which is electronically deactivated by the two MeOCO groups at C(1) and C(2) shows no more thermal reactivity in the presence of ADM at the five-membered ring (*cf. Scheme 11*). The tricyclic tetracarboxylates **22** and **23** react with excess ADM at 200° in a slow *Diels-Alder* reaction to form the tetracyclic hexacarboxylates **32**, *'anti'*-**33**, and *'anti'*-**34** (*cf. Schemes 10–12* as well as *Scheme 13*). A structural correlation of the tri- and tetracyclic compounds is only feasible if thermal equilibration *via* [1,5]-C shifts between all six possible tricyclic tetracarboxylates (**22**, **23**, and **35**–**38**; *cf. Scheme 13*) is assumed. The tetracyclic hexacarboxylates **32**, *'anti'*-**33**, and *'anti'*-**34** seem to arise from the most strained tricyclic intermediates (**36**–**38**) by the *Diels-Alder* reaction with ADM.

Introduction. – In the preceding communication [1], we have shown that the thermal reaction of azulenes with dimethyl acetylenedicarboxylate (ADM) in apolar solvents such as decalin or tetralin leads to the formation of two primary intermediates **A** and **B** which arise from the reversible *Diels-Alder*-type addition of ADM to the five-membered ring of the azulenes and from the – under the reaction conditions – irreversible *Diels-Alder*-type addition of ADM to the seven-membered ring of the azulenes (*Scheme 1*). These two primary reaction paths are controlled by the corresponding HOMO(azulene)/LUMO-

Scheme 1[a])



[a]) R represents varying numbers of alkyl substituents at the possible skeletal positions. [b]) '*anti*' refers to the relative position of the two maleic ester substructures within the tetracyclic skeletons, *i.e.*, its relative position with respect to the sites of the original azulene skeleton.

(ADM) and SHOMO(azulene)/LUMO(ADM)[1]) interactions resulting in the formation of **A** and **B**, respectively. Both primary intermediates may be trapped by excess ADM in a consecutive *Diels-Alder* reaction yielding the 'isoskeletal' tetracyclic compounds of type '*anti*'-**I** and '*anti*'-**II**, respectively[2]). The known products from the thermal reaction of azulenes with ADM in apolar media, mainly heptalene- and azulene-1,2-dicarboxylates (*cf.* [2–5] as well as [1]), are derived from the primary intermediate **A** by rearrangement *via* zwitterionic intermediates (→heptalene-1,2-dicarboxylates (*cf.* [6])) or *retro-Diels-Alder* reaction (→azulene-1,2-dicarboxylates (*cf.* [2–5])).

The formation of the tricyclic intermediates **B** that competes energetically with the formation of the tricyclic intermediates **A** due to the fact of a large difference of > 80 kJ·mol^{-1} in the $\Delta H_f°$ values of the two tricyclic skeletons (*cf.* [1]) seems to be dependent especially on the steric encumbrance of alkyl substituents at C(6) of the involved azulenes. A Me group at C(6) allows the formation of **B** or its trapping product '*anti*'-**II** or '*syn*'-**II** with ADM in yields of 1–6%, whereas no products of these types are observed with azulenes carrying a Pr or *t*-Bu group at C(6) (*cf.* [1]). Therefore, we investigated the thermal reaction of azulenes, which carry no alkyl substituents at C(6), with ADM in apolar solvents (*cf.* also [7]) and chose, for this study, guaiazulene (**1**) and its 3-methyl derivative **2**, since **1** gives the highest yield, so far observed, of a corresponding heptalene-1,2-dicarboxylate **3a** when heated with ADM in tetralin (*Scheme 2*) [4][3]). The frontier-

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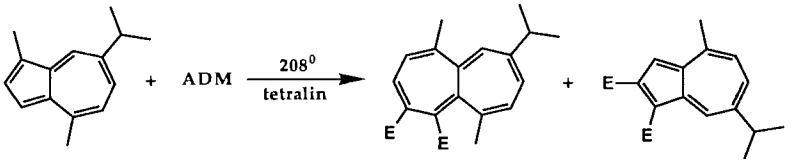
[1]) SHOMO = subjacent HOMO.

[2]) The formation of the corresponding '*syn*'-addition products of **A** was not observed so far. On the other hand, **B** may react with ADM in the '*anti*'- or '*syn*'-mode (*cf.* [1]).

[3]) The Ru-catalyzed reaction of **1** with ADM in different solvents (toluene, MeCN, dioxan) at 100–125° gives nearly quantitative yields of **3a** [8].

Scheme 2[a])



1 **3a** (63.5%) **4** (5.7%)

[a]) *Cf.* [4]; molar ratio **1**/ADM *ca.* 1:1.1.

orbital energies of methyl analogues of **1** and **2** are as expected quite similar to those of 1,3,4,6- and 1,4,6,8-tetramethylazulene (*cf. Table 1*) which gave in the presence of excess ADM in decalin at 200° *ca.* 1 and 5%, respectively, of the corresponding tetracyclic compounds of type **II** (*cf.* [1]).

Table 1. *Comparison of the Frontier-Orbital Energies* [eV] *of Some Me-Substituted Azulenes*[a])

Position of Me groups at the azulene ring	$\Delta H_f°$ [kJ·mol^{-1}]	SHOMO	HOMO	LUMO	NLUMO	Δ_1	Δ_2	$\Delta_1 - \Delta_2$
1,4,7[b])	221.8	−8.64	−7.63	−0.88	−0.56	7.5	6.5	1.0
1,3,4,6 [1]	201.3	−8.47	−7.52	−0.89	−0.51	7.3	6.4	0.9
1,3,4,7[c])	200.4	−8.62	−7.51	−0.83	−0.55	7.5	6.4	1.1
1,4,6,8 [1]	210.5	−8.45	−7.61	−0.89	−0.46	7.3	6.5	0.8

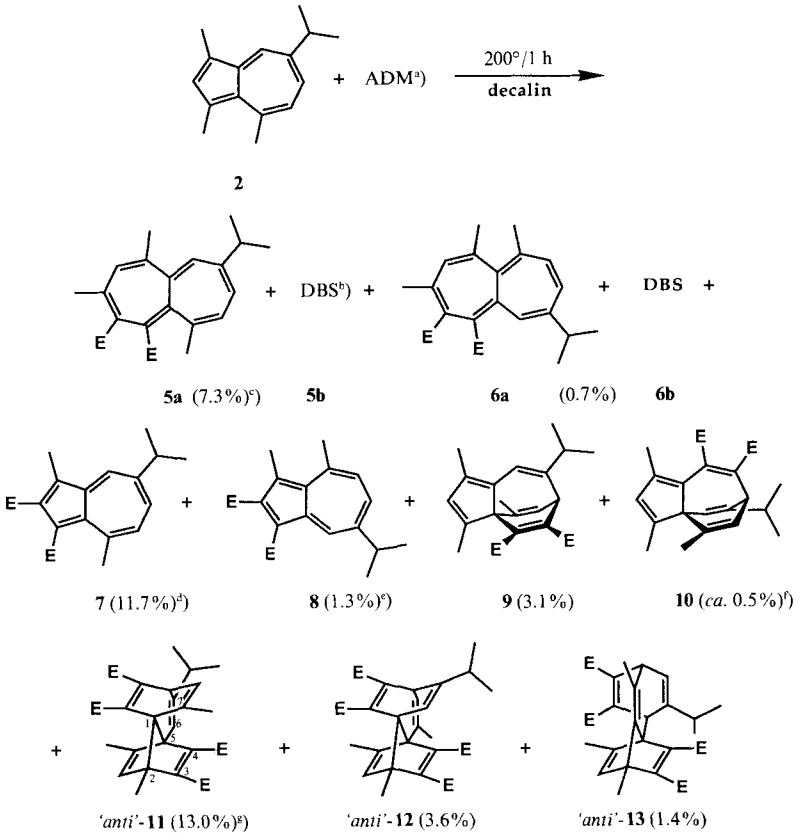
[a]) AM1 calculations (*cf.* [1]); Δ_1 = SHOMO(azulene) − LUMO(ADM) (as di-acid; −1.16 eV); Δ_2 = HOMO-(azulene) − LUMO(ADM).
[b]) As analogue for **1**.
[c]) As analogue for **2**.

Results and Discussion. – Heating of 5-isopropyl-1,3,8-trimethylazulene (3-methylguaiazulene; **2**) in the presence of a 3.8 molar excess of ADM in decalin during 1 h at 200° led to a complex reaction mixture (*Scheme 3*) which was separated by TLC on Al_2O_3 followed by crystallization and HPLC (*cf. Exper. Part*).

The structure of the two isomeric heptalene-1,2-dicarboxylates **5a** and **6a** were unequivocally established by comparison of their ^{1}H-NMR data ($CDCl_3$) with those of **3a** [4][4]). Both crystalline heptalene-1,2-dicarboxylates, when dissolved in $CDCl_3$, started already at room temperature to rearrange reversibly into their corresponding DBS isomers **5b** and **6b**, respectively. The assignment of the position of the C=C bond in the two pairs of DBS isomers is clearly attained by the observed J_{vic}(H,H) values of 6.5 (**5a**), 12.0 (**5b**), 11 (**6a**), and 6 Hz (**6b**) (*cf. Scheme 4*). The structure of **6a** is also secured by an observed strong ^{1}H-NOE between CH_3–C(5) and CH_3–C(6). The equilibrium ratio for **5a**/**5b** and **6a**/**6b** are, as expected, quite similar (*cf. Scheme 4*), and the interconversion of **5a** and **5b** was also realized photochemically (*cf.* [5b]).

[4]) The structure of **3a** has already been secured by an X-ray diffraction analysis (*cf.* [9]).

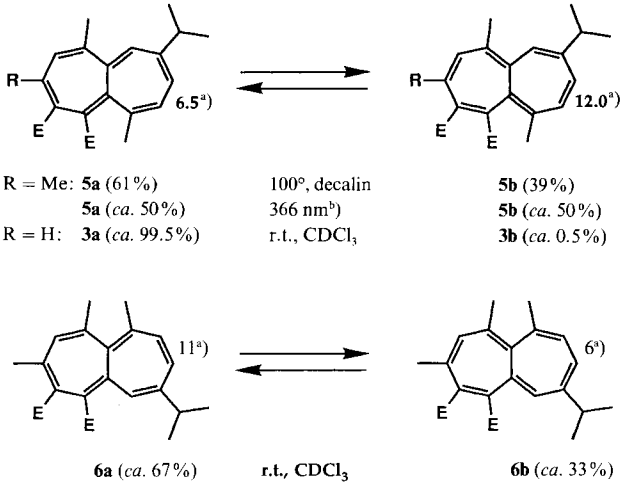
Scheme 3[a])



[a]) Molar ratio **2**/ADM 1:3.8. [b]) DBS denotes the double-bond-shifted isomer which was not isolated from the original reaction mixture, since the DBS process occurred already at room temperature (see later). [c]) The chromatographic fraction containing all heptalenes and the tricyclic compounds **9** and **10** amounted to 12% (15% in second run). [d]) The chromatographic fraction containing the two azulene-1,2-dicarboxylates amounted to 13% (8% in a second run). [e]) Only obtained in an enriched mixture with **7**. [f]) Identified in the original reaction mixture but not isolated. [g]) The chromatographic fraction containing all three tetracyclic compounds amounted to 18% (15% in a second run). The ratio *'anti'*-**11**/*'anti'*-**12**/*'anti'*-**13** was determined by ^{1}H-NMR spectroscopy, because the three compounds showed nearly the same chromatographic behaviour. Pure samples of the tetracyclic compounds were obtained by mechanical separation of the mixture of different crystals of *'anti'*-**11**, *'anti'*-**12**, and *'anti'*-**13**.

The ^{1}H-NMR data of **5a**/**5b** and **6a**/**6b** allow also to estimate the chemical shifts for the so far unknown DBS isomer **3b** of **3a**. *Table 2* shows these estimated chemical-shift values in comparison to observed positions of signals and signal patterns, when a twice recrystallized sample of **3a** was dissolved at room temperature in $CDCl_3$ and measured at 300 MHz. The ratio of integrals of comparable signals of **3a** and **3b** was found to be 99.5:0.5, showing that the equilibrium concentration of **5b** is strongly enhanced by the

Scheme 4[a])



R = Me: **5a** (61%) 100°, decalin **5b** (39%)
5a (*ca.* 50%) 366 nm[b]) **5b** (*ca.* 50%)
R = H: **3a** (*ca.* 99.5%) r.t., $CDCl_3$ **3b** (*ca.* 0.5%)

6a (*ca.* 67%) **r.t., $CDCl_3$** **6b** (*ca.* 33%)

[a]) Observed ^3J values of the corresponding vicinal H,H couplings (R = Me). [b]) In hexane/CH_2Cl_2 9:1.

Me group at C(3) (*cf.* $\Delta G_{298} \approx -13$ kJ·mol^{-1} for **3a**/**3b** and -2.1 kJ·mol^{-1} for **5a**/**5b**). Effects on ΔG of similar magnitude have also been observed for comparable pairs of tetra- and pentamethylheptalene-1,2-dicarboxylates (*cf.* [1]).

Table 2. *Comparison of Estimated and Observed ^{1}H-NMR Chemical Shifts for the DBS Isomer* (**3b**) *of Dimethyl 7-Isopropyl-5,10-dimethylheptalene-1,2-dicarboxylate* (**3a**)[a])

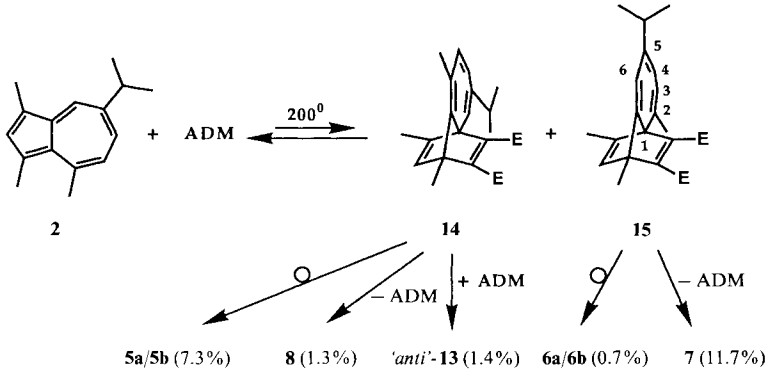
Substituents in **3b**	δ(estim.) [ppm]	Multiplicity, ^3J(estim.) [Hz]	δ(obs.) [ppm]	Multiplicity, ^3J(obs.) [Hz]
H–C(2)/H–C(3)	6.58[b])	*AB*, ~ 12	6.56/6.45	*AB*, ~ 12
H–C(7)/H–C(8)	6.35	*AB*, ~ 12	6.36	br. *s*[c])
H–C(10)	5.70	br. *s*	5.71	br. *s*
MeOCO–C(4)	3.66	*s*	3.70	*s*
MeOCO–C(5)	3.88	*s*	3.88	*s*
Me–C(1)	1.74	*s*	1.74	*s*
Me–C(6)	1.65	*s*	1.67	*s*
Me_2CH–C(9)[d])	1.12	2*d*, 7	1.13/1.14	2*d*, 7

[a]) 300 MHz; in $CDCl_3$. The amount of **3b** detected in **3a** was *ca.* 0.5%.
[b]) Estimated according to δ(H–C(2)) and δ(H–C(3)) (= 6.58 and 6.56 ppm) of dimethyl 8-(*tert*-butyl)-1,6,10-trimethylheptalene-4,5-dicarboxylate [5].
[c]) Not observable.
[d]) The signal for Me_2CH–C(9) of **3b** seems to be hidden under the same signal for **3a**.

The structural assignment of the two azulene-1,2-dicarboxylates **7** and **8** is based on the chemical-shift difference ($CDCl_3$) of the isolated H-atom at the seven-membered ring which appears at 8.394 ppm in **7** and at 9.701 ppm in **8** due to the strong deshielding effect of MeOCO–C(1) in **8**. The azulene-1,2-dicarboxylate **4** (*Scheme 2*) representing the 3-demethylated derivative of **8** shows the signal due to H–C(8) at 9.44 ppm (CCl_4) [4].

The appearance of structurally isomeric heptalene- (**5a**/**5b** and **6a**/**6b**) and azulene-dicarboxylates (**7** and **8**) in the reaction mixture of **2** and ADM demonstrates that two isomeric primary intermediates, namely **14** and **15** (*Scheme 5*), must have been formed as the corresponding precursors for **5a**/**5b** and **8** as well as for **6a**/**6b** and **7**, respectively. Moreover, there is no doubt that the primary intermediate **14** is also the precursor for '*anti*'-**13**. That no analogous structure is derived from the other intermediate **15** can be attributed to the fact that both C-termini in **15** for the *Diels-Alder* reaction with ADM are occupied by alkyl groups (*cf.* Me–C(2) and i-Pr–C(5); see also later). The general thermal behaviour of **14** and **15** is as expected (*cf.* [1]), *i.e.*, **14** with i-Pr–C(3) and Me–C(6) shows preferentially rearrangement to the corresponding heptalenes **5a**/**5b** and only little tendency to undergo the *retro-Diels-Alder* reaction yielding **8** ((**5a**/**5b**)/**8** ~ 6:1) whereas **15** with no alkyl substituent at C(3) and C(6) exhibits just the inverse reactivity trend, thus yielding mainly **7** ((**6a**/**6b**)/**7** ~ 1:15).

Scheme 5[a])



[a]) The circled arrows indicate rearrangement *via* zwitterionic intermediates followed by formation of corresponding *Dewar* heptalenes which yield the final heptalenes by electrocyclic opening (*cf.* [1] [6]).

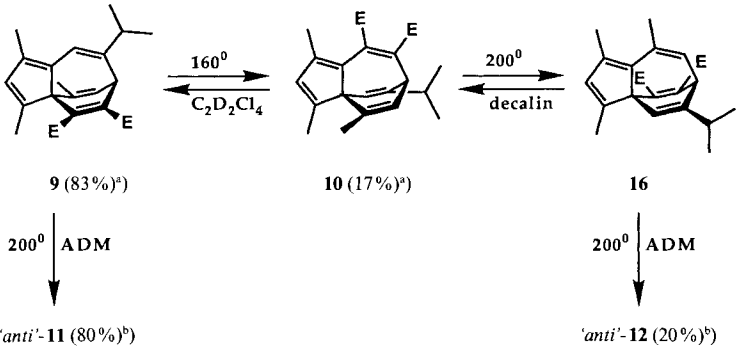
The remaining four compounds (**9** to '*anti*'-**12**) in the reaction mixture of **2** and ADM are structurally interrelated. The tricyclus **9** which represents the SHOMO(azulene)/LUMO(ADM)-controlled primary *Diels-Alder*-addition product of ADM to the seven-membered ring of **2** is thermally stable at room temperature. However, when heated to 160° in 1,1,2,2-tetrachloro[1,2-$^2H_2$]ethane, **9** rearranges reversibly into the tricyclus **10** to an equilibrium concentration of up to 17% (*Scheme 6*). A structurally possible third tricyclic compound, namely **16**, was not detected in the equilibrium mixture of **9** ad **10** at 160°[5]). However, when **9** was heated in decalin in the presence of a nine-fold molar excess of ADM the formation of '*anti*'-**11** and '*anti*'-**12** was observed in a ratio of 4:1[6]). The structure of '*anti*'-**12** reflects the structure of a tricyclic precursor that is only compatible with that of **16**, *i.e.*, at 200°, **9** and **10** must be in equilibrium also with **16**. This trapping experiment with ADM shows that the tetracyclic compounds of the general type '*anti*'-**II**

[5]) At temperatures > 160°, **9** and **10** decomposed rapidly in the equilibrium mixture in solution.

[6]) Both tetracyclic compounds are stable at 200° in decalin, *i.e.* '*anti*'-**11** and '*anti*'-**12** are not interconverted or yield the mixture of **9** and **10**.

(or '*syn*'-**II**) are indeed derived from their precursor structures **B** and not from **A** (*cf. Scheme 1*), because addition of ADM to the partial diene system C(4) to C(7) of **A** would also result in the formation of '*anti*'-**II** (or '*syn*'-**II**). It should be noted that both **9** and **16** may represent the two site-selective addition products of ADM to the seven-membered ring of **2**. However, since both are interconverted at the reaction temperature of **2** with ADM, these two possible primary reaction paths cannot be distinguished[7]).

Scheme 6[a])



[a]) Equilibrium mixture at 160° in $C_2D_2Cl_4$. [b]) Relative percentages after heating of **9** in the presence of a nine-fold molar excess of ADM. The yield of the isolated mixture of '*anti*'-**11** and '*anti*'-**12** amounted to 64%.

The observed thermal equilibrium between **9** and **10** is comparable to those for tricyclic compounds of type **B** (*Scheme 1*) with R = Me substituents at C(2), C(4), C(6), C(8), C(11) as well as with an additional Me group at C(3) (*cf.* [1]). Indeed, the equilibrium ratios show in all cases a preference for the tricyclic structures with the MeOCO groups at C(9), C(10). So far, we cannot decide, whether [1,5]-C shifts of the E–C(10) take part in the establishment of the equilibrium between **9**, **10**, and **16**, or not. [1,5]-C Shifts of E–C(10) would mean that **9** and **16** are directly related dynamically and not only *via* **10**[8]).

The structures of **9** and **10** were mainly established on the basis of their ^{1}H-NMR spectra in comparison with those of the penta- and hexamethyl-substituted analogues on which we have already reported [1]. In particular, the ^{1}H chemical shifts of the Me groups placed at C(11) of the tricyclic skeleton and, therefore, well above the cyclopentadiene substructure are quite similar (*e.g.* 1.487 ppm in the case of the pentamethyl-substituted tricyclus and 1.590 ppm in the case of **9** as well as 1.550 ppm for **10**). Irradiation of these Me groups induces strong ^{1}H-NOE at Me–C(2) in all investigated cases. This observation excludes the possibility that the compound in thermal equilibrium with **9** would have structure **16**, because in this case strong ^{1}H-NOE should have been determined between

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[7]) On grounds of relief of peri-strain between Me–C(3) and Me–C(4) in the transition state of the *Diels-Alder* reaction of **2** with ADM as well as on grounds of the larger orbital coefficients at C(3a) (0.353; *cf. Table 1*) as compared to C(8a) (0.296) in the reaction-determining SHOMO of the methyl analogue of **2**, the formation of **9** should clearly be favoured over that of **16**.

[8]) We will report on this type of rearrangement in detail later in this journal.

Me–C(4), which appears as a *s*, and the assumed Me–C(6) which appears as a *d* due to the allylic coupling (^4J = 1.6 Hz) with the vicinal olefinic H-atom. However, the observed ^{1}H-NOE are between two Me groups that appear both as *d*. What also supports the structure of **9** and **10** is the observed order of magnitude of the ^3J(H,H) values of 6.6 and 6.7 Hz, respectively, which is in agreement with the assigned structures, since both structures possess a torsion angle in the H–C(8)–C(12)–H fragment of *ca.* 24°[9]). On the other hand, the corresponding torsion angle in **16** (H–C(7)–C(8)–H) amounts to 0°, and one would expect a ^3J(H,H) value in the order of 8.5 Hz[10]).

The structure of '*anti*'-**11** and '*anti*'-**12** is unambiguously established by their ^{1}H-NMR data. Both compounds show an H-atom (H–C(8)) in trisallylic position (3.545 and 3.630 ppm, respectively; $CDCl_3$) as *dd* with distinctly different ^3J(H,H) (7.2 and 8.6 Hz, respectively) and ^4J(H,H) (1.2 and 1.8 Hz, respectively) due to the fact that in one case, namely '*anti*'-**12**, the vicinal torsion angle as well as the allylic coupling angle ϕ (*cf.* [10]) amount to *ca.* 0°, whereas in the other case, namely '*anti*'-**11**, these angles lie in a range of *ca.* 20° (*cf.* [7]), in agreement with the observed smaller vicinal and allylic H,H coupling constants. Both compounds possess one Me group which appears as a sharp *s* and, therefore, it has to be placed at C(2). Irradiation of this Me group causes strong ^{1}H-NOE with H–C(14) in both compounds. However, the additionally observed ^{1}H-NOE are different. In one compound, namely '*anti*'-**11**, it is the olefinic Me group at 2.008 ppm that exhibits a strong ^{1}H-NOE, whereas in the other compound, *i.e.*, '*anti*'-**12**, it is the olefinic H-atom at 5.661 ppm, which is allylicly coupled with the H-atom in trisallylic position (3.630 ppm) and the methine-H of the i-Pr group (at C(12)) that shows a strong ^{1}H-NOE.

The third tetracyclic compound '*anti*'-**13** shows in the ^{1}H-NMR spectrum ($CDCl_3$) two H-atoms (H–C(2) and H–C(5)) in tris- and bisallylic position. Therefore, its structure, on the basis of further ^{1}H-NMR data (*cf. Exper. Part*), is also well established.

When guaiazulene (**1**) was reacted with a five-fold molar excess of ADM in decalin at 190°, a whole variety of tetracyclic compounds (*cf. Scheme 7*) was observed alongside with the known products **3a** and **4** (*cf. Scheme 2*). In the polar fractions containing the (1 + 2) adducts, we observed two further compounds of similar polarity which turned out to be the tricyclic compounds **22** and **23**. However, we could detect no tetracyclic compounds in the reaction mixture which would belong to the structure type of '*anti*'-**I**.

The structure of the tetracyclic compounds **17** to **21**, which in all cases was unequivocally established on the basis of the ^{1}H-NMR data (*cf. Exper. Part* as well as [1] [7]), clearly evidences that the two possible primary addition products resulting from the SHOMO(azulene)/LUMO(ADM)-controlled *Diels-Alder* reaction of ADM with the seven-membered ring of **1** are thermally transformed by [1,5]-C shifts into tricyclic isomers, before they are trapped by ADM in a consecutive *Diels-Alder* reaction (*Scheme 8*)[11]). Indeed, all the observed tetracyclic compounds can be traced back structurally to

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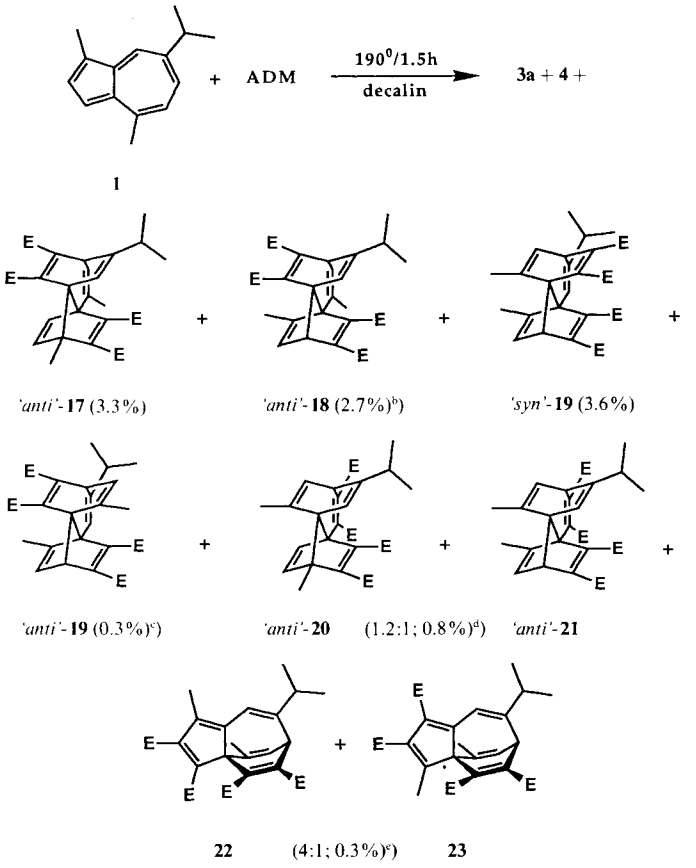
[9]) According to MM3 calculations of the basal skeleton (*cf.* [1]).

[10]) This is the order of magnitude of ^3J(H–C(7), H–C(8)) for all tetracyclic structures of type '*anti*'- or '*syn*'-**II** (*cf. Scheme 1*) which all possess the analogous substructures as **16** (*cf.* also [1]).

[11]) The orbital coefficients of the SHOMO of the methyl analogue of **1** (*cf. Table 1*) are similar at C(3a) (0.344) and C(8a) (0.318), *i.e.*, there should be no pronounced site selectivity in the primary addition step of ADM to the seven-membered ring of **1**.

Scheme 7[a])

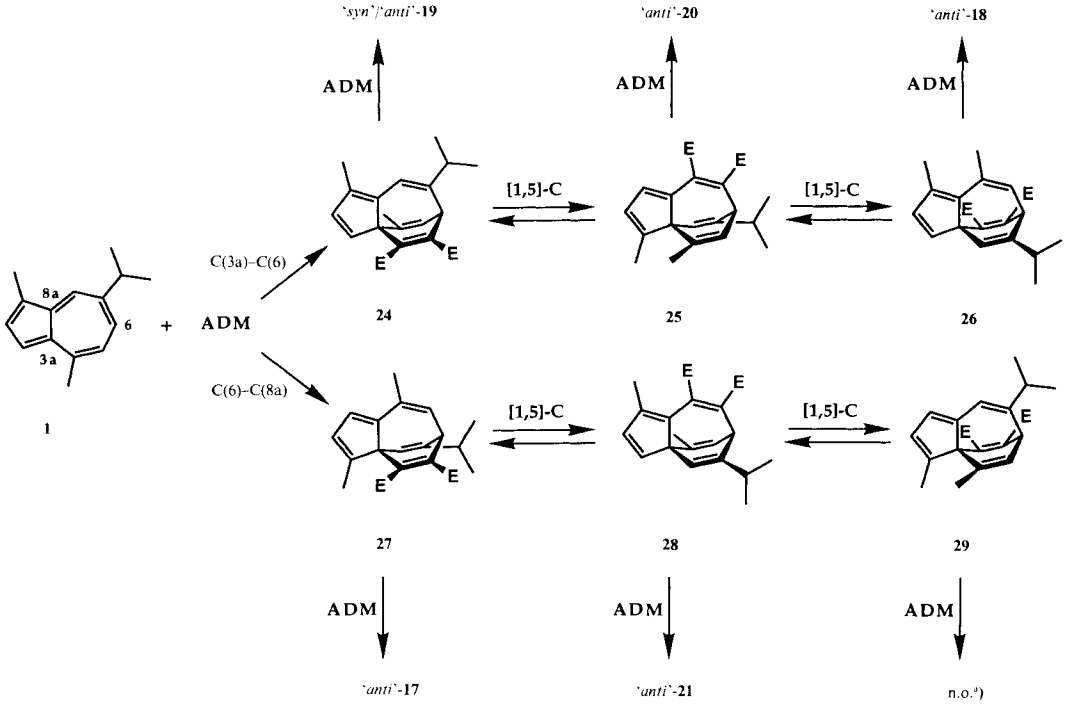


[a]) Guaiazulene (**1**) was reacted with a five-fold molar excess of ADM in a 0.25M (0.12) solution in decalin. Only the fraction of polar compounds, containing the shown tri- and tetracyclic compounds in a total yield of 19.3% (28.5%), was isolated (*cf. Scheme 2*). If not otherwise stated, the yields refer to HPLC-pure material. [b]) Isolated in a mixture with 10% of '*anti*'-**19**. [c]) Only observed in mixtures with other tetracyclic compounds (*cf. Exper. Part*). [d]) A mixture of 55% of '*anti*'-**20** and 45% of '*anti*'-**21** was isolated by prep. HPLC. '*anti*' refers to the spatial relation of Me–C(3) and MeOCO–C(10). [e]) Obtained as a 4:1 thermal equilibrium mixture after two HPLC separations (*cf. Exper. Part*, and later).

corresponding tricyclic structures (*cf.* **24** to **26** and **27** to **29**, respectively) which should arise from the primary tricyclic structures **24** and **27**, respectively by [1,5]-shifts of the sp^2-C-atoms carrying a Me group or an H-atom. If we postulate the involvement of [1,5]-shifts of the sp^2-C-atoms substituted by a MeOCO group all six possible tricyclic compounds (**24**–**29**) would be structurally interrelated by [1,5]-C shifts[8]).

One of the expected tetracyclic compounds, namely that derived from **29**, was not observed in the reaction mixture. It may be that the thermal reactivity of **29** towards ADM cannot compete with that of **27** and **28** which should be more strained due to substituents at C(4) and C(6). In principle, the tricycle **29** with its 'site-selective' counter-

Scheme 8[a])



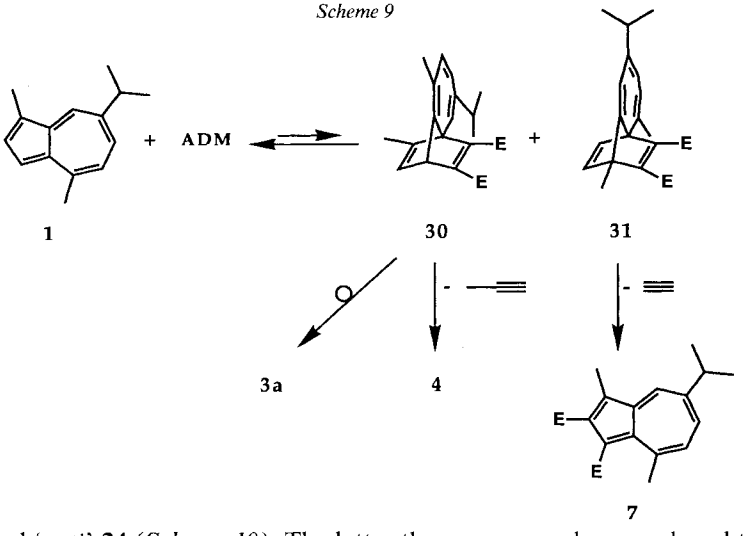
[a]) n.o. = not observed; *cf.* Footnote 5 in [1].

part **26** should also be accessible by the thermal reaction of the unknown 'isoguaiazulene', *i.e.* 5-isopropyl-1,8-dimethylazulene, with ADM. The observable ratio of the tetracyclic compounds **17** to **21** may give an answer to the question, whether **29** is reactive in competition with **27** and **28** in the presence of ADM, and whether there are two series of equilibrating tricyclic compounds (**24** to **26** and **27** to **29**, respectively) at 190°, or only one comprising all six tricyclic compounds[8]).

The presence of the two tricyclic compounds with four MeOCO substituents (**22** and **23**) in the reaction mixture is of interest, since they may represent rearranged thermal degradation products of *'anti'*-**17** or *'anti'*-**20**. However, these compounds are stable in solution under the reaction conditions. Another possibility is that **22** and **23** are addition products resulting from the thermal reaction of ADM with dimethyl 5-isopropyl-3,8-dimethylazulene-1,2-dicarboxylate (**7**) which may arise from the so far not realized second primary intermediate of the reaction of guaiazulene (**1**) with ADM (*Scheme 9*). Indeed, we would expect, in analogy to the thermal reaction of the tricyclic intermediate **15** (*cf. Scheme 5*), that the postulated second tricyclic compound **31** of the thermal reaction of ADM with **1** should mainly undergo the *retro-Diels-Alder* reaction to yield **7**.

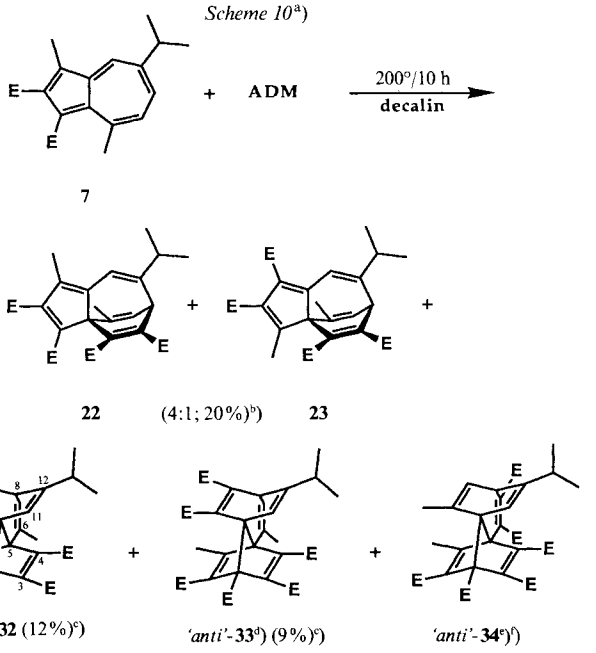
When **7** from the thermal reaction of **2** with ADM was heated in decalin in the presence of a 4.4 molar excess of ADM, a slow reaction was observed leading to the formation of the 4:1 mixture **22**/**23** as well as of the three tetracyclic compounds **32**,

Scheme 9



'*anti*'-**33**, and '*anti*'-**34** (*Scheme 10*). The latter three compounds were also obtained in the 4.5:4.5:1 ratio, when the thermal 4:1 equilibrium mixture of **22** and **23** was heated with excess ADM in decalin at 200°. Two further addition experiments with

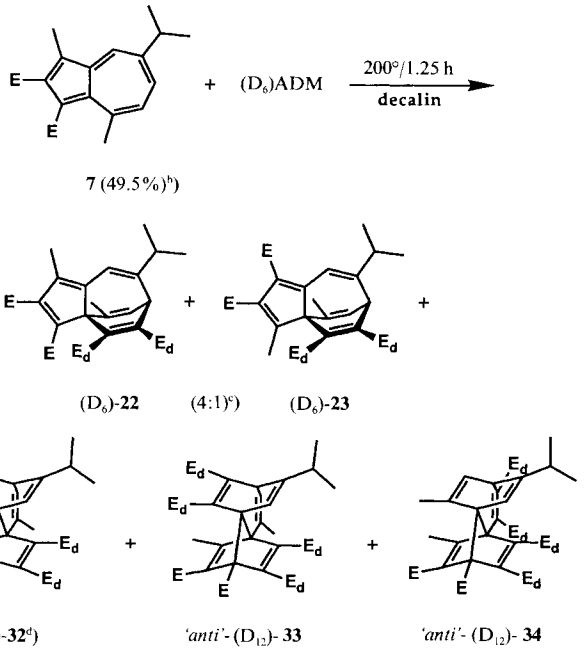
Scheme 10[a])



[a]) ADM was applied in a 4.4 molar excess. [b]) Equilibrium mixture of **22** and **23**. [c]) Amount of crystallized material. The ratio of **32**/'*anti*'-**33**/'*anti*'-**34** was 4.5:4.5:1. [d]) '*anti*' refers to the spatial relation of the two maleic-ester substructures in **33**. [e]) Found in the mother liquors of the crystallization of crude **32**. Enriched probes contained up to 57% of '*anti*'-**34** beside 43% of **32**. [f]) '*anti*' refers to the spatial relation of Me–C(3) and MeOCO–C(10) (*cf. Footnote d* in *Scheme 7*).

di(trideuteriomethyl) acetylenedicarboxylate ((D$_6$)ADM) showed that the two tricyclic compounds **22** and **23** are formed irreversibly under the reaction conditions, and that the *Diels-Alder* reaction of these compounds with ADM takes place in the '*anti*'-mode. When **7** was reacted with excess (D$_6$)ADM to *ca.* 50% conversion the 4:1 mixture (D$_6$)-**22**/(D$_6$)-**23** with the labelled methoxycarbonyl groups at C(9) and C(10) was obtained. The tetracyclic compounds (D$_{12}$)-**32** to (D$_{12}$)-'*anti*'-**34** showed the labelled methoxycarbonyl groups in the indicated positions (*cf. Scheme 11*). Furthermore, the recovered azulene-

Scheme 11[a])

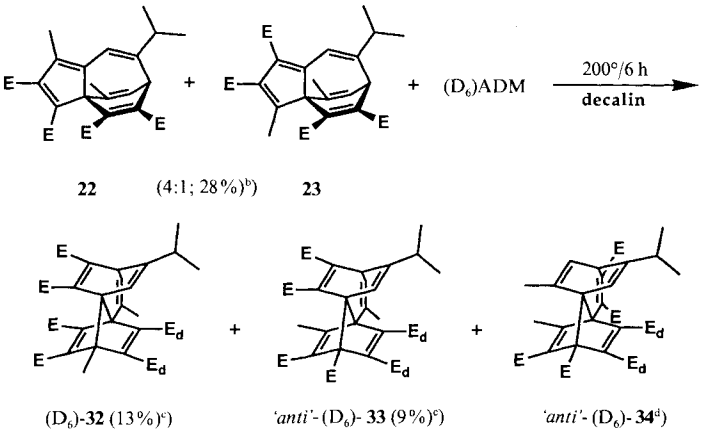


[a]) (D$_6$)ADM was applied in a 2.9-fold molar excess. [b]) Amount of recovered **7**; no incorporation of [^{2}H$_3$]COOC in **7** was detected. [c]) The mixture (D$_6$)-**22**/(D$_6$)-**23** was isolated. [d]) The 4.5:4.5:1 mixture (D$_{12}$)-**32**/(D$_{12}$)-'*anti*'-**33**/(D$_{12}$)-'*anti*'-**34** was isolated.

1,2-dicarboxylate **7** showed no incorporation of (D$_6$)ADM, *i.e.*, **7** seems to exhibit no more *Diels-Alder* reactivity with (D$_6$)ADM at the five-membered ring, whereas the reactivity at the seven-membered ring is maintained. On the other hand, when the 4:1 mixture **22**/**23** was heated in the presence of a ten-fold molar excess of (D$_6$)ADM in decalin at 200° during 6 h the recovered 4:1 mixture **22**/**23** (13%) showed no labelled methoxycarbonyl groups at C(9) and C(10), and the purified tetracyclic compounds had incorporated just 1 equiv. of (D$_6$)ADM (*cf. Scheme 12*).

The two tricyclic compounds **22** and **23** equilibrate thermally already slowly at room temperature. Therefore, we were not able to get isomerically pure samples of these compounds. Nevertheless, HPLC separations yielded samples of **22** enriched in **23** and *vice versa*, so that the thermal equilibrium could be established at 100° in toluene (*cf.*

Scheme 12[a])



[a]) (D_6)ADM was applied in a ten-fold molar excess. [b]) Amount of recovered 4:1 mixture **22**/**23**; no incorporation of $[^2H_3]$COOC was detected. [c]) Amount of crystallized material. [d]) Obtained in a *ca.* 2:3 mixture with (D_6)-**32**.

Scheme 13). It shows that **22** is sligthly more stable than **23** ($\Delta G_{373} = -2.7$ kJ·mol^{-1}), probably mainly due to the more extended conjugated π system in **22** as compared to **23**[12]).

Scheme 13 shows the whole set of the six tricyclic compounds which should be thermally interconvertible. The two compounds which can be directly formed by site-selective thermal addition of ADM to the seven-membered ring of **7** are **22** and **37**. The establishment of the thermal equilibrium between **22** and **23** which slowly takes place already at room temperature necessarily affords the participation of at least two further tricyclic compounds (**35** and **36** as well as **37** and **38**). This means that, in this case, the [1,5]-shifts must include the migration of the sp^2-C-atoms carrying a MeOCO group[13]). In principle, the cycle of equilibrating tricyclic compounds can also be entered by the

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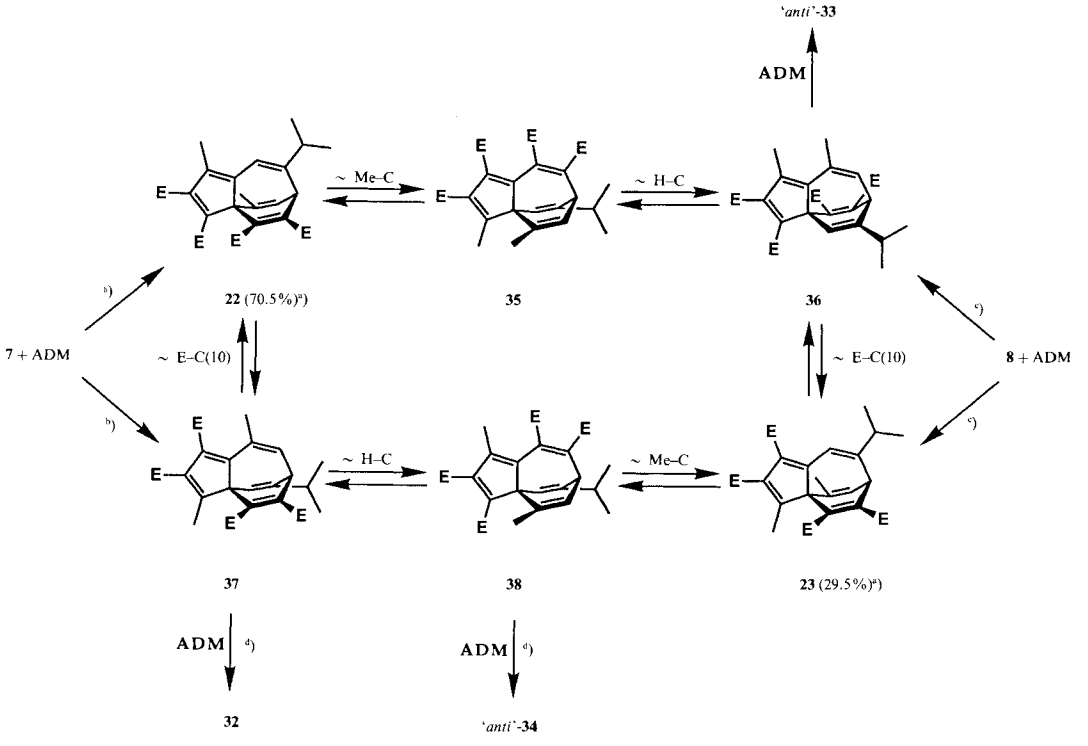
[12]) The longest-wavelength absorption of **22** is found at 375.6 nm (hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1) and that of **23** at 355.0 nm under the HPLC conditions. That the observed difference of 21 nm is mainly caused by the different positions of the MeOCO groups at the cyclopentadiene substructure can be realized as follows: cyclopentene-1,2-dicarboxylates show their longest-wavelength absorption at 228 nm (*cf.* [11]). As an increment for the extension of conjugation ($\Delta\lambda$) may be taken the difference in the UV absorptions of cyclopentadiene (239 nm) and cyclopentene (193 nm; *cf.* [11]), *i.e.* $\Delta\lambda = 46$ nm. It means that we expect the longest-wavelength absorption for cyclopentadiene-1,2-dicarboxylates at (228 + 46) = 274 nm. The longest-wavelength absorption for cyclopentadiene-2,3-dicarboxylates can be estimated from the corresponding absorption band position of cyclohexa-1,3-diene-2,3-dicarboxylates (267 nm; *cf.* [11] as well as [12]). For the contraction to the five-membered ring system, we have to consider a contraction increment of −18 nm, *i.e.* the difference in the absorptions of cyclopentadiene (238 nm) and cyclohexa-1,3-diene (256 nm). Therefore, we expect the longest-wavelength absorption for cyclopentadiene-2,3-dicarboxylates at (267 − 18) = 249 nm. Hence, the estimated difference amounts to (274 − 249) = 25 nm, in good agreement with the observed difference (λ(**22**) − λ(**23**)) of 21 nm.

[13]) We suppose that the transition state of the migration of E–C(10) (*e.g.* **22** → **37**) resembles a corresponding 6*H*-azulenyl and α-maleinyl-ester radical due to the decrease of the energy of the HOMO (6*H*-azulenyl system) caused by electron-attracting methoxycarbonyl groups at C(2) and C(3) in **22** and **23**[8]).

Scheme 13



a) Amount in thermal equilibrium at 100° in toluene ($\Delta G_{373} = -2.7$ kJ · mol^{-1}). b) In decalin at 200° (*cf. Scheme 10*). c) A 3:2 mixture **7**/**8** was reacted in the presence of a 5.7 molar excess of ADM during 0.75 h at 180° in decalin. Recovery of 68% of a *ca.* 3:2 mixture **7**/**8**. The tricyclic compounds were isolated as the 4:1 mixture **22**/**23**. d) In decalin at 200° (*cf. Scheme 12*).

thermal reaction of dimethyl 7-isopropyl-3,4-dimethylazulene-1,2-dicarboxylate (**8**; *cf. Scheme 3*) with ADM. Indeed, when a 3:2 mixture **7**/**8**[14]) was reacted with excess ADM at 180° in decalin the formation of the 4:1 mixture **22**/**23** was again observed (*Scheme 13*). The primary tricyclic adducts that can be formed by site-selective reaction of ADM with the seven-membered ring of **8** are **23** and **36**. Therefore, the equilibrium mixture of the tricyclic compounds **22** and **23** had been approached from both sides.

The structure of the tetracyclic compounds **32**, '*anti*'-**33**, and '*anti*'-**34** show that their direct precursors are neither **22** nor **23**, but **37**, **36**, and **38**, respectively, *i.e.*, we have again a structural proof of at least five of the six possible tricyclic compounds which are in thermal equilibrium at 200°. A comparison of the tricyclic structures reveals that compounds with the sterically most demanding substituents (Me and E), *i.e.* causing most of the ground state strain, at C(4) and C(6), exhibit *Diels-Alder* reactivity in the presence of ADM.

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[14]) It was the mixture **7**/**8** isolated from the thermal reaction mixture of **2** with ADM (*cf. Scheme 3*). After 32% conversion, the composition of the 3:2 mixture had nearly not changed, *i.e.*, both **7** and **8** had reacted to the same extent with ADM.

The structural assignment of **22** and **23** as well as of the *Diels-Alder* adducts with ADM is mainly based on their ^{1}H-NMR data. The two fundamental arguments for the structure of **22** and **23** are the following: *1*) both compounds exhibit ^3J(H,H) values of 6.6 and 6.5 Hz. This observation indicates that the torsion angle of the vicinal H-atoms is $\neq 0°$ in both compounds (*cf.* ^3J(H,H) = 6.6 and 6.7 Hz, respectively, for the analogous tricyclic structures **9** and **10**). Therefore, the structures **36** and **37**, where the discussed torsion angle will be *ca.* 0°, can be excluded. *2*) Irradiation of the Me group that appears as a *d* (^4J = 1.5 Hz) in the main product causes a strong ^{1}H-NOE only at the allylic coupling partner (H–C(12)). In addition, a medium ^{1}H-NOE is observed at one of the MeOCO groups, which, therefore, has to be placed at C(2). On the other hand, when the Me group that appears as an *s* in the main product is irradiated, a strong ^{1}H-NOE is induced at the olefinic H-atom which is allylically coupled (^4J = 1.2 Hz) with the methine-H-atom of the i-Pr group as well as with the H-atom in trisallylic position (H–C(8)). These observations in combination with additional ^{1}H-NOE measurements (*cf. Exper. Part*) are only compatible with the tricyclic structure **22**. In the other tricyclic compounds, present in minor amounts in the thermal equilibrium mixture, both Me groups (*s* and *d*) are in spatial neighbourhood, since they show strong reciprocal ^{1}H-NOE when irradiated. Therefore, its structure must be **23**, because the other possible structure, namely **36**, has already been excluded on the basis of the observed ^3J(H,H) value (*vide supra*).

The two main products of the tetracyclic hexacarboxylates show ^3J(H,H) values of 8.8 Hz, being only in agreement with the structures **32** and *'anti'*-**33** (torsion angle H–C(7)–C(8)–H $\approx 0°$), because all the other four possible tetracyclic structures should possess torsion angles of the vicinal H-atoms in the range of *ca.* 24°, *i.e.*, their coupling constants will be in the order of 7 Hz. Indeed, the third tetracyclic hexacarboxylate, found in minor amounts, exhibits a ^3J(H,H) value of 7.0 Hz. The relative position of the substituents at the tetracyclic skeleton of all three compounds follows from corresponding ^{1}H-NOE measurements (*cf. Exper. Part*). The assignment of the positions of the six MeOCO groups is also based on ^{1}H-NOE experiments as well as on the results of the addition reactions with (D_6)ADM (*cf. Schemes 11* and *12*).

We thank Prof. *M. Hesse* and his coworkers for mass spectra, Prof. *W. von Philipsborn* and his coworkers for NMR support and numerous ^{1}H-NOE measurements, Dr. *R. W. Kunz* for AM1 calculations, and *H. Frohofer* for elemental analyses. The financial support of this work by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* as well as by *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged.

Experimental Part

General. See [1] [5] [7] [9].

1. *Synthesis of 7-Isopropyl-1,3,4-trimethylazulene* (= *3-Methylguaiazulene*; **2**; *cf.* [13]). 1.1. *5-Isopropyl-3,8-dimethylazulene-1-carbaldehyde* (**39**). *Guaiazulene* (**1**; 1.62 g; 8.17 mmol; *Fluka*; purified by CC) was formylated under *Vilsmeier* conditions in the usual way (*cf.* [1] [13]). The product was purified by CC on Al_2O_3 (Et_2O) and crystallized from acetone/hexane to yield **39** in wine-red crystals (1.38 g; 75%). M.p. 84.4–84.5°. R_f (Et_2O/hexane 7:3) 0.30. UV (hexane): λ_{max} 398 (4.10), 383 (4.03), 315 (4.54), 309 (sh, 4.51), 277 (4.08), 247 (4.32), 221 (4.21); λ_{min} 387 (4.03), 341 (3.54), 281 (4.07), 269 (4.04), 224 (4.20). IR ($CHCl_3$): 3007*m*, 2965*m*, 2929*w*, 1618*s*, 1545*m*, 1465*m*, 1437*m*, 1394*s*, 1367*s*, 1304*w*, 1262*w*, 1162*s*, 1094*m*, 1024*w*. ^{1}H-NMR (300 MHz): 10.650 (*s*, CHO); 8.294 (*d*, *J* = 2.1, H–C(4)); 8.234 (*s*, H–C(2)); 7.590 (*dd*, *J* = 10.8, 2.1, H–C(6)); 7.424 (*d*, *J* = 10.8, H–C(7)); 3.161 (*sept.*, partly covered, *J* = 6.9, Me_2CH); 3.153 (*s*, Me–C(8)); 2.589 (*d*, *J* $\approx$ 0.6, Me–C(3)); 1.395 (*d*, *J* = 6.8, Me_2CH).

MS: 226 (100, $M^{+\cdot}$), 211 (73), 209 (40), 183 (16), 168 (13), 167 (13), 165 (18). Anal. calc. for $C_{16}H_{18}O$ (226.32): C 84.91, H 8.02; found: C 84.70, H 8.26.

1.2. *Reduction of* **39** *to* **2** was performed in the usual way (*cf.* [1] [14]) by reacting **39** (1.30 g, 5.24 mmol) with $NaBH_4/BF_3 \cdot Et_2O$ in diglyme/Et_2O. Workup and CC on Al_2O_3 (Et_2O/hexane 7:3) yielded 1.08 g (89%) of **2** as a blue oil which turned out to be rather unstable in air (*cf.* [13]). R_f (Et_2O/hexane 7:3): 0.60. UV (hexane): λ_{max} 372 (3.61), 354 (3.67), 347 (sh, 3.50), 338 (sh, 3.47), 306 (4.01), 288 (4.55), 248 (4.22), 220 (4.07); λ_{min} 366 (3.38), 318 (3.27), 303 (3.99), 259 (4.09), 229 (4.01), 211 (4.05). IR ($CHCl_3$): 3005*s*, 2962*s*, 2927*s*, 2869*s*, 1603*w*, 1544*s*, 1461*s*, 1433*m*, 1396*w*, 1380*m*, 1371*m*, 1328*w*, 1289*w*, 1262*m*, 1154*w*, 1089*m*, 1054*m*, 1015*m*. ^{1}H-NMR (300 MHz): 7.998 (*d*, ^4J(H,H–C(6)) = 2.1, H–C(8)); 7.390 (*s*, H–C(2)); 7.194 (*dd*, ^3J(H,H–C(5)) = 10.7, ^4J(H,H–C(8)) = 2.1, H–C(6)); 6.744 (*d*, ^3J(H,H–C(6)) = 10.7, H–C(5)); 2.974 (*sept.*, Me_2CH); 2.956 (*s*, Me–C(4)); 2.841 (*s*, Me–C(3)); 2.584 (*s*, Me–C(1)); 1.317 (*d*, J = 6.9, Me_2CH). MS: 212 (100, $M^{+\cdot}$), 197 (17), 182 (7), 171 (7), 167 (5), 165 (3).

2. *Thermal Reaction of* **2** *with ADM.* The azulene **2** (0.226 g; 1.06 mmol) and ADM (0.580 g; 4.08 mmol) were heated in degassed decalin (4.0 ml) under Ar at 200° during 1 h. Prep. TLC (Al_2O_3; hexane/Et_2O 7:3) yielded a heptalene fraction (0.045 g; 12%), a fraction of a 9:1 mixture (0.051 g; 13%) of *dimethyl 5-isopropyl-3,8-dimethyl-* and *7-isopropyl-3,4-dimethylazulene-1,2-dicarboxylate* (**7** and **8**, resp.), and a fraction of the (1 + 2) adducts '*anti*'-**11**, '*anti*'-**12**, and '*anti*'-**13** in a ratio (^{1}H-NMR) of 9:2.5:1 (0.095 g; 18%).

Crystallization of the heptalene fraction from hexane at −20° yielded yellow needles (0.0085 g; 2.3%) of *dimethyl 7-isopropyl-3,5,10-trimethylheptalene-1,2-dicarboxylate* (**5a**) which, in soln. at 20°, isomerized partially (*ca.* 20%) into its DBS isomer, namely *dimethyl 9-isopropyl-1,3,6-trimethylheptalene-4,5-dicarboxylate* (**5b**; see below). The mother liquor of the heptalene fraction contained additional amounts of **5a**/**5b**, two further isomeric heptalenes (**6a**/**6b**), and the tricyclic compound **9**. Prep. HPLC (hexane/(CH_2Cl_2 + 0.5% MeOH) 5.7:1) yielded 0.0086 g (2.3%) of **5a**, 0.0117 g (3.1%) of the tricyclus **9**[15]), and **6a** as well as **6b**. The yellow oil of **5a** crystallized from hexane at −20° (0.0023 g; 0.6%). The other heptalene, **6a** (*ca.* 0.6%), isomerized in soln. at 20° to yield a mixture of *ca.* 70% of **6a** and 30% of **6b** (see below).

Data of **5a**: yellow needles. M.p. 102.5–104.8°. R_f (Et_2O/hexane 3:2) 0.38. UV (Et_2O): λ_{max} 330 (3.61), 258 (4.25), 216 (4.32); λ_{min} 314 (3.58), 242 (4.20). IR ($CHCl_3$): 3008*w*, 2960*s*, 2864*w*, 1721*s*, 1436*m*, 1373*w*, 1261*s*, 1096*s*, 1015*s*. ^{1}H-NMR (400 MHz): 6.293 (*dq*, ^3J(H,H–C(8)) = 6.6, ^4J(H,Me–C(10)) ≈ 1.3, H–C(9)); 6.135 (*dd*, ^3J(H,H–C(9)) = 6.5, ^4J(H,H–C(6)) ≈ 1.2, H–C(8)); 6.006 (*q*-like, ^4J(H,Me–C(5)) ≈ 1.3, H–C(4)); 5.863 (br. *s*, H–C(6)); 3.687, 3.627 (2*s*, 2 MeOCO); 2.500 (br. *sept.*, Me_2CH); 2.271 (*s*, Me–C(3)); 2.018 (*d*, ^4J(Me,H–C(4)) = 1.4, Me–C(5)); 2.004 (br. *s*, Me–C(10)); 1.102, 1.069 (2*d*, J = 6.9, Me_2CH). MS: 354 (51, $M^{+\cdot}$), 339 (41), 295 (18), 280 (10), 257 (19), 256 (100, $[M - MeC{\equiv}CCOOMe]^{+\cdot}$), 241 (17), 225 (11), 221 (11), 212 (17, $[M - ADM]^{+\cdot}$), 209 (12), 197 (10), 191 (10), 178 (10), 165 (13). Anal. calc. for $C_{22}H_{26}O_4$ (354.45): C 74.55, H 7.39; found: C 74.31, H 7.67.

The heptalene **5a** isomerized thermally in $CDCl_3$ already at r.t. to yield its DBS isomer **5b** in *ca.* 30%. At 100° in decalin, a ratio of 61% of **5a** and 39% of **5b** was established (^{1}H-NMR). Irradiation of **5a** in hexane/CH_2Cl_2 9:1 at 366 nm resulted in a 1:1 mixture **5a**/**5b** (HPLC).

Data of **5b**: R_f (Et_2O/hexane 3:2) 0.38. ^{1}H-NMR (400 MHz; in the presence of *ca.* 60% of **5a**): 6.436 (br. *s*, H–C(2)); 6.373 (*dd*, ^3J(H,H–C(8)) = 12.0, ^5J(H,H–C(10)) ≈ 0.5, H–C(7)); 6.345 (*dd*, ^3J(H,H–C(7)) = 12.0, ^4J(H,H–C(10)) = 1.1, H–C(8)); 5.723 (br. *s*, H–C(10)); 3.877, 3.655 (2*s*, 2 MeOCO); ~ 2.52 (*sept.*, Me_2CH); 2.002 (br. *s*, Me–C(3)); 1.741 (br. *s*, Me–C(1)); 1.648 (*s*, Me–C(6)); 1.129, 1.122 (2*d*, J = 6.9, Me_2CH).

Fractions enriched in **5b** showed that **5b** isomerized already at r.t. to yield a *ca.* 2:1 mixture **5a**/**5b** (^{1}H-NMR).

Dimethyl 9-Isopropyl-3,5,6-trimethylheptalene-1,2-dicarboxylate (**6a**). Yellow crystals. M.p. 104.7–106.3°. R_f (Et_2O/hexane 3:2) 0.38. UV (hexane): λ_{max} 332 (3.64), 264 (4.28), 217 (4.34); λ_{min} 308 (3.54), 242 (4.19), 200 (4.26). IR ($CHCl_3$): 3690*w*, 3021*m*, 2961*s*, 1717*s*, 1651*w*, 1601*w*, 1571*w*, 1436*m*, 1375*w*, 1138*s*, 1084*s*, 1013*s*. ^{1}H-NMR (300 MHz): 6.439 (*AB*, J_{AB} ≈ 11, ^4J(H,H–C(10)) ≈ 1, H–C(7,8) with δ(H–C(7)) > 6.439 > δ(H–C(8)); 6.121 (br. *s*, H–C(10)); 6.012 (*q*-like, ^4J(H,Me–C(5)) ≈ 1.1, H–C(4)); 3.649, 3.628 (2*s*, 2 MeOCO); 2.581 (*sept.d*, Me_2CH); 2.227 (*s*, Me–C(3)); 1.936 (*d*, ^4J(Me,H–C(4)) = 1.4, Me–C(5)); 1.805 (*s*, Me–C(6)); 1.164, 1.146 (2*d*, J = 6.8, Me_2CH). ^{1}H-NOE (400 MHz; $CDCl_3$): 2.227 (Me–C(3))→6.012 (*s*, H–C(4)); 1.936 (Me–C(5))→6.012 (*s*, H–C(4)), 1.805 (*m*, Me–C(6)); 1.805 (Me–C(6))→6.439 (*s*, H–C(7)), 1.936 (*m*, Me–C(5)). CI-MS: 355 (33, $[M + 1]^+$), 323 (100), 309 (3), 240 (6). Anal. calc. for $C_{22}H_{26}O_4$ (354.45): C 74.55, H 7.39; found: C 74.84, H 7.56.

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[15]) *Later* (*cf. 2.1.3*), we found that **9** was accompanied already in the original reaction mixture by a second tricyclic compound, namely **10**, in an amount of *ca.* 18% with respect to the amount of **9** (HPLC).

The heptalene **6a** isomerized readily in soln. at r.t. to yield a *ca.* 3:1 mixture with its DBS isomer **6b** (^{1}H-NMR).

Dimethyl 7-Isopropyl-1,3,10-trimethylheptalene-4,5-dicarboxylate (**6b**). R_f (Et_2O/hexane 3:2) 0.38. ^{1}H-NMR (300 MHz; in the presence of *ca.* 70% of **6a**): 6.423 (*q*-like, ^4J(H,Me–C(3)) ≈ 1, H–C(2)); 6.418 (*AB*, J_{AB} ≈ 6, H–C(8,9)); 5.678 (*s*, H–C(6)); 3.884, 3.678 (2*s*, 2 MeOCO); 2.441 (*sept.d*, Me_2CH); 2.029 (*d*, ^4J(Me,H–C(9)) = 1.2, Me–C(10)); 1.999 (br. *s*, Me–C(3)); 1.758 (*s*, Me–C(1)); 1.054, 1.021 (2*d*, *J* = 6.8, 6.9, Me_2CH).

Dimethyl 7-Isopropyl-2,4,11-trimethyltricyclo[6.2.2.0^{1,5}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate (**9**). Pale yellow oil. R_f (Et_2O/hexane 3:2) 0.38. UV (hexane): λ_{max} 339 (sh, 3.50), 312 (3.61), 234 (sh, 3.72), 214 (sh, 4.05); λ_{min} 272 (3.41). IR ($CHCl_3$): 3030*m*, 2953*m*, 1720*s*, 1625*w*, 1462*w*, 1436*s*, 1329*w*, 1272*s*, 1148*m*, 1102*m*, 1007*m*, 950*m*, 806*w*. ^{1}H-NMR (400 MHz): 6.728 (*q*, ^4J(H,Me–C(2)) = 1.5, H–C(3)); 6.004 (*dq*, ^3J(H,H–C(8)) = 6.6, ^4J(H,Me–C(11)) = 1.5, H–C(12)); 5.797 (*t*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me_2CH) ≈ 1.2, H–C(6)); 4.166 (*dd*, ^3J(H,H–C(12)) = 6.6, ^4J(H,H–C(6)) = 1.5, H–C(8)); 3.720 (*s*, MeOCO–C(9)); 3.691 (*s*, MeOCO–C(10)); 2.455 (*sept. d*, Me_2CH); 2.069 (*d*, ^4J(Me,H–C(3)) = 1.4, Me–C(2)); 1.936 (*s*, Me–C(4)); 1.590 (*d*, ^4J(Me,H–C(12)) = 1.6, Me–C(11)); 1.092, 1.075 (2*d*, *J* = 6.9, Me_2CH). ^{1}H-NOE (400 MHz): 2.069 (Me–C(2))→6.278 (*s*, H–C(3)), 1.590 (*s*, Me–C(11)), 3.691 (*m*, MeOCO–(10)); 3.691 (MeOCO–C(10))→2.069 (*m*, Me–C(2)); 1.936 (Me–C(4))→5.797 (*s*, H–C(6)), 6.278 (*s*, H–C(3)); 1.590 (Me–C(11))→2.069 (*s*, Me–C(2)), 6.004 (*s*, H–C(12)).

From the azulene-1,2-dicarboxylate mixture, pure **7** crystallized. The mother liquor contained the enriched **8** (*ca.* 40%).

Data of **7**: dark blue crystals. M.p. 74.9–75.7° (hexane). R_f (Et_2O/hexane 3:2) 0.36. UV (hexane): λ_{max} 369 (sh, 3.39), 356 (3.84), 341 (3.73), 311 (4.51), 299 (4.61), 249 (4.43), 220 (4.19); λ_{min} 344 (3.72), 329 (3.63), 308 (4.51), 263 (4.19), 228 (4.14). IR ($CHCl_3$): 3024*w*, 2962*m*, 1715*s*, 1557*w*, 1522*w*, 1445*s*, 1412*m*, 1160*m*, 1096*s*, 1017*s*, 867*w*. ^{1}H-NMR (300 MHz): 8.394 (*d*, ^4J(H,H–C(6)) = 2.0, H–C(4)); 7.506 (*dd*, ^3J(H,H–C(5)) = 10.5, ^4J(H,H–C(4)) = 2.0, H–C(6)); 7.121 (*d*, ^3J(H,H–C(6)) = 10.6, H–C(7)); 3.954, 3.938 (2*s*, 2 MeOCO); 3.070 (*sept.*, Me_2CH); 2.824 (*s*, Me–C(8)); 2.775 (*s*, Me–C(3)); 1.355 (*d*, *J* = 6.6, Me_2CH). CI-MS: 316 (5.5, $[M+2]^+$), 315 (29, $[M+1]^+$), 284 (18), 283 (100). Anal. calc. for $C_{19}H_{22}O_4$ (314.39): C 72.59, H 7.05; found: C 72.44, H 6.91.

Data of **8**: R_f (Et_2O/hexane 3:2) 0.36. UV (hexane/CH_2Cl_2 85:15; qual.): λ_{max} 382 (0.19), 351 (0.14), 311 (sh, 0.90), 306 (sh, 0.96), 301 (1.0), 248 (0.48), 221 (0.45); λ_{min} 357 (0.137), 336 (0.12), 269 (0.20), 228 (0.43). ^{1}H-NMR (300 MHz; in the presence of *ca.* 60% **7**): 9.701 (*d*, ^4J(H,H–C(6)) = 2.2, H–C(8)); 7.548 (*dd*, ^3J(H,H–C(5)) = 10.5, ^4J(H,H–C(8)) = 2.1, H–C(6)); 7.256 (*d*, ^3J(H,H–C(6)) = 10.9, H–C(5)); 3.984, 3.902 (2*s*, 2 MeOCO); 3.101 (*sept.*, Me_2CH); 3.072 (*s*, Me–C(3)); 2.739 (*s*, Me–C(4)); 1.368 (*d*, *J* = 6.7, Me_2CH).

The mixture of the three (1 + 2) adducts crystallized from Et_2O/hexane in colourless crystals of different shape (0.072 g), allowing separation of individual crystals under a magnifying glass. Recrystallization of these selected crystals from Et_2O/hexane yielded the pure tetracyclic compounds.

*Tetramethyl (1*RS,*2*RS,*5*RS,*8*SR*)-7-isopropyl-2,11,13-trimethyltetracyclo[6.2.2.2^{2,5}0^{1,5}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate* (*'anti'*-**11**). Colourless crystals. M.p. 99.3–101.2°. R_f (Et_2O/hexane 3:2) 0.32. UV (CH_2Cl_2): λ_{max} 249 (3.77), 224 (3.90); λ_{min} 239 (3.74). IR ($CHCl_3$): 3028*m*, 2953*m*, 1718*s*, 1613*m*, 1436*s*, 1384*m*, 1331*m*, 1259*s*, 1150*w*, 1099*m*, 1075*m*, 1019*m*. ^{1}H-NMR (300 MHz): 6.138 (*dq*, ^3J(H,H–C(8)) = 7.2, ^4J(H,Me–C(11)) = 1.5, H–C(12)); 5.975 (*q*, ^4J(H,Me–C(13)) = 1.8, H–C(14)); 5.480 (*t*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me_2CH) ≈ 1.3, H–C(6)); 3.786, 3.707, 3.700 (3*s*[1:2:1], 4 MeOCO); 3.545 (*dd*, ^3J(H,H–C(12)) = 7.2, ^4J(H,H–C(6)) = 1.2, H–C(8)); 2.455 (*sept. d*, *J* = 6.8, ^4J(Me_2CH,H–C(6)) ≈ 1, Me_2CH); 2.008 (*d*, ^4J(Me,H–C(12)) = 1.5, Me–C(11)); 1.752 (*s*, Me–C(2)); 1.730 (*d*, ^4J(Me,H–C(14)) = 1.8, Me–C(13)); 1.074, 1.071 (2*d*, *J* = 6.9, Me_2CH). ^{1}H-DR (400 MHz): 2.008 (*d*, Me–C(11))→6.138 (*d*, *J* = 7.3, H–C(12)); 1.730 (*d*, Me–C(13))→5.975 (*s*, H–C(14)); 5.480 (*t*-like, H–C(6))→3.545 (*d*, *J* = 7.3, H–C(8)), 2.455 (*sept.*, *J* = 6.8, Me_2CH); 3.545 (*dd*, H–C(8))→6.138 (*d*-like, *J* ≈ 1.6, H–C(12)), 5.480 (*d*, *J* = 1.1, H–C(6)). ^{1}H-NOE (400 MHz): 6.138 (H–C(12))→3.545 (*s*, H–C(8)), 2.008 (*s*, Me–C(11)); 5.480 (H–C(6))→1.730 (*s*, Me–C(13)), 2.455 (*s*, Me_2CH); 2.455 (Me_2CH)→5.480 (*s*, H–C(6)), 3.545 (*s*, H–C(8)), 1.074/1.071 (*s*, Me_2CH); 2.008 (Me–C(11))→1.752 (*s*, Me–C(2)), 6.138 (*s*, H–C(12)); 1.752 (Me–C(2))→5.975 (*s*, H–C(14)), 2.008 (*s*, Me–C(11)); 1.730 (Me–C(13))→5.975 (*s*, H–C(14)), 5.480 (*s*, H–C(6)). MS: 496 (0.7, M^+), 437 (100), 405 (61), 377 (27), 345 (17), 303 (13), 245 (14), 233 (15). Anal. calc. for $C_{28}H_{32}O_8$ (496.56): C 67.73, H 6.50; found: C 67.56, H 6.73.

*Tetramethyl (1*RS,*2*RS,*5*SR,*8*SR*)-12-Isopropyl-2,6,13-trimethyltetracyclo[6.2.2.2^{2,5}0^{1,5}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate* (*'anti'*-**12**). Colourless crystals. M.p. 146.7–147.5°. R_f (Et_2O/hexane 3:2) 0.32. UV (CH_2Cl_2): λ_{max} 246 (3.74), 230 (3.75); λ_{min} 238 (3.73). IR ($CHCl_3$): 3030*m*, 2953*m*, 1715*s*, 1615*m*, 1435*s*, 1280*s*, 1140*w*, 1087*w*, 1070*w*. ^{1}H-NMR (300 MHz): 6.114 (*q*, ^4J(H,Me–C(13)) = 1.8, H–C(14)); 6.112 (*dq*,

^3J(H,H–C(8)) = 8.6, ^4J(H,Me–C(6)) = 1.4, H–C(7)); 5.661 (*t*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me$_2$C*H*) ≈ 1.3, H–C(11)); 3.759, 3.727, 3.712, 3.686 (4*s*, 4 MeOCO); 3.630 (*dd*, ^3J(H,H–C(7)) = 8.6, ^4J(H,H–C(11)) = 1.8, H–C(8)); 2.344 (*sept.d*, *J* = 6.6, ^4J(Me$_2$C*H*,H–C(11)) ≈ 1.2, Me$_2$C*H*); 1.819 (*d*, ^4J(Me,H–C(14)) = 1.8, Me–C(13)); 1.705 (*s*, Me–C(2)); 1.657 (*d*, ^4J(Me,H–C(7)) = 1.4, Me–C(6)); 1.005, 0.994 (2*d*, *J* = 6.8, *Me*$_2$CH). ^{1}H-DR (400 MHz): 5.661 (*t*-like, H–C(11))→3.630 (*d*, *J* = 8.6, H–C(8)), 2.334 (*sept.*, *J* = 6.6, Me$_2$C*H*); 3.630 (*dd*, H–C(8))→6.11 (br. *d*-like, H–C(7), H–C(14)); 1.819 (*d*, Me–C(13))→6.114 (*s*, H–C(14)), 6.112 (*dq*-like, *J* = 8.6, 1.4, H–C(7)); 1.657 (*d*, Me–C(6))→6.114 (*q*-like, *J* = 1.7, H–C(14)), 6.112 (*d*, *J* = 8.6, H–C(7)). ^{1}H-NOE (400 MHz): 5.661 (H–C(11))→2.344 (*s*, Me$_2$C*H*), 1.705 (*s*, Me–C(2)), 1.005/0.994 (*m*, *Me*$_2$CH); 1.819 (Me–C(13))→6.114 (*s*, H–C(14)), 3.686 (*w*, MeOCO–C(10)), 1.657 (*s*, Me–C(6)); 1.705 (Me–C(2))→6.114 (*s*, H–C(14)), 5.661 (*s*, H–C(11)); 1.657 (Me–C(6))→6.112 (*s*, H–C(7)), 3.727 (*m*, MeOCO–C(4)), 1.819 (*s*, Me–C(13)). MS: 496 (0, $M^{+\cdot}$), 437 (100), 405 (70), 377 (28), 345 (27), 317 (17), 303 (12), 275 (7), 259 (8), 245 (5), 219 (18), 215 (9), 202 (9). CI-MS: 497 (100, $[M+1]^+$), 465 (98), 437 (61), 287 (14), 211 (5). Anal. calc. for $C_{28}H_{32}O_8$ (496.56): C 67.73, H 6.50; found: C 67.56, H 6.65.

*Tetramethyl (1*RS,*2*SR,*5*SR,*8*SR*)-14-Isopropyl-6,8,11-trimethyltetracyclo[6.2.2.2^{2,5}0^{1,7}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate* ('*anti*'-**13**). Colourless crystals. M.p. 145.1–146.5°. R_f (Et$_2$O/hexane 3:2): 0.32. UV (CH_2Cl_2): λ_{max} 249 (sh, 3.00), 224 (4.03). IR ($CHCl_3$): 3028*m*, 2953*m*, 1715*s*, 1633*w*, 1603*w*, 1435*s*, 1269*s*, 1140*m*, 1080*m*, 1068*m*, 1030*m*. ^{1}H-NMR (300 MHz): 6.150 (*q*, ^4J(H,Me–C(11)) = 1.7, H–C(12)); 5.963 (*dt*, ^3J(H,H–C(5)) = 7.0, ^4J(H,H–C(2)) ≈ ^4J(H,Me$_2$C*H*) ≈ 1.6, H–C(13)); 4.248 (*d*, ^4J(H,H–C(13)) = 1.9, H–C(2)); 3.781, 3.761, 3.754, 3.739 (4*s*, 4 MeOCO); 3.255 (*d*, ^3J(H,H–C(13)) = 7.0, H–C(5)); 2.211 (*sept. d*, *J* = 6.5, ^4J(Me$_2$C*H*,H–C(13)) = 1.2, Me$_2$C*H*); 1.841 (*s*, Me–C(6)); 1.830 (*d*, ^4J(Me,H–C(12)) = 1.7, Me–C(11)); 1.642 (*s*, Me–C(8)); 1.027 (br. *d*, *J* ≈ 6.7, *Me*$_2$CH). ^{1}H-NOE (400 MHz): 1.642 (Me–C(8))→6.150 (*s*, H–C(12)), 1.841 (*s*, Me–C(6)); 1.830 (Me–C(11))→6.150 (*s*, H–C(12)), 4.248 (*s*, H–C(2)), 3.781 (*m*, MeOCO–C(3)); 1.841 (Me–C(6))→3.255 (*s*, H–C(5)), 1.642 (*s*, Me–C(8)); 4.248 (H–C(2))→2.211 (*s*, Me$_2$C*H*), 1.830 (*s*, Me–C(12)), 1.027 (*m*, Me$_2$CH); 5.963 (H–C(13))→3.255 (*s*, H–C(5)), 1.027 (*m*, *Me*$_2$CH). MS: 496 (30, $M^{+\cdot}$), 464 (34), 437 (16), 421 (47), 405 (24), 389 (19), 377 (17), 361 (19), 345 (15), 260 (25), 228 (100), 165 (11).

In a second experiment, 0.808 g of **2** (3.805 mmol) were heated with 1.79 ml of ADM (14.55 mmol) in 14.3 ml of decalin under Ar at 200° during 1 h. The separated mixture of heptalenes and tricycle **9**[15]) amounted to 0.202 g (15%) and the mixture of (1 + 2) adducts to 0.183 g (15%). The mixture of azulene-1,2-dicarboxylates **7** and **8** was obtained in a yield of 8.1% (0.114 g).

2.1. *Control Experiments.* 2.1.1. *Thermal Stability of the Tetracycle* 'anti'-**11**. The tetracycle (0.010 g) could be distilled in a *Kugelrohr* at *ca.* 10^{-3} Torr and 130° without decomposition (HPLC). Also, when '*anti*'-**11** (0.009 g) was heated in decalin (0.5 ml) up to 200° and as long as 20 h no decomposition was observed.

2.1.2. *Thermal Reaction of the Tricyclus* **9** *with ADM.* A soln. of **9** (0.011 g; 0.031 mmol) and ADM (0.039 g; 0.274 mmol) in decalin (0.2 ml) was heated at 200° under N_2. The reaction was followed by HPLC. After 2 h, only '*anti*'-**11** and '*anti*'-**12** were present in a ratio of 4:1. The mixture was isolated after distillative removal of decalin and excess ADM by prep. TLC on silica gel (hexane/Et$_2$O 3:2) to yield pure material (0.0096 g; 64%). ^{1}H-NMR showed that the mixture contained '*anti*'-**11** and '*anti*'-**12** in a ratio of 4:1.

2.1.3. *Thermal Behaviour of the Tricycle* **9**. *Formation of Dimethyl 9-Isopropyl-2,4,11-trimethyltricyclo[6.2.2.0^{1,5}]dodeca-2,4,6,9,11-pentaene-6,7-dicarboxylate* (**10**). Tricycle **9** (0.020 g; 0.056 mmol) was dissolved in 1,1,2,2-tetrachloro[1,2-$^2H_2$]ethane (1.0 ml) and a trace of $CDCl_3$ added. The soln. was filled in a NMR tube, purged with N_2, and the tube sealed. It was heated at 160° for 3.5 h and for additional 1.5 h. At both times, the formation of a second tricyclic compound, namely **10**, to an extent of 17% with respect to **9** was observed (^{1}H-NMR). UV of **10** (hexane/(CH_2Cl_2 + 0.5% MeOH) 5.7:1; qual.): λ_{max} 357. ^{1}H-NMR (300 MHz; $C_2D_2Cl_4$; **9**/**10** 83:17): 6.189/6.109 (*q*-like, ^4J = 1.6/1.5, H–C(3)/H–C(3)); 5.90/5.90 (*dq*, ^3J = 6.5/6.5, H–C(12)/H–C(12)); 5.665/5.403 (*t*-like, ^4J ≈ 1.3/1.3, H–C(6)/H–C(10)); 4.036/4.280 (*dd*, ^3J = 6.6/6.7, ^4J = 1.3/1.8, H–C(8)/H–C(8)); 3.620, 3.594/3.694, 3.671 (2*s*, MeOCO–C(9,10)/MeOCO–C(6,7)); *ca.* 2.35/2.35 (*sept.d*, *J* ≈ 6.5, Me$_2$C*H*–C(7)/C(9)); 1.952/2.032 (*d*, ^4J ≈ 1.2/1.2, Me–C(2)/Me–C(2)); 1.845/1.832 (*s*, Me–C(4)/Me–C(4)); 1.482/1.443 (*d*, ^4J = 1.4/1.4, Me–C(11)/Me–C(11)); 0.991, 0.981/0.918, 0.906 (2*d*, *J* = 6.7/6.7, Me$_2$CH–C(7)/C(9)). ^{1}H-NMR (300 MHz; C_6D_6; **9**/**10** 83:17): 6.183/5.975 (*q*-like, ^4J = 1.5/1.5, H–C(3)/H–C(3)); 6.027/6.088 (*dq*, ^3J = 6.7/6.6, ^4J = 1.6/1.6, H–C(11)/H–C(11)); 5.957/5.647 (*t*-like, ^4J ≈ 1.3/1.3, H–C(6)/H–C(10)); 4.442/4.742 (*dd*, ^3J = 6.7/6.6, ^4J = 1.5/1.7, H–C(8)/H–C(8)); 3.527, 3.437/3.719, 3.540 (2*s*, MeOCO–C(9,10)/MeOCO–C(6,7)); 2.524/2.480 (*sept.d*, *J* = 6.6/6.6, Me$_2$C*H*–C(7)/C(9)); 2.208/1.977 (*d*, ^4J = 1.3/1.2, Me–C(2)/Me–C(2)); 1.848/2.068 (*s*, Me–C(4)/Me–C(4)); 1.622/1.553 (*d*, ^4J = 1.5/1.5, Me–C(11)/Me–C(11)); 1.168, 1.127/1.112, 1.100 (2*d*, *J* = 6.7/6.7, *Me*$_2$CH–C(7)/C(9)). ^{1}H-NOE (400 MHz; C_6D_6; **10** in the presence of 83% of **9**): 2.068 (Me–C(4))→5.975 (*s*, H–C(3)), 3.719 (*m*, MeOCO–C(6)); 1.977 (Me–C(2))→5.975 (*s*, H–C(3)), 5.647 (*s*, H–C(10)), and 1.553 (*m*, Me–C(11)).

3. *Thermal Reaction of 7-Isopropyl-1,4-dimethylazulene* (*Guaiazulene*; **1**) *with ADM* (*cf.* [4–5]). Azulene **1** (0.350 g; 1.765 mmol) and ADM (1.08 ml; 8.83 mmol) were heated in decalin (7.0 ml) at 190° during 1.5 h. The solvent was removed by distillation and the residue chromatographed on silica gel (hexane/AcOEt 3:2) to remove **3a** and **4**. The polar fractions were combined to yield the mixture of (1 + 2) adducts and small amounts of tricyclic compounds (in total 0.164 g; 19.3% [16]). The polar fractions were further separated by prep. HPLC to yield the following purified fractions: 0.0284 g (3.3%) of '*anti*'-**17** which crystallized from Et_2O/hexane (0.013 g); 0.0306 g (3.6%) of '*syn*'-**19**; 0.023 g (2.7%) of '*anti*'-**18**, contaminated with 10% of '*anti*'-**19**; 0.007 g (0.8%) of a mixture of '*anti*'-**20** (55%) and '*anti*'-**21** (45%). Two additional fractions contained beside the compounds already mentioned two further substances, namely the tricycle **22** and **23**. An additional purification by prep. HPLC yielded 0.002 g of a 4:1 mixture **22**/**23**.

*Tetramethyl (1*RS,*2*RS,*5*SR,*8*SR*)-12-Isopropyl-2,6-dimethyltetracyclo[6.2.2.2*^{2,5}*0*^{1,5}*]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate* ('*anti*'-**17**). Colourless crystals. M.p. 130.2–131.4°. t_R (hexane/(CH_2Cl_2 + 0.5% MeOH) 85:15): 9.35 min (1.5 ml/min). UV (CH_2Cl_2): λ_{max} 244 (3.89), 224 (3.79); λ_{min} 238 (3.78). ^{1}H-NMR (300 MHz): 6.636 (*d*, ^3J(H,H–C(13)) = 5.3, H–C(14)); 6.581 (*d*, ^3J(H,H–C(14)) = 5.3, H–C(13)); 6.037 (*dq*, ^3J(H,H–C(8)) = 8.5, ^4J(H,Me–C(6)) = 1.5, H–C(7)); 5.688 (*t*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me$_2$C*H*) ≈ 1.5, H–C(11)); 3.778, 3.729, 3.708 (3*s*[1:1:2], 4 MeOCO); 3.661 (*dd*, ^3J(H,H–C(7)) = 8.6, ^4J(H,H–C(11)) = 1.8, H–C(8)); 2.340 (*sept. d*, Me$_2$C*H*); 1.721 (*s*, Me–C(2)); 1.644 (*d*, ^4J(Me,H–C(7)) = 1.5, Me–C(6)); 1.010, 1.001 (2*d*, *J* = 6.8, *Me*$_2$CH). ^{1}H-NOE (400 MHz): 1.721 (Me–C(2))→6.636 (*s*, H–C(14)), 5.688 (*s*, H–C(11)), 3.778, 3.708 (*w*, MeOCO–C(3,10)); 1.644 (Me–C(6))→6.581 (*s*, H–C(13)), 6.037 (*s*, H–C(7)), 3.708 (*m*, MeOCO–C(4)); 5.688 (H–C(11))→2.340, 1.010/1.001 (*s*, *Me*$_2$C*H*), 1.721 (*s*, Me–C(2)). MS: 482 (0, $M^{+\cdot}$), 423 (100, $[M - COOCH_3]^+$), 391 (40), 363 (38), 359 (17), 331 (19), 289 (12), 219 (12), 202 (12).

*Tetramethyl (1*RS,*2*SR,*5*SR,*8*SR*)-7-Isopropyl-11,13-dimethyltetracyclo[6.2.2.2*^{2,5}*0*^{1,5}*]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate* ('*syn*'-**19**). t_R (hexane/(CH_2Cl_2 + 0.5% MeOH) 85:15): 11.77 min (1.5 ml/min). ^{1}H-NMR (300 MHz): 6.399 (*sext.*-like, ^4J(H,Me–C(13)) ≈ 0.5·^3J(H,H–C(2)) ≈ 1.8, H–C(14)); 6.117 (*dq*, ^3J(H,H–C(8)) = 7.1, ^4J(H,Me–C(11)) = 1.6, H–C(12)); 5.277 (*q*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me$_2$C*H*) ≈ ^5J(H,H–C(2)) ≈ 1, H–C(6)); 4.272 (*dd*, ^3J(H,H–C(14)) = 3.4, ^5J(H,H–C(6)) = 0.65, H–C(2)); 3.761, 3.732, 3.696, 3.668 (4*s*, 4 MeOCO); 3.535 (*dd*, ^3J(H,H–C(12)) = 7.1, ^4J(H,Me–C(6)) = 1.2, H–C(8)); 2.446 (*sept. d*, Me$_2$C*H*); 1.826 (*d*, ^4J(Me,H–C(12)) = 1.6, Me–C(11)); 1.747 (*d*, ^4J(Me,H–C(14)) = 1.8, Me–C(13)); 1.074, 1.052 (*t*-like, *J* ≈ 6.7, *Me*$_2$CH). ^{1}H-DR (400 MHz): 5.277 (*q*-like, H–C(6))→4.272 (*d*, ^3J = 3.4, H–C(2)); 4.272 (*dd*, H–C(2))→5.277 (*t*-like, ^4J ≈ 1.1, H–C(6)). ^{1}H-NOE (400 MHz): 1.747 (Me–C(13))→6.399 (*s*, H–C(14)), 5.277 (*s*, H–C(6)); 1.826 (Me–C(11))→6.399 (*s*, Me–C(14)), 6.117 (*s*, H–C(12)), 4.272 (*s*, H–C(2)); 5.277 (H–C(6))→2.446, 1.074/1.052 (*s*, *Me*$_2$C*H*), 1.747 (*m*, Me–C(13)).

*Tetramethyl (1*RS,*2*RS,*5*SR,*8*SR*)-12-Isopropyl-6,13-dimethyltetraclo[6.2.2.2*^{2,5}*0*^{1,5}*]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate* ('*anti*'-**18**). In the mixture with *ca.* 10% of '*anti*'-**19**. t_R (hexane/(CH_2Cl_2 + 0.5% MeOH) 85:15): 16.47 min (1.5 ml/min; t_R('*anti*'-**19**): 17.15 min). ^{1}H-NMR (300 MHz): 6.278 (*sext.*-like, ^4J(H,Me–C(13)) ≈ 0.5·^3J(H,H–C(2)) ≈ 1.8, H–C(14)); 6.132 (*dq*, ^3J(H,H–C(8)) = 8.8, ^4J(H,Me–C(6)) = 1.5, H–C(7)); 5.671 (*t*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me$_2$C*H*) ≈ 1.7, H–C(11)); 4.203 (*d*, ^3J(H,H–C(14)) = 3.5, H–C(2)); 3.768 (*s*, MeOCO–C(3)); 3.765 (*s*, MeOCO–C(4)); 3.720, 3.713 (2*s*, MeOCO–C(9,10)); 3.558 (*dd*, ^3J(H,H–C(7)) = 8.7, ^4J(H,H–C(11)) = 1.8, H–C(8)); 2.318 (*sept. d*, Me$_2$C*H*); 1.838 (*d*, ^4J(Me,H–C(14)) = 1.8, Me–C(13)); 1.662 (*d*, ^4J(Me,H–C(7)) = 1.5, Me–C(6)); 0.980 (*d*, *J* = 6.8, *Me*$_2$CH). ^{1}H-NOE (400 MHz): 1.662 (Me–C(6))→6.132 (*s*, H–C(7)), 3.765 (*m*, MeOCO–C(4)), 1.838 (*m*, Me–C(13)); 1.838 (Me–C(13))→6.278 (*s*, H–C(14)), 1.662 (*m*, Me–C(6)); 5.671 (H–C(11))→4.203 (*s*, H–C(2)), 3.768 (*w*, MeOCO–C(3)), 2.318, 0.980 (*s*, *Me*$_2$C*H*).

*Tetramethyl (1*RS,*2*RS,*5*SR,*8*SR*)-7-Isopropyl-11,13-dimethyltetracyclo[6.2.2.2*^{2,5}*0*^{1,5}*]tetradeca-3,6,9,11-13-pentaene-3,4,9,10-tetracarboxylate* ('*anti*'-**19**). Only observed in mixtures with the other tetracyclic compounds. t_R (hexane/(CH_2Cl_2 + 0.5% MeOH) 85:15): 17.15 min (1.5 ml/min). ^{1}H-NMR (300 MHz; taken from a mixture with 69% of '*anti*'-**18** and 4% of '*anti*'-**17**): 6.207 (*sext.*-like, ^4J(H,Me–C(13)) ≈ 0.5·^3J(H,H–C(2)) ≈ 1.8, H–C(14)); 6.157 (*dq*, ^3J(H,H–C(8)) = 7, ^4J(H,Me–C(11)) = 1.5, H–C(12)); 5.268 (*q*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me$_2$C*H*) ≈ ^5J(H,H–C(2)) ≈ 1, H–C(6)); 4.324 (*dd*, ^3J(H,H–C(14)) = 3.4, ^5J(H,H–C(6)) ≈ 0.7, H–C(2)); 3.773, 3.767, 3.752, 3.695 (4*s*, 4 MeOCO); 3.610 (*dd*, ^3J(H,H–C(12)) = 7, ^4J(H,H–C(6)) = 1.5, H–C(8)); 2.445 (*sept. d*, Me$_2$C*H*); 1.832 (*d*, ^4J(Me,H–C(12)) = 1.5, Me–C(11)); 1.752 (*d*, ^4J(Me,H–C(14)) = 1.8, Me–C(13)); 1.067, 1.062 (2*d*, *J* = 6.8, *Me*$_2$CH).

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[16]) In a second experiment, **1** (0.741 mmol) reacted with a five-fold molar excess of ADM (3.68 mmol) in decalin (6.0 ml) at 190° during 3 h. The total amount of the fraction of tetracyclic compounds was 28.5%.

Tetramethyl (1RS,2SR,5RS,8RS)-9-Isopropyl-2,11-dimethyltetracyclo[6.2.2.2^{2,5}0^{1,5}]tetradeca-3,6,9,11,13-pentaene-3,4,6,7-tetracarboxylate ('*anti*'-**20**). In a mixture with *ca.* 45% of '*anti*'-**21**. t_R (hexane/(CH_2Cl_2 + 0.5% MeOH) 85:15): *ca.* 14.6 min (1.5 ml/min). ^{1}H-NMR (300 MHz): 6.689 (*d*, ^3J(H,H–C(13)) = 5.2, H–C(14)); 6.623 (*d*, ^3J(H,H–C(14)) = 5.2, H–C(13)); 6.235 (*dq*, ^3J(H,H–C(8)) = 7.2, ^4J(H,Me–C(11)) = 1.8, H–C(12)); 5.798 (*t*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me$_2$C*H*), H–C(10)); 3.845, 3.820, 3.814, 3.803 (4*s*, 4 MeOCO); 3.311 (*dd*, ^3J(H,H–C(12)) = 7.0, ^4J(H,H–C(10)) = 1.7, H–C(8)); 2.360 (*sept.d*, Me$_2$C*H*); 1.920 (*d*, ^4J(Me,H–C(12)) = 1.5, Me–C(11)); 1.609 (*s*, Me–C(2)); 1.018, 1.006 (2*d*, *J* = 6.8, *Me*$_2$CH). ^{1}H-NOE (400 MHz): 1.609 (Me–C(2))→6.689 (*s*, H–C(14)); 5.798 (*s*, H–C(10)); 3.814 (*w*, MeOCO–C(3)), 1.920 (*m*, Me–C(11)); 1.920 (Me–C(11))→6.689 (*s*, H–C(14)), 6.623 (*w*, H–C(13)), 6.235 (*s*, H–C(12)), 1.609 (*m*, Me–C(2)); 5.798 (H–C(10))→2.360, 1.018/1.006 (*s*, *m*, *Me*$_2$C*H*), 1.609 (*s*, Me–C(2)).

Tetramethyl (1RS,2SR,5SR,8SR)-9-Isopropyl-11,13-dimethyltetracyclo[6.2.2.2^{2,5}0^{1,5}]tetradeca-3,6,9,11,13-pentaene-3,4,6,7-tetracarboxylate ('*anti*'-**21**): In a mixture with *ca.* 55% of '*anti*'-**20**. t_R('*anti*'-**21**) ≈ t_R('*anti*'-**20**; hexane/(CH_2Cl_2 + 0.5% MeOH) 85:15). ^{1}H-NMR (300 MHz): 6.497 (*sext.*-like, ^4J(H,Me–C(13)) ≈ 0.5·^3J(H,H–C(2)) ≈ 1.7, H–C(14)); 6.235 (*dq*, H–C(12); overlapping with H–C(12) in '*anti*'-**20**); 5.732 (*t*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me$_2$C*H*), H–C(10)); 3.976 (*d*, ^3J(H,H–C(14)) = 3.5, H–C(2)); 3.699, 3.622, 3.614 (3*s*[1:1:2], 4 MeOCO); 3.357 (*dd*, ^3J(H,H–C(12)) = 7.0, ^4J(H,H–C(10)) = 1.8, H–C(8)); 2.337 (*sept.d*, Me$_2$C*H*); 1.787 (*d*, ^4J(Me,H–C(12)) = 1.5, Me–C(11)); 1.639 (*d*, ^4J(Me,H–C(14)) = 1.7, Me–C(13)); 0.985, 0.971 (2*d*, *J* = 6.8, *Me*$_2$CH). ^{1}H-NOE (400 MHz): 1.636 (Me–C(13))→6.497 (*s*, H–C(14)), 1.787 (*w*, Me–C(11)); 1.787 (Me–C(11))→6.497 (*s*, H–C(14)), 6.235 (*s*, H–C(12)), 3.976 (*s*, H–C(2)), 1.636 (*w*, Me–C(13)).

Tetramethyl 7-Isopropyl-4,11-dimethyltricyclo[6.2.2.0^{1,5}]dodeca-2,4,6,9,11-pentaene-2,3,9,10-tetracarboxylate (**22**). In a mixture with *ca.* 20% of **23**. t_R(**22**)/t_R(**23**) 10.7:9.5 min (hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1; flow rate: 1 ml/min). UV (hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1; qual.): λ_{max} 375.6 (0.58), 310 (sh, 0.22), 226.8 (1.0); λ_{min} 273.0 (0.17). ^{1}H-NMR (300 MHz; $CDCl_3/C_6D_6$): 6.054/5.816 (*dq*, ^3J(H,H–C(8)) = 6.6, ^4J(H,Me–C(11)) = 1.5, H–C(12)); 5.855/5.739 (*t*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me$_2$C*H*) ≈ 1.2, H–C(6)); 4.236/4.274 (*dd*, ^3J(H,H–C(12)) = 6.6, ^4J(H,H–C(6)) = 1.4, H–C(8)); 3.941, 3.744, 3.730, 3.614/3.635, 3.460, 3.385, 3.345 (4*s*, 4 MeOCO); 2.498/covered (*sept.d*, Me$_2$C*H*); 1.947/1.766 (*s*, Me–C(4)); 1.599/1.642 (*d*, ^4J(Me,H–C(12)) = 1.5, Me–C(11)); 1.092, 1.075/0.954, 0.902 (2*d*, *J* = 6.8, *Me*$_2$CH). ^{1}H-NOE (400 MHz; $CDCl_3$): 1.599 (Me–C(11))→6.054 (*s*, H–C(12)), 3.774 (*m*, MeOCO–C(2)); 1.947 (Me–C(4))→5.855 (*m*, H–C(6)), 3.941 (*w*, MeOCO–C(3)); 4.236 (H–C(8))→6.054 (*s*, H–C(12)), 2.489, 1.092/1.075 (*m*, *s*, *Me*$_2$C*H*); 5.855 (H–C(6))→2.489, 1.092/1.075 (*m*, *s*, Me$_2$C*H*), 1.947 (*s*, Me–C(4)); 6.054 (H–C(12))→4.236 (*s*, H–C(8)), 1.599 (*m*, Me–C(11)).

Tetramethyl 7-Isopropyl-2,11-dimethyltricyclo[6.2.2.0^{1,5}]dodeca-2,4,6,9,11-pentaene-3,4,9,10-tetracarboxylate (**23**). In a mixture with *ca.* 80% of **22**. t_R (**23**): *cf.* **22**. UV (hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1; qual.); λ_{max} 355.0 (0.35), 291 (0.21), 224.4 (1.0); λ_{min} 270.0 (0.21). ^{1}H-NMR (300 MHz; $CDCl_3/C_6D_6$): 6.432/6.691 (*t*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me$_2$C*H*) ≈ 1, H–C(6)); 6.168/5.861 (*dq*, ^3J(H,H–C(8))=6.6, ^4J(H,Me–C(11)) = 1.7, H–C(12)); 4.301/4.316 (*dd*, ^3J(H,H–C(12)) = 6.5, ^4J(H,H–C(6)) = 1.4, H–C(8)); 3.839, 3.795, 3.741, 3.688/3.502, 3.422, 3.365, 3.301 (4*s*, 4 MeOCO); *ca.* 2.50/covered (*sept. d*, Me$_2$C*H*); 2.163/2.270 (*s*, Me–C(2)); 1.611/1.375 (*d*, ^4J(Me,H–C(12)) = 1.7, Me–C(11)); *ca.* 1.03/0.902, 0.876 (2*d*, *J* = 6.8, Me$_2$CH). ^{1}H-NOE (400 MHz; $CDCl_3$): 1.611 (Me–C(11))→6.168 (*s*, H–C(12)), 2.163 (*s*, Me–C(2)); 2.163 (Me–C(2))→3.688 (*m*, MeOCO–C(10)), 1.611 (*m*, Me–C(11)). ^{1}H-NOE (400 MHz; C_6D_6): 1.375 (Me–C(11))→5.861 (*s*, H–C(12)), 2.270 (*s*, Me–C(2)).

3.1. *Control Experiments. 3.1.1. Thermal Reversible Isomerization of* **22** *and* **23**. Starting with the 4:1 mixture **22**/**23**, enriched probes of **22** (90% of **22** and 10% of **23**) and of **23** (25% of **22** and 75% of **23**) were obtained by prep. HPLC (hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1). After 4 h at 25° in $CDCl_3$, the first sample showed a composition of 83% of **22** and 17% of **23** (^{1}H-NMR; 300 MHz) and the second one such of 43.5% of **22** and 56.5% of **23**. $CDCl_3$ was exchanged by toluene, and both probes were heated at 100° for 1 h. ^{1}H-NMR revealed that both probes consisted of 70.5% of **22** and 29.5% of **23**.

3.1.2. *Thermal Reaction of* **7** *with ADM*. The dicarboxylate **7** (0.173 g; 0.550 mmol) and ADM (0.347 g; 2.44 mmol) were heated in decalin (4.0 ml) at 200° during 10 h. Prep. TLC (silica gel; hexane/Et_2O 9:1) yielded alongside with trimethyl 5-methoxyfuran-2,3,4-tricarboxylate (*cf.* [15]) two fractions containing mainly the 4:1 mixture **22**/**23** (R_f (hexane/Et_2O 1:4) 0.27) and a mixture of the new tetracyclic compounds **32**, '*anti*'-**33**, and '*anti*'-**34** (R_f 0.15) in a ratio of *ca.* 4.5:4.5:1. Prep. HPLC (hexane/(CH_2Cl_2 + 0.5% MeOH) 85:15) of the fraction of the tricyclic compounds gave pure mixtures of **22** and **23** (in total 0.049 g; 20%). HPLC separation (hexane/(CH_2Cl_2 + 0.5% MeOH) 4:1) of the mixture of tetracyclic compounds yielded crystalline **32** (0.040 g; 12%) and a greenish oil (0.029 g; 9%) which mainly contained '*anti*'-**33**. Crystallization from Et_2O/hexane gave colourless needles of pure '*anti*'-**33**. Fractions enriched in '*anti*'-**34** (up to 57%) were obtained from the mother liquor of the crystallization of **32**.

Hexamethyl (1RS,8SR)-12-Isopropyl-2,6-dimethyltetracyclo[6.2.2.2^{2,5}0^{1,5}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10,13,14-hexacarboxylate (**32**). Colourless crystals from hexane/AcOEt. M.p. 169.1–170.2°. R_f (hexane/Et_2O 1:4): 0.27. UV (MeCN): λ_{max} 211 (sh, 4.23), 188 (4.44). IR ($CHCl_3$): 3028*m*, 2954*m*, 1726*s*, 1610*m*, 1435*m*, 1261*m*, 1127*m*, 1102*m*, 1029*m*. ^{1}H-NMR (300 MHz; $CDCl_3/C_6D_6$; C*H*Cl_3 at 7.260/C_6D_5H at 7.159): 6.093/6.128 (*dq*, ^3J(H,H–C(8)) = 8.85/8.78, ^4J(H,Me–C(6)) = 1.52/1.45, H–C(7)); 5.660/5.952 (*t*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me$_2$C*H*) ≈ 1.4/1.4, H–C(11)); *ca.* 3.75/3.927 (*dd*, ^3J(H,H–C(7)) = 10.6[17])/8.78, ^4J(H,H–C(11)) = 10.6[17])/1.80, H–C(8)); 3.792, 3.773, 3.751, 3.737, 3.728, 3.660/3.598, 3.360, 3.304, 3.295, 3.241 (6*s*/5*s*[1:2:1:1:1], 6 MeOCO); 2.382/2.165 (*sept. d*, *J* = 6.3/6.5, Me$_2$C*H*); 1.852/2.310 (*s*, Me–C(2)); 1.500/1.702 (*d*, ^4J(Me,H–C(7)) = 1.4/1.32, Me–C(6)); 1.022, 1.015/0.953, 0.943 (2*d*, *J* = 6.6, 6.8, *Me*$_2$CH). ^{1}H-NOE (400 MHz; C_6D_6): 0.95 (*Me*$_2$CH)→6.128 (*w*, H–C(7)), 5.952 (*s*, H–C(11)), 3.927 (*s*, H–C(8)), 2.615 (Me$_2$C*H*); 1.702 (Me–C(6))→6.128 (*s*, H–C(7)); 2.310 (Me–C(2))→5.952 (*s*, H–C(11)), 3.598, 3.360 (*w*, *m*, MeOCO–C(3, 14)). CI-MS: 601 (10, [*M* + 3]$^+$), 600 (27, [*M* + 2]$^+$), 599 (100, [*M* + 1]$^+$), 568 (15), 567 (65). MS: 598 (0, *M*$^{+\cdot}$), 567 (8), 540 (28), 539 (100), 480 (10), 479 (39), 364 (23). Anal. calc. for $C_{31}H_{34}O_{12}$ (598.61): C 62.20, H 5.73; found: C 62.15, H 5.85.

Hexamethyl (1RS,2RS,5RS,8RS)-12-Isopropyl-6,13-dimethyltetracyclo[6.2.2.2^{2,5}0^{1,5}]tetradeca-3,6,9,11,13-pentaene-2,3,4,9,10,14-hexacarboxylate ('*anti*'-**33**). Colourless needles from Et_2O/hexane. M.p. 161.2–162.4°. R_f: see **32**. UV (MeCN): λ_{max} 246 (sh, 3.77), 189 (4.44). IR ($CHCl_3$): 3021*m*, 2954*m*, 1725*s*, 1622*m*, 1437*s*, 1258*m*, 1155*w*, 1086*w*, 1023*w*, 950*w*. ^{1}H-NMR (300 MHz; $CDCl_3/C_6D_6$; C*H*Cl_3 at 7.260; C_6D_5H at 7.159): 6.215/6.667 (*t*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me$_2$C*H*) ≈ 1.3/1.5, H–C(11)); 6.199/6.135 (*dq*, ^3J(H,H–C(8)) = 8.8/8.77, H–C(7)); 3.805, 3.778, 3.776, 3.765, 3.714/3.827, 3.664, 3.550, 3.367, 3.280 (5*s*[1:1:1:2:1/1:1:1:1:2], 6 MeOCO); 3.648/3.800 (*dd*, ^3J(H,H–C(7)) = 8.7/8.82, ^4J(H,H–C(11)) = 1.9/1.96, H–C(8)); 2.379/2.177 (*sept.d*, *J* = 6.7/6.4, Me$_2$C*H*); 1.925/1.903 (*s*, Me–C(13)); 1.669/1.538 (*d*, ^4J(Me,H–C(7)) = 1.4/1.36, Me–C(6)); 1.034,1.013/0.975, 0.931 (2*d*, *J* = 6.7/6.7, *Me*$_2$CH). ^{1}H-NOE (400 MHz; $CDCl_3$): 0.95 (*Me*$_2$CH)→6.667 (*s*, H–C(11)), 6.135 (*w*, H–C(7)), 3.800 (*s*, H–C(8)), 2.177 (*s*, Me$_2$C*H*); 1.538 (Me–C(6))→6.135 (*s*, H–C(7)), 3.367 (*m*, MeOCO–C(4)), 1.903 (*s*, Me–C(13)); 1.903 (Me–C(13))→3.827, 3.550 (*m*, MeOCO–C(10,14)), 1.538 (*s*, Me–C(6)). MS: 599 (100, [*M* + 1]$^+$), 584 (58), 568 (30), 567 (100), 552 (11), 539 (83), 535 (10). Anal. calc. for $C_{31}H_{34}O_{12}$ (598.61): C 62.20, H 5.73; found: C 62.28, H 5.81.

Hexamethyl (1RS,2RS,5SR,8SR)-9-Isopropyl-11,13-dimethyltetracyclo[6.2.2.2^{2,5}0^{1,5}]tetradeca-3,6,9,11,13-pentaene-2,3,4,6,7,14-hexacarboxylate ('*anti*'-**34**). Enriched in the mother liquors of the crystallization of **32**. ^{1}H-NMR (300 MHz; $CDCl_3/C_6D_6$; C*H*Cl_3 at 7.260/C_6D_5H at 7.159; in a mixture with 43% of **32**): 6.259/6.161 (*dq*, ^3J(H,H–C(8)) = 7.00/7.05, ^4J(H,Me–C(11)) = 1.65/1.60, H–C(10)); 6.117/6.553 (*t*-like, ^4J(H,H–C(8)) ≈ ^4J(H,Me$_2$C*H*), H–C(10)); 3.830, 3.818, 3.814, 3.786, 3.672, 3.610/3.530, 3.512, 3.460, 3.447, 3.346, 3.142 (6*s*, 6 MeOCO); 3.401/3.511 (*dd*, ^3J(H,H–C(12)) = 7.00/7.0, ^4J(H,H–C(10)) = 1.80/2.0, H–C(8)); 2.37/2.322 (*sept. d*, Me$_2$C*H*); 1.886/2.128 (*d*, ^4J(Me,H–C(12)) = 1.62/1.52, Me–C(11)); 1.824/1.923 (*s*, Me–C(13)); 0.997/1.056 and 1.047 (*d*/2*d*, *J* = 6.76, 6.84, *Me*$_2$CH). ^{1}H-NOE (400 MHz; C_6D_6): 1.923 (Me–C(13))→6.161 (*w*, H–C(12)), 3.530 and 3.142 (*m* and *s*, MeOCO–C(6,14)), 2.128 (*m*, Me–C(11)); 2.128 (Me–C(11))→6.161 (*s*, H–C(12)), 3.346 (*m*, MeOCO–C(2)), 1.923 (*m*, Me–C(13)); 6.553 (H–C(10))→2.322, 1.056/1.047 (*m*, *Me*$_2$C*H*).

3.1.3. *Thermal Reaction of* **7** *with (D$_6$)ADM.* Azulene **7** (0.0305 g; 0.154 mmol) and (D$_6$)ADM (0.065 g; 0.439 mmol; prepared from the corresponding di-acid and CD_3OD by *Fischer*'s method) were heated in decalin (0.7 ml) at 200° for 1.25 h. Workup as described in *3.1.2* yielded the starting azulene (0.0151 g; 49.5%) and fractions containing mainly a 4:1 mixture (D$_6$)-**22**/(D$_6$)-**23** as well as a mixture (46%, 45%, and 9%, resp.) of (D$_{12}$)-**32**, (D$_{12}$)-'*anti*'-**33**, (D$_{12}$)-'*anti*'-**34**.

Recovered **7**: ^{1}H-NMR (300 MHz) indicated no incorporation of (D$_6$)ADM (2*s*, 2 MeOCO).

*Mixture (4:1) (D$_6$)-***22**/*(D$_6$)-***23**: ^{1}H-NMR (300 MHz; $CDCl_3/C_6D_6$): Ester signals of (D$_6$)-**22**: 3.941/3.635 (*s*, MeOCO–C(3)), 3.773/3.460 (*s*, MeOCO–C(2)); ester signals of (D$_6$)-**23**: 3.831/3.502 (*s*, MeOCO–C(3)), 3.787/3.422 (*s*, MeOCO–C(2)); all the signals were the same as for **22** and **23**.

*Mixture (46:45:9) (D$_{12}$)-***32**/'anti'-*(D$_{12}$)-***33**/'anti'-*(D$_{12}$)-***34**: ^{1}H-NMR (300 MHz; $CDCl_3/C_6D_6$): Ester signals of (D$_{12}$)-**32**: 3.774/3.360 (*s*, MeOCO–C(14)), 3.752/3.304 (*s*, MeOCO–C(13)); ester signals of '*anti*'-(D$_{12}$)-**33**: 3.806/3.827 (*s*, MeOCO–C(14)), 3.779/3.664 (*s*, MeOCO–C(2)); ester signals of '*anti*'-(D$_{12}$)-**34**: 3.819/3.530 (*s*, MeOCO–C(14)), 3.786/3.346 (*s*, MeOCO–C(2)). No change in the other signals.

3.1.4. *Thermal Reaction of a 3:2 Mixture* **7**/**8**. The mixture of azulenes (*cf. 2*; 0.022 g; 0.069 mmol) and ADM (0.056 g; 0.39 mmol) was heated in decalin (0.6 ml) at 180° for 0.75 h. Workup as described yielded the recovered mixture of azulenes (0.015 g; 68%) and a fraction containing the 4:1 mixture **22**/**23**. HPLC analysis of the mixture **7**/**8** indicated the presence of 64.5% of the first and 35.5% of the second one. The ^{1}H-NMR (300 MHz) data of the mixture **22**/**23** were identical with those described in *3*.

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[17]) Sum of ^3J and ^4J.

3.1.5. *Heating of the 4:1 Mixture* **22**/**23** *in the Presence of* (D_6)*ADM*. The mixture (0.032 g; 0.070 mmol) and (D_6)ADM (0.110 g; 0.743 mmol) were heated in decalin (1.0 ml) at 200° for 6 h. Prep. TLC on silica gel (Et_2O/hexane 9:1) yielded the fraction of the starting mixture together with some not identifiable material and the fraction of the tetracyclic compounds **32**, '*anti*'-**33**, and '*anti*'-**34**. Both fractions were rechromatographed (silica gel; hexane/AcOEt 1:1) and then subjected to prep. HPLC (hexane/(CH_2Cl_2 + 0.5% MeOH) 3:1) to yield fractions from which **32** (0.005 g) and '*anti*'-**33** (0.0039 g) crystallized in pure form. The mother liquor of **32** contained the third tetracyclus, *i.e.* '*anti*'-**34**. The tricyclic compounds **22** and **23** (0.009 g) were recovered as a 4:1 mixture. The ^{1}H-NMR (400 MHz; $CDCl_3$) of this mixture showed the typical *s* for the ester Me groups at 3.941, 3.744, 3.730, and 3.614 in **22**, and at 3.839, 3.795, 3.741, and 3.688 in **23** in the expected ratios, *i.e.* neither **22** nor **23** indicated an incorporation of [$^2H_3$]COOC groups. The ^{1}H-NMR (400 MHz; $CDCl_3$) of **32** showed the complete lack of the *s* for MeOCO–C(3,4), whereas the other 4*s* (3.774, 3.751, 3.738, and 3.660) were present in a ratio of 1:1:1:1. Similarly, '*anti*'-**33** showed no signals for MeOCO–C(3,4). On the other hand, the *s* for MeOCO–C(2,9,10,14) were present (ratio 1:1:1:1) at 3.827, 3.665, 3.552, and 3.282. No change in all the other signals of **32** and '*anti*'-**33** was observed. The mother liquor of **32** showed in the ^{1}H-NMR (300 MHz; $CDCl_3$) the presence of 38% of '*anti*'-**34** with ester Me signals at 3.833, 3.817, 3.789, and 3.613 in a ratio of 1:1:1:1, *i.e.* the signals for MeOCO–C(3,4) at 3.821 and 3.675[18]) were completely missing.

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[18]) δ corrected by 0.003 ppm (*cf.* ^{1}H-NMR data of '*anti*'-**34**).