43. Some Unusual Products from the Thermal Reaction of Azulenes with Dimethyl Acetylenedicarboxylate

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The thermal reaction of azulene-1-carbaldehydes **5** and **6** with excess dimethyl acetylenedicarboxylate (ADM) in decalin leads mainly to the formation of (1 + 1) and (1 + 2) adducts arising from the addition of ADM at the seven-membered ring of the azulenes (*cf. Schemes 2* and *4*). The (1 + 2) adducts are formed in a homo-*Diels-Alder* reaction of ADM and isomeric tricyclic carbaldehydes which are derived from the primary tricyclic carbaldehydes by reversible [1*s*,5*s*]-C shifts (*cf. Schemes 3* and *5*). The thus formed pentacyclic carbaldehydes seem to undergo deep-seated skeletal rearrangements (*cf. Scheme 7*) which result finally in the formation of the formyl-tetrahydrocyclopenta[*bc*]acenaphthylene-tetraesters **12** and **19**, respectively. In other cases, *e.g.*, azulene-1-carbaldehydes **7** and **8** (*cf. Scheme 8*), the thermal reaction with excess ADM furnishes only the already known tetracyclic (1 + 2) adducts of type '*anti*'-**26** to '*anti*'-**29**. The thermal reaction of 1,3,4,8-tetramethylazulene (**9**) with excess ADM in decalin resulted in the formation of two (1 + 2) and one (1 + 3) adduct in low yields (*cf. Scheme 9*). The latter turned out to be the 2,6-bridged barrelene derivative **32**. There are structural evidences that **32** is formed by similar pathways as the formyl-tetrahydrocyclopenta[*bc*]acenaphthylene-tetraesters (*cf. Schemes 7* and *11*). [$^2H_3$]Me-Labelling experiments are in agreement with the proposed mechanisms (*cf. Scheme 13*).

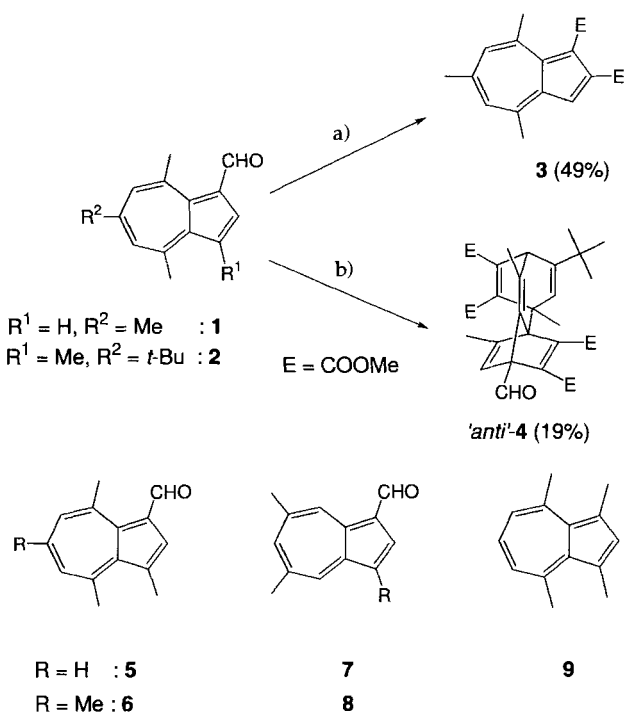
1. Introduction. – Four years ago, we reported that the thermal reaction of azulenes with dimethyl acetylenedicarboxylate (ADM) leads not only to the addition of ADM at the five-membered ring of the azulenes but also at the seven-membered ring [1]. Both reactions can be regarded as *Diels-Alder*-type additions controlled by the HOMO and SHOMO, respectively, of the azulenes. The thermal reaction at the seven-membered ring of the azulenes, which occurs irreversibly under the applied conditions, is strongly favored in cases where the reaction at the five-membered ring is highly reversible, or where the five-membered ring carries π-acceptor substituents such as the CHO or MeOCO group at C(1) or C(3) [1–3]. Since we observed already in our earlier work [2] [4] that the additional substituents at the azulene core have also a great influence on the thermal addition of ADM at the seven-membered ring, we varied the position of Me substituents at the seven-membered ring systematically. We now report on the results of this work. As we will see, the yields of the new products are altogether low, since most of the azulenes reacted to highly polar, intractable materials. However, the elucidated structures of the (1 + 1) to (1 + 3) adducts cast some light on unprecedented combined reactivities of strained molecules.

2. Thermal Reactions of Azulenes in the Presence of Excess of Dimethyl Acetylenedicarboxylate. – 2.1. *Reactions with Azulene-1-carbaldehydes.* Since we already observed

[1]) Part of the Ph. D. thesis of *A. M.*, University of Zurich, 1996.

that neither 4,6,8-trimethyl- nor 6-(*tert*-butyl)-3,4,8-trimethylazulene-1-carbaldehyde (**1** and **2**, resp.) gave, in the thermal reaction with ADM, products that could be derived from the addition of ADM at the seven-membered ring of the reactants (*cf. Scheme 1*), we included in our studies the azulene-1-carbaldehydes **5**–**8** (*Scheme 2*) in order to look specifically into the influence of the substituent at C(6) – one of the bonding termini of the primary adduct formation at the seven-membered ring. For comparison, the tetramethylazulene **9** was also involved in our investigations.

Scheme 1



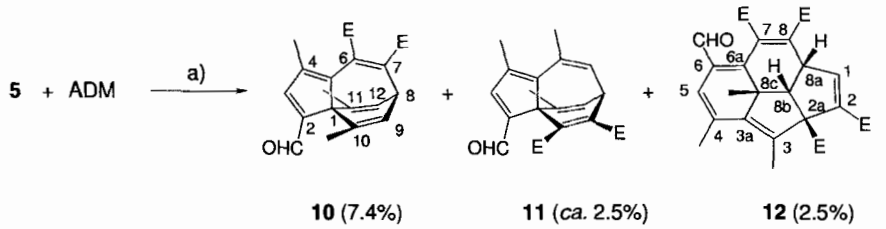
a) Carbaldehyde **1** was reacted with 4,5 mol-equiv. of ADM at 200°/3.5 h; recovery of 18% of **1** [2]. b) Carbaldehyde **2** was reacted with 4.4 mol-equiv. of ADM at 200°/2.5 h; recovery of 38% of **2** [2].

The synthesis of carbaldehydes **6** to **8** has already been described (*cf.* [1] [4] [5]). Azulene **9** and carbaldehyde **5** were synthesized by the usual formylation/reduction procedures (*cf.* [1]) starting with 4,8-dimethylazulene [5].

The thermal reaction of carbaldehyde **5** with a 3.5 mol-equiv. of ADM in decalin led to the formation of three new yellow-colored formyl-esters **10**–**12** (*Scheme 2*). The compounds **10** and **12** could be separated by column chromatography on silica gel (hexane/Et_2O 2:3), then further purified by preparative HPLC and finally crystallized from Et_2O. The third carbaldehyde **11**, which is structurally related to **10**, could only be characterized by its ^{1}H-NMR spectrum in the mixture with **10**.

The C_s-symmetric structure of **10** was clearly indicated by its ^{1}H-NMR spectrum ($CDCl_3$) which showed for the three Me groups only two signals (*s* and *d*) in the ratio

Scheme 2



10 (7.4%) **11** (*ca.* 2.5%) **12** (2.5%)

a) A 0.2M solution of **5** in decalin was heated in the presence of 3.5 mol-equiv. of ADM at 180°/1.5 h. Carbaldehyde **11** could not be isolated in pure form, since it isomerized slowly at room temperature to yield a thermal 3:1 equilibrium mixture **10**/**11**. The other yields refer to pure material.

of 1:2 at 2.04 and 1.39 ppm, respectively. The signal for H–C(9) and H–C(12) in enantiotopic position appeared as *dd* at 6.03 ppm with ^3J(H–C(9,12),H–C(8)) = 6.8 Hz and ^4J(H–C(9,12), Me–C(10,11)) = 1.2 Hz. The observed chemical shifts, especially the high-field shift for Me–C(10,11), and the coupling constants are typical for this type of structure (*cf.* [1–4]). To secure the NMR-derived structure as model for all tricyclic carbaldehydes of this type, we performed an X-ray crystal-structure analysis of **10** (*Fig. 1*). It clearly documents, on one hand, the almost perfect s-*cis*- and s-*trans*-conformation of the C=O group of the ester function at C(7) and the CHO group at C(2), respectively, *i.e.*, at the two termini of the incorporated hexa-1,3,5-triene substructure. The MeOCO group at C(6), which is only in cross-conjugation with the triene system, is turned by exactly 90° out of conjugation in the crystals. On the other hand, the almost ideal s-*trans*-conformation of the CHO group at C(2) shows that the two trajectories of this group for a nucleophilic attack are interrupted by the two spheres of the Me groups at C(10) and C(11). Indeed, all attempts to reduce the CHO group in such types of tricyclic carbaldehydes, without affecting other parts of these molecules, have failed so far. This is also true for addition reaction with other nucleophiles. The only reaction that could be performed easily was the decarbonylation reaction with the *Wilkinson* catalyst (*cf.* [2]).

The structure of the other formyl-ester **11** that slowly isomerized thermally into **10** and *vice versa* was only deduced from its ^{1}H-NMR spectrum ($CDCl_3$). It indicated the presence of three different olefinic H-atoms in a ratio of 1:1:1. The one at lowest field

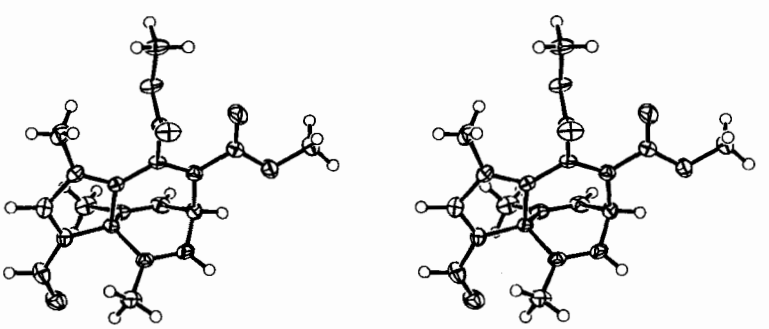
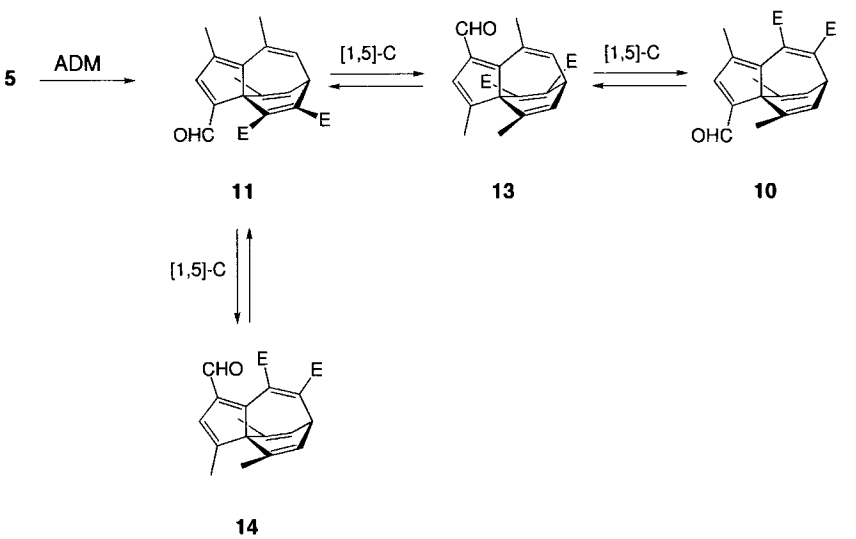


Fig. 1. *Stereoscopic view of the X-ray crystal structure of the tricyclic formyl-diester* **10**

(7.41 ppm) appeared as the sharp *s* and had to be assigned to H–C(3). The signals of the two other olefinic H-atoms occurred as *dq* at 6.20 and 6.06 ppm, respectively. The coupling constants of the two *d* amounted to 8.5 and 6.7 Hz, respectively. The signal with $^3J = 8.5$ Hz had to be assigned to H–C(7) which shares with H–C(8) a rigid torsion angle of 0°, whereas H–C(12) and H–C(8) form a rigid torsion angle of *ca.* 19°[2]) in accordance with the reduced ^3J value of 6.7 Hz. The structure of **11** is also reflected in the signals of three different Me groups which are found at 2.32 ppm (sharp *s*), 2.05 as well as 1.52 ppm (both as *d* with $^4J = 1.2$ and 1.3 Hz, resp.). The fact that the signals of H–C(3) and the Me group at the five-membered ring appear both as sharp *s* permits only placing the Me group at C(4) and, as a consequence, the CHO group at C(2), because the reverse situation (*cf.* **13** in *Scheme 3*) would result in a ^4J coupling between H–C(3) and the adjacent Me group.

Scheme 3



The thermal interconversion of **10** and **11** requires the presence of at least one further tricyclic formyl-diester **13** which carries its Me group at the five-membered ring at C(2). It might also be that the tricyclic formyl-diester **14** as the last possible structure takes also part in the thermal equilibrium.

The structure of the formyl-tetraester **12** was without precedence, and the spectroscopic data of **12** (see later) did not allow an unequivocal establishment of its structure. Therefore, the structure of **12** was solved by an X-ray crystal-diffraction analysis (*Fig. 2*).

The analysis revealed the presence of a tetrahydrocyclopenta[*bc*]acenaphthylene core which carried all the substituents at the sp^3-centers in *cis*-relation leading to a bowl-like

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[2]) This torsion angle is taken from the X-ray crystal structure of the analogous dimethyl 2-formyl-7-isopropyl-4,11-dimethyltricyclo[6.2.2.$0^{1,5}$]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate whose synthesis we have already described [2] (see *Exper. Part, Footnote 7*).

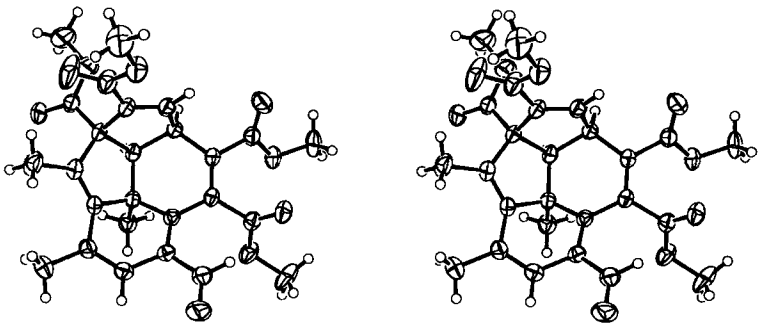


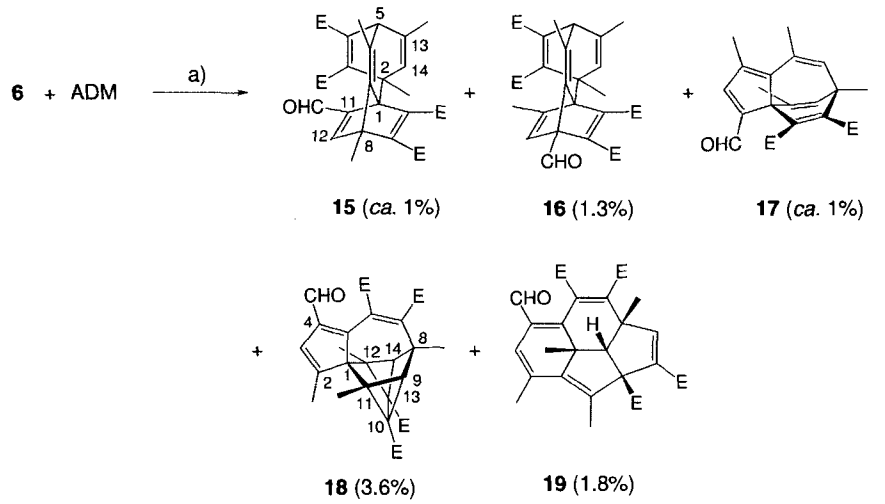
Fig. 2. *Stereoscopic view of the X-ray crystal structure of the formyl-cyclopenta[*bc*]acenaphthylene-tetracarboxylate* **12**

arrangement of the C-skeleton. The four contiguous C=C bonds are only moderately twisted to each other as indicated by θ(C(3)–C(3a)–C(4)–C(5)) = – 138.6(3)°, θ(C(4)–C(5)–C(6)–C(6a)) = – 19.1(4)°, and θ(C(6)–C(6a)–C(7)–C(8)) = 157.3(2)°, which may account for the intense yellow color of **12** in the crystals as well as in solution. The Me group at C(8c) is well placed in the middle of the surrounding octatetraene substructure. This explains its appearance as a sharp *s* at 1.29 ppm in the ^{1}H-NMR spectrum ($CDCl_3$), *i.e.*, its signal is shifted to high field due to the shielding effect of the π-system. The two adjacent H-atoms at C(8a) and C(8b) are clearly differentiated by their chemical shifts (4.04 and 2.98 ppm, resp.) and the additional coupling constant of H–C(8a) which couples weakly (^3J = 2.2 Hz) with H–C(1), whereas H–C(8a) and H–C(8b) couple with ^3J = 8.7 Hz. The signal of H–C(1) turns up at 6.56 ppm as *d*(^3J = 2.1 Hz) and that of H–C(5) appears as a broad *s* at 6.34 ppm, since the ^4J coupling with Me–C(4) is small, being also evident from the comparable broad *s* of this group at 2.22 ppm. The chemical shift of the H-atom of the CHO group (9.59 ppm) is in agreement with the conjugation of the aldehyde function with the extended π-system.

The thermal reaction of the carbaldehyde **6** with ADM in decalin gave, in comparison to **5**, a more complex reaction mixture (*Scheme 4*). The chromatographic workup of the mixture on silica gel (hexane/Et_2O 1:9) gave three fractions. The fractional crystallization of the first chromatographic crop from Et_2O yielded crystals of **18**, followed by crystals of **19** and finally of **16**. The latter carbaldehyde crystallized in fine colorless needles as well as in colorless cubes, whereas **18** was obtained in yellow-orange prisms, and **19** as an intensely yellow crystal powder. From the two other chromatographic fractions, the formyl-esters **15** and **17** were isolated, by preparative HPLC, in small amounts. Both compounds were identified by their characteristic ^{1}H-NMR spectra (*vide supra* as well as [2]). Moreover, **17** is the Me–C(8) analogoue of **11** and displayed, therefore, a similar ^{1}H-NMR spectrum (*cf. Exper. Part*).

The ^{1}H-NMR spectra ($CDCl_3$) of **15** and **16** resembled each other with the difference that **15** showed the signal of the Me group at C(8) as a sharp *s* in contrast to **16** which displaced the signal for the corresponding Me group in the olefinic region at as *d* (^4J(Me–C(11), H–C(12)) = 1.4 Hz). In accordance with this findings appears the

Scheme 4



a) A 0.14M solution of **6** in decalin was treated with 4.5 mol-equiv. of ADM at 180°/2 h. Yields are given for the purified and crystallized materials. Formyl-esters **13** and **15** were only obtained in solution after purification by preparative HPLC.

signal for H–C(12) of **15** as an *s* at 7.66 ppm, *i.e.*, strongly shifted to low field due to the presence of the CHO group in vinylogous position. The isomeric formyl-tetraester **16**, on the other hand, shows the signal for H–C(12) as *q*-like (^4J(H–C(12),Me–C(11)) = 1.4 Hz) at 6.70 ppm. The chemical shift of the H-atom of the CHO group in both isomers (**15**: 9.52 ppm; **16**: 10.05 ppm) is an additional support for the correct assignment of the structure of **15** and **16**.

The structure of **19** was assigned on the basis of its almost identical UV/VIS spectrum as compared with **12**. Also the ^{1}H-NMR spectrum ($CDCl_3$) of **19** resembled very much that of **12**. The signal of H–C(8b) appeared in **19** as a sharp *s* at 2.59 ppm, since the neighboring C(8a)-atom carried now, instead of an H-atom as in **12**, a Me group, the signal of which turned up as an *s* at 1.34 ppm. The Me group at C(8c) is again shielded by the surrounding octatetraene substructure, and, therefore, its signal occurred as an *s* at 1.28 ppm (*cf.* **12**: 1.29 ppm). This *cis*-relation of the substituents at C(8a) to C(8c) was further confirmed by ^{1}H-NOE measurements which gave strong reciprocal effects for the substituents in these positions. Furthermore, irradiation of the signal of Me–C(8a) gave, in addition to the effect on H–C(8b), also an effect on H–C(1), indicating the vicinal relation of these two substituents. The spatial relationship of Me–C(3) and Me–C(4) was also evident from corresponding ^{1}H-NOE measurements (*cf. Exper. Part*).

The ^{1}H-NMR spectrum ($CDCl_3$) of formyl-tetraester **18** disclosed already at a first glance that the structure of this compound must be unusual and new. The integral of the signals of the MeCO groups revealed it to be a (1 + 2) adduct of **6** and ADM. In addition, the signal ratios of the MeOCO and Me groups of 1:1:2 as well as that of the H-atom of the CHO group, one olefinic H-atom (small *q*-like with an allylic coupling of 1.4 Hz with one of the Me groups at 2.10 ppm) at 6.74 ppm, and two equivalent H-atoms,

appearing as a sharp *s* at 1.77 ppm, indicated the presence of a mirror plane in the molecule. The location of the signal of the H-atom of the CHO group at 9.81 ppm implied that the CHO group occupied also an olefinic position. Noteworthy was also the position of the signal of the two equivalent Me groups at 0.70 ppm suggesting that they were linked to a cyclopropane ring and concomitantly placed above a cyclopentadiene subunit. The ^{13}C-NMR spectrum of **18** fully supported this view (see *Exper. Part*). The final resolution of the structure of **18** came from an X-ray crystal-diffraction analysis (*Fig. 3*), disclosing indeed the presence of two three-membered rings in mirror-image position and the rest of the skeletal C-atoms placed in the mirror plane.

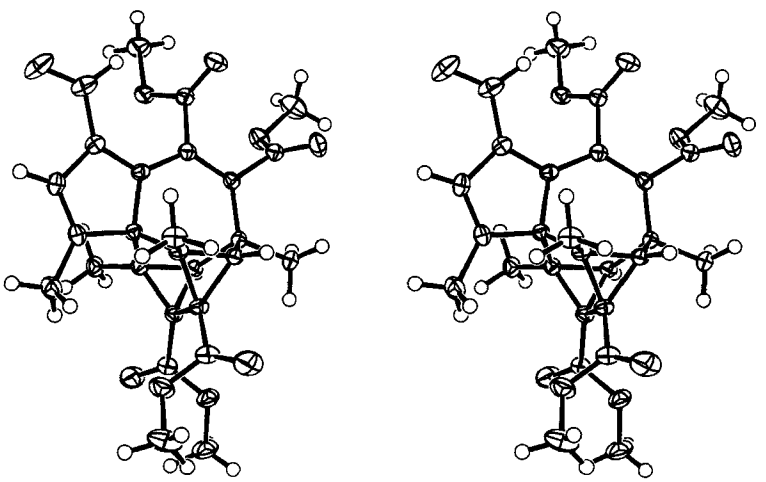


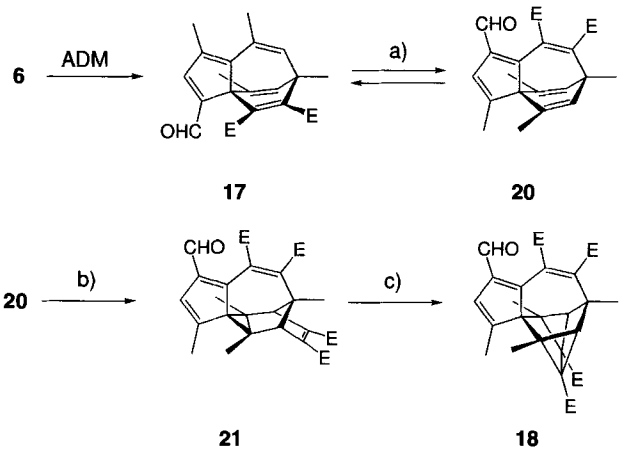
Fig. 3. *Stereoscopic view of the X-ray crystal structure of the pentacyclic formyl-tetraester* **18**

Formation of **18** from a symmetric tricyclic precursor of type **20** and ADM as depicted in *Scheme 5* seems, therefore, reasonable. The presence of **17** in the reaction mixture has already been demonstrated (*Scheme 4*). A reversible [1*s*,5*s*]-C shift will lead to the formation of the C_s-symmetric tricycle **20** which can react thermally with ADM in a homo-*Diels-Alder* reaction to **21**. The thermal rearrangement of the latter will result in the formation of the observed pentacyclic structure of **18**[3]).

The tetrahydrocyclopenta[*bc*]acenaphthylene structure of **12** and **19** evidences that the formation of **12** and **19** must be the result of a deep-seated skeletal rearrangement of the azulene nucleus, since both compounds contain instead of an adjacent five- and seven-membered ring two annelated six-membered rings. In addition, we had found that a compound of type **12**/**19** has also been formed in the thermal reaction of 1,3,4,6,8-pentamethylazulene (**22**) and ADM, beside all other products [1], when we had been repeat-

[3]) Rearrangements of this type are well known from cyclopropanated norbornadienes that are transformed into homoquadricyclane derivatives (*cf.* [6] [7]). In a control experiment the tricycle **10** (*Scheme 2*) was heated with excess ADM in decalin at 180°. The tetrahydrocyclopenta[*bc*]acenaphthylene derivative **12** could unequivocally be identified in the reaction mixture (see *Exper. Part*).

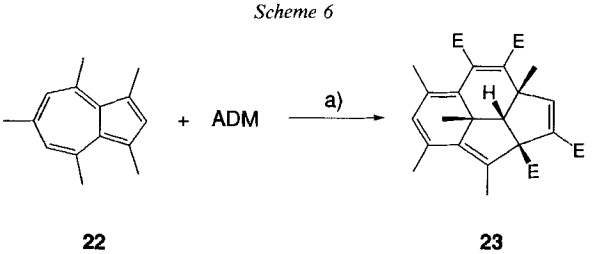
Scheme 5



a) Thermal [1*s*,5*s*]-C shifts. b) Homo-*Diels-Alder* reaction. c) Bicyclo[4.1.0]hex-3-ene → tricyclo[4.1.0.$0^{2,4}$]hexane rearrangement (*cf.* [6]).

ing the original reaction [7] (*Scheme 6*). The structure of **23** had been solved by an X-ray crystal-diffraction analysis [7]. Therefore, it seems that the CHO group in the azulenes **5** and **6** is not responsible for the generation of the tetrahydrocyclopenta[*bc*]-acenaphthylene structure of **12** and **19**, respectively. On the other hand, all three azulenes have in common that they form isolable tricyclic adducts by addition of ADM at the

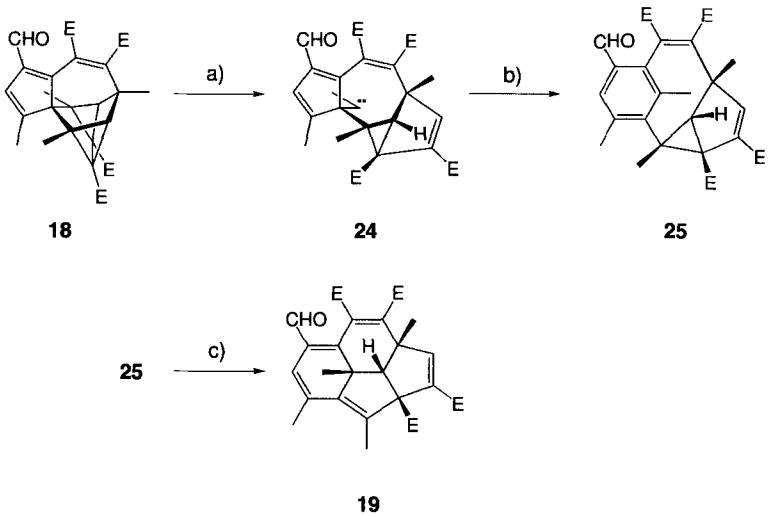
Scheme 6



a) A. 0.5M solution of **22** in decalin was heated in the presence of 4 mol-equiv. of ADM at 200°/2 h. See [1] for all the other formed products; m.p. of **23** 179–181° (Et_2O) [7].

seven-membered ring, and the formation of the pentacyclic bisadduct **18** discloses that the primary adducts of type **17** can rearrange to derived tricycles (*e.g.* **20**) which are able to take up thermally a second ADM molecule in a homo-*Diels-Alder* reaction (*cf. Scheme 5*). If we assume now that strained pentacycles of type **18** can undergo a thermal cheletropic cleavage reaction to a corresponding singlet carbene (*e.g.* **24**) which then endures an aromatic ring-enlargement reaction, we are not far away from the final product **19** (*Scheme 7*). An aromatic vinylcyclopropane → cyclopentene rearrangement of the strained *meta*-bridged intermediate **25** will then result in the formation of the final product **19**. The formation of **12** and **23** can be formulated in the same way.

Scheme 7



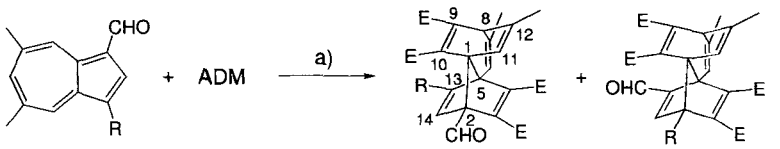
a) Cheletropic ring-cleavage reaction. b) Cyclopentadienylmethylene → benzene rearrangement. c) Cyclopropylbenzene → indene rearrangement.

The generation of singlet carbenes from cyclopropanes is a well-known photochemical process (see, *e.g.*, [8]). Ring-enlargement reactions of cycloalkylmethylenes in the sense of a *Bamford-Stevens* reaction are well established (see, *e.g.*, [9]). Of interest in this connection is the observation that (1-phenylcyclopentyl)methylene leads in 80% yield to the formation of 1-phenylcyclohexene [10]. It seems that the rearrangement of (cyclopentadien-5-yl)methylenes into benzene derivatives has so far not been investigated (see, *e.g.*, [11]). The thermal rearrangement of strained *meta*-bridged **25** into **19** will be an energetically favorable process despite the fact that the benzene nucleus loses its aromatic character. Thermal vinylcyclopropane → cyclopentene rearrangements are well investigated (*e.g.*, [12]); however, their aromatic variants have so far only been observed photochemically (see, *e.g.*, [8]).

The thermal reactions of the carbaldehydes **7** and **8** with ADM did not lead to the formation of product types so far discussed. From both reaction mixtures, we isolated by chromatography on silica gel two tetracyclic compounds of the same type (*Scheme 8*). It has already been demonstrated by us that tetracyclic compounds of the shown type are the result of the thermal addition of ADM at the seven-membered ring, followed by a second thermal addition of ADM at the cyclopentadiene ring of the primary adducts of type **7** *etc.* (*cf.* [1–4]). The '*anti*'-addition mode of ADM in the second step that leads to the '*anti*'-structures shown in *Scheme 8* was established by the X-ray crystal-structure analysis of '*anti*'-**27** and '*anti*'-**28** (*cf. Exper. Part*).

In conclusion, we can state that the primary adducts of azulenes with ADM at the seven-membered ring, as a rule, will react in a second *Diels-Alder* addition with ADM at the five-membered ring to form tetracyclic compounds of type '*anti*'-**26** to '*anti*'-**29**. However, when the second addition step of ADM is impeded on steric grounds (*e.g.*, Me

Scheme 8



R = H : **7** — *'anti'*-**26** (1.3%) — *'anti'*-**27** (8%)

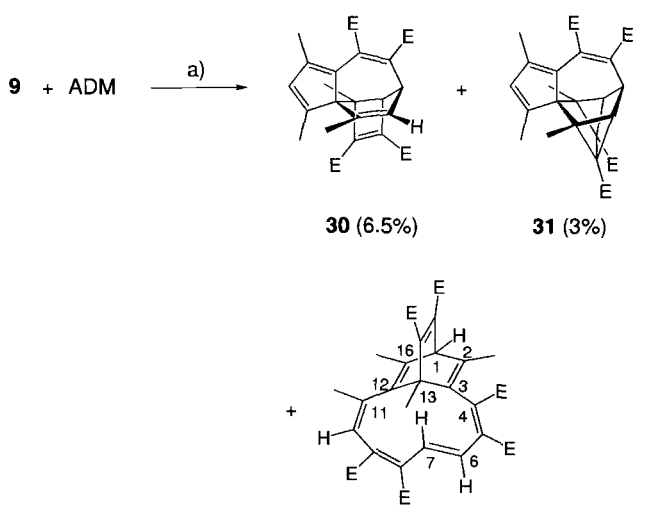
R = Me : **8** — *'anti'*-**28** (23%) — *'anti'*-**29** (2%)

a) R = H: A 0.16M solution of **7** in decalin was heated with 4 mol-equiv. of ADM at 180°/1.5 h; R = Me: a 0.1M solution of **8** in decalin was heated with 4.9 mol-equiv. of ADM at 180°/1.5 h.

groups at C(2) and C(4)) or retarded for electronic reasons (Me and CHO group at C(2) and C(4)), a homo-*Diels-Alder* reaction can occur with ADM at the homo-diene substructure of the homo-barrelene part of the primary adducts. The so formed pentacyclic compounds with two cyclopropane units are then the starting materials for further products, *e.g.*, **12**, **19**, or **23**.

2.1. *Reactions with 1,3,4,8-Tetramethylazulene* (**9**) *and Its 1-([$^2H_3$]Methyl) Isotopomer 1-[$^2H_3$]Me-***9**. To study the thermal behavior of the 6-normethyl analogue of **22**, the azulene **9** was heated in the presence of 4.7 mol-equiv. of ADM in the usual manner (*Scheme 9*). Chromatography of the reaction mixture on silica gel with hexane/Et_2O 1:4 led to three fractions. The first one contained the pure compound **30**, which, after recrystallization from Et_2O, was obtained as a colorless crystal powder. The second

Scheme 9



30 (6.5%) — **31** (3%)

32 (0.6%)

a) A 0.35M solution of **9** in decalin was heated in the presence of 4.7 mol-equiv. of ADM at 180°/2 h. Yields are given for purified and crystallized material.

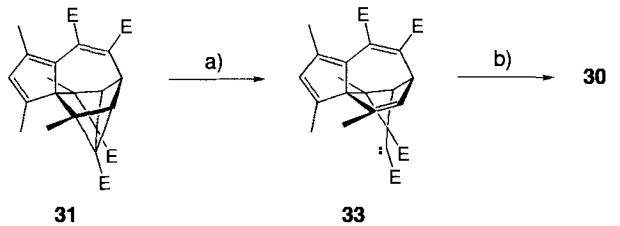
fraction was further purified by preparative HPLC and gave then, after crystallization, colorless irregular prisms of **31**. The third yellow fraction contained the barrelene derivative **32** which crystallized in bright-orange prisms.

The structure of **31** was derived from its ^{1}H-NMR spectrum ($CDCl_3$) which was, according to the average C_s-symmetry of the molecule, quite simple. The H-atom at C(3) appeared as the sole olefinic H-atom as a *q*-like signal at 6.20 ppm. The signal of H–C(8) occurred as a t (^3J = 5.5 Hz) at 4.20 ppm, followed by sharp *s* in a ratio of 1:1:2 of four MeOCO groups. The signals of the four Me groups appeared also in a ratio of 1:1:2 with the *s* for Me–C(11) and Me–C(13) at 0.66 ppm. The d (^3J = 5.5 Hz) for H–C(9) and H–C(12) at 1.84 ppm completed the spectrum. The structure of **31** was finally solved by an X-ray crystal-diffraction analysis (*cf. Exper. Part*).

The assignment of the structure of **30** is based on its ^{1}H- and ^{13}C-NMR spectrum, supplemented by the corresponding COSY and NOESY spectra. The ^{1}H-NMR spectrum ($CDCl_3$) showed clearly that **30** represented a (1 + 2) adduct of **9** and ADM, since it exhibited the signals of four MeOCO groups. It showed further signals of two olefinic and two aliphatic H-atoms. The latter two were coupled to each other with J = 2.1 Hz. On the other hand, one of the olefinic H-atoms was coupled with the H-atom whose signal appeared at comparably low field (4.17 ppm). This means that this H-atom had to be placed in a bis-allylic position. The appearance of two signals of Me groups in the high-field region (*d* at 1.55 and *s* at 1.03 ppm) suggested that one of the Me groups was linked to an sp^2-C-atom and the other one to an sp^3-C-atom, in close vicinity to a shielding subunit such as a cyclopentadiene ring. The presence of a cyclopentadiene ring was indeed indicated by the position and the shape of the signals of the two remaining Me groups. One signal appeared as a *s* at 1.98 ppm (Me–C(4)) and the other one as a d (^4J = 1.3 Hz) at 1.92 ppm (Me–C(2)). The chemical shifts of the four MeOCO groups (3.84 to 3.76 ppm) indicated that all four were fixed at sp^2-C-atoms. The ^{13}C-NMR spectrum of the compound fully supported this view. Moreover, the observed long-range ^{1}H,^{13}C couplings allowed only the assignment of the shown structure of **30**. The last open question was that of the relative position of the cyclobutene ring with respect to the C(6)=C(7) bridge. The ^{1}H-NOESY spectrum of **30** showed that no polarization transfer was observable between H–C(12) and Me–C(13) as well as between H–C(9) and H–C(14). On the other hand, whereas Me–C(13) and Me–C(2) showed a strong polarization effect as it is usually observed in other tricycles with this substructure, there was only a weak ^{1}H-NOE observable between Me–C(12) and Me–C(2), *i.e.*, only the shown '*anti*'-relation of **30** was in agreement with the observed ^{1}H-NOE. It might be that the formation of **30** is the result of a cheletropic cleavage reaction and a subsequent *Bamford-Stevens* rearrangement of the intermediate singlet carbene **33** (*Scheme 10*). This reaction sequence would explain the '*anti*'-position of the cyclobutene substructure of **30** with respect to the C(6)=C(7) bridge. Nevertheless, the radical rearrangement of a corresponding homo-diene adduct of type **21** (*cf. Scheme 5*) could also account for the stereo-structure of **30**.

Compound **32** showed, in comparison to all the other compounds, a completely different and unusual ^{1}H-NMR spectrum ($CDCl_3$). Noteworthy was the presence of 6*s* of 6 non-equivalent MeOCO groups and 4*s* of 4-nonequivalent Me groups which indicated that **32** represented a (1 + 3) adduct of **9** and ADM in agreement with the $M^{+\cdot}$ peak at *m/z* 610 in the MS of **32**. The appearance of an *AB* system with J_{AB} = 16.0 Hz

Scheme 10



a) Cheletropic ring-cleavage reaction. b) Cyclopropylmethylene → cyclobutene rearrangement (*cf.* [9]).

at 6.73 and 5.97 ppm revealed the presence of a *trans*-configured ethylene bond with two H-atoms in a distinctly different chemical surrounding. A third olefinic H-atom occurred as a broad *s* at 6.00 ppm showing a weak allylic coupling with one of the Me groups that appeared as a broad *s* at lowest field (1.95 ppm) of the Me groups. The signal (sharp *s*) of a fourth H-atom at 4.59 ppm was in agreement with the bonding of this H-atom to a C-atom in bis-allylic and possibly bridgehead position. The UV/VIS spectrum (CH_2Cl_2) exhibited two broad absorption bands at 401 (log $\varepsilon = 3.06$) and 316 nm (log $\varepsilon = 3.88$), *i.e.*, they implied the presence of an extended π-system.

The final structure of **32** was then determined by an X-ray crystal-diffraction analysis (*Fig. 4*) which revealed the unusual structure of a 2,6-bridged barrelene derivative.

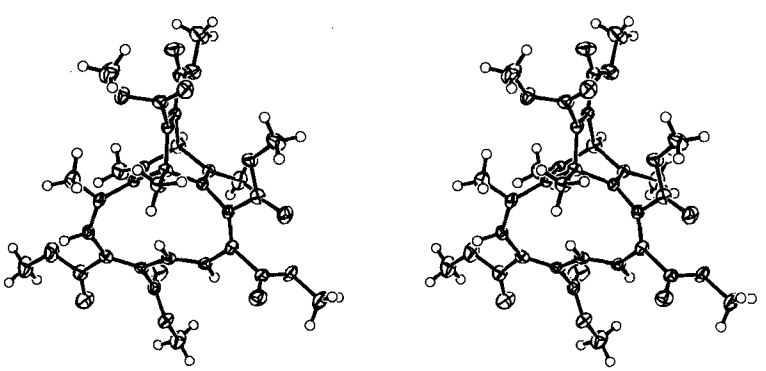
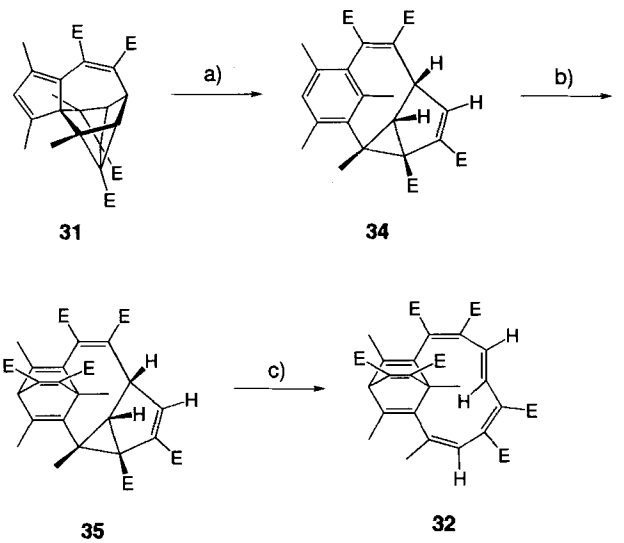


Fig. 4. *Stereoscopic view of the X-ray crystal structure of the barrelene derivative* **32**

The presence of a maleic-ester bridge in the barrelene part of the molecule can be interpreted as the result of an interception of a strained *meta*-bridged benzene derivative **34** by ADM in *Diels-Alder*-type reaction (*Scheme 11*). The precursor molecule **34** corresponds to the postulated intermediate molecules of type **25** in the thermal rearrangement of the pentacycles of type **18** into the tetrahydrocyclopenta[*bc*]acenaphthylenes of type **19** (*cf. Scheme 7*).

The ring opening of the residual bicyclic structure in the '*meta*-bridge' is consistent with a thermal bicyclo[3.1.0]hex-3-ene → hexa-1,3,5-triene rearrangement[4]) that turns obligatorily the H–C bond next to the C=C bond in a *trans*-position with respect to the

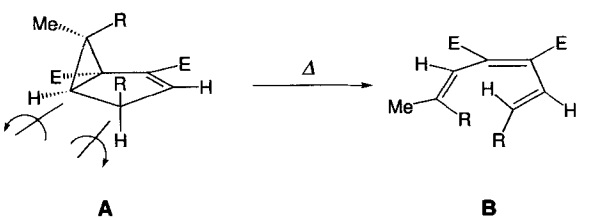
Scheme 11



a) See step a) and b) in *Scheme 8*. b) *Diels-Alder* reaction with ADM. c) Thermal bicyclo[3.1.0]hexene → hexa-1,3,5-triene rearrangement.

olefinic H–C bond, since the conservation of orbital symmetry requires a suprafacial ring opening in the indicated sense (*cf. Scheme 12*). Unfortunately, heating of **31** in the presence of ADM as a control experiment did not lead to detectable amounts of the final product **32**. However, the small amounts of **31** that were available to us did not allow to repeat this control experiment under altered conditions.

Scheme 12[a])



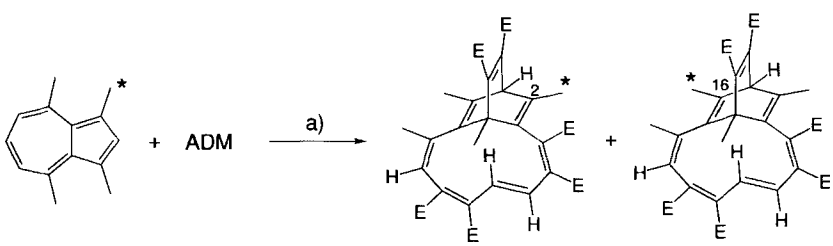
[a]) **A** and **B** partial structures of **35** and **32**, respectively. R = residual cyclic part.

On the other hand, another experiment was successful. The proposed mechanism for the formation of **32** from **9** and ADM *via* **31** places Me–C(1,3) of **9** at C(2) and C(4) in **31**. Since the cyclopentadiene will undergo ring enlargement to the aromatic nucleus of the postulated intermediate **34**, the discussed two Me groups have to appear at C(2)

[4]) The reverse reaction is a well-known photochemical process (see [13] and ref. cit. there) which has also been observed thermally in some cases (*cf.* [14]).

and C(16) in **32** according to the proposed mechanism. This is indeed the case. Heating of 1-[$^2H_3$]Me-**9**[5]) in the described manner with ADM resulted in the formation of the expected isotopomeric 1:1 mixture of 2- and 16-[$^2H_3$]Me-**32** (*Scheme 13*). The position of the [$^2H_3$]Me groups could easily be determined by ^{1}H-NMR spectroscopy. The signals of Me–C(2) and Me–(16) at 1.68 and 1.73 ppm, respectively, showed just half of the integrated intensities of the Me groups at 1.95 (Me–C(11)) and 1.90 ppm (Me–C(13)). All the other signals were unchanged. The assignment of all ^{1}H-signals of **32** are based on corresponding ^{1}H-NOE measurements. Noteworthy is the observation that irradiation of the signal of Me–C(13) at 1.90 ppm caused a strong ^{1}H-NOE only on H–C(7) at 6.73 ppm, *i.e.*, the spatial arrangement of the *trans*-configured C=C bond is in solution just the same as in the crystals or, in other words, there is no easy rotation around the single bonds of the C(6)=C(7) bond that would give rise to a pair of diastereoisomers.

Scheme 13



1-[$^2H_3$]Me-**9** 2-[$^2H_3$]Me-**32** (1:1) 16-[$^2H_3$]Me-**32**

a) The reaction was performed with 7.3 equiv. of ADM in decalin.

We thank Dr. *A. Linden* for the X-ray crystal-structure analyses, Prof. *M. Hesse* and his coworkers for mass spectra, Prof. *W. von Philipsborn* and his coworkers for NMR support and ^{1}H-NOE measurements, and *J. Kessler* for elemental analyses. The financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. All reactions were performed under N_2 or Ar atmosphere (purity > 99.998%) in a *Schlenk* reaction vessel. The solvents were dried over NaH, destilled, and stored under N_2. HPLC: on a *Waters 991* instrument with a photodiode-array detector and a *Bischof HPLC* pump using a *Spherisorb CN* column (ODS 5 μm, length 250 mm, diameter 4.5 mm). Prep. HPLC: on a *Du Pont 830* instrument with a *Spherisorp S5 CN* column (length 250 mm, diameter 20 mm). M.p.: on *Büchi FP5* (heating rate 3°/min). The values are uncorrected. UV/VIS Spectra: on a *Perkin-Elmer Lambda 9*. IR Spectra: on a *Perkin-Elmer FT-IR 1600* spectrophotometer (only bands with > 50% absorbance are reported). ^{1}H- and ^{13}C-NMR spectra: on the *Bruker* spectrometers *AC 300*, *ARX 300*, *AM 400*, and *AMX 600*. Chemical shifts in ppm with respect to TMS (= 0). *J* in Hz. The intensities in COSY and NOE measurements are characterized as: s = strong, w = weak, m = medium. All spectra were taken in $CDCl_3$, with the signal of residual $CHCl_3$ as internal standard (δ = 7.26 ppm). Anal. MS: *Finnigan MAT SSQ 700* spectrometer (EI at 70 eV). All X-ray crystal-structure analyses were performed on a *Rigaku AFC 5R* diffractometer, with graphite monochromated MoK_α (I = 0.71069 Å) and CuK_α (I = 1.54178 Å) radiation.

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[5]) The synthesis of 1-[$^2H_3$]Me-**9** was realized by the *Vilsmeier* reaction of 1,4,8-trimethylazulene with (D_7)DMF followed by the reduction of the [^{2}H]carbaldehyde of **8** with NaB[$^2H_4$]/$BF_3 \cdot OEt_2$.

1. Synthesis of the Azulenes. – Azulene, 4,6,8-trimethylazulene and 5,7-dimethylazulene were prepared as described in [15–17]. 4,8-Dimethylazulene was prepared *via* two consecutive methylation (MeLi) and dehydrogenation steps from azulene [4]. Formylation of the azulenes at C(1) was realized *via Vilsmeier* reactions with $DMF/POCl_3$ [18] [19]. After hydrolysis, the products were extracted with Et_2O and crystallized. Further reduction with $NaBH_4/BF_3 \cdot Et_2O$ led to the corresponding 1-methylazulenes, which were extracted with Et_2O, filtered over a Al_2O_3 column (basic, act. IV) with hexane as mobile phase, and crystallized [1].

3,4,8-Trimethylazulene-1-carbaldehyde (**5**): violett crystals. ^{1}H-NMR (300 MHz): 10.64 (*s*, CHO); 8.16 (*s*, H–C(2)); 7.42 (*t*-like, H–C(6), $^3J = 10.1$); 7.27, 7.25 (2*d*, H–C(5,7), $^3J = 9.8$); 3.13, 3.08, 2.82 (3*s*, 3 Me).

3,4,6,8-Tetramethylazulene-1-carbaldehyde (**6**): see [1].

5,7-Trimethylazulene-1-carbaldehyde (**7**) *and 3,5,7-Trimethylazulene-1-carbaldehyde* (**8**). See [4].

1,3,4,8-Tetramethylazulene (**9**): blue crystals. M.p. 112.0–113.0°. ^{1}H-NMR (300 MHz): 7.33 (*s*, H–C(2)); 7.07 (*t*, $^3J = 10.2$, H–C(6)); 6.65 (*d*, $^3J = 10.9$, H–C(5,7)); 2.98 (*s*, Me–C(4,8)); 2.85 (*s*, Me–C(1,3)).

2. Thermal Reactions of the Azulenes with Dimethyl Acetylendicarboxylate (ADM). – *General.* All reactions were performed in decalin at 180–190° for 1.5–2 h in a *Schlenk* reaction vessel. After heating, decalin and excess ADM were distilled off *in vacuo*.

2.1. *Carbaldehyde* **5**. Compound **5** (0.2 g, 1 mmol) was heated with 0.5 g (3.5 mmol) of ADM in 5 ml of decalin. The mixture was subjected to CC on silica gel with hexane/Et_2O 2:3 and collected in two fractions (R_f 0.16, 0.10). Further purification of the first fraction with prep. HPLC (hexane + 10% i-PrOH, $t_R = 14.5$ min) gave the main product **10** which was crystallized from Et_2O at r.t. The second isomer **11** could only be obtained in a mixture with **10**. Compound **12** could be crystallized from the second fraction from Et_2O at r.t.

Dimethyl 2-Formyl-4,10,11-trimethyltricyclo[6.2.2.0^{1,5}]dodeca-2,4,6,9,11-pentaene-6,7-dicarboxylate (**10**): 25 mg (7.4%). Yellow prisms. M.p. 140.0–142.6°. UV/VIS (CH_2Cl_2): λ_{max} 373 (4.2); λ_{min} 280 (3.4). IR (KBr): 1727, 1711, 1660, 1249, 1218. ^{1}H-NMR (300 MHz): 9.88 (*s*, CHO); 7.38 (*s*, H–C(3)); 6.03 (*dd*, $^3J = 6.77$, $^4J = 1.2$, H–C(9,12)); 4.39 (*t*, $^3J = 6.81$, H–C(8)); 3.77, 3.74 (2*s*, CO_2Me); 2.04 (*s*, Me–C(4)); 1.39 (*d*, $^4J = 1.13$, Me–C(10,11)). ^{13}C-NMR (75 MHz): 186.2 (*d*, CHO); 168.3, 166.4 (*s*, 2 *C*O_2Me); 157.1 (*d*, CH); 155.3, 141.1, 138.7, 132.0, 130.5 (*s*, 5 C(sp^2)); 124.3 (*d*, CH); 68.8 (*s*, C(sp^3)); 52.5, 52.2 (*q*, 2 CO_2*Me*); 38.6 (*d*, CH); 18.2, 14.3 (*q*, 2 Me). EI-MS: 340 (22, M^+); 308 (36); 293 (100). Anal. calc. for $C_{20}H_{20}O_5$ (340.37): C 70.58, H 5.92; found: C 70.93, H 5.00. X-Ray crystal structure of **10**. See *Fig. 1* and the *Table*.

Dimethyl 2-Formyl-4,6,11-trimethyltricyclo[6.2.2.0^{1,5}]dodeca-2,4,6,10,11-pentaene-9,10-dicaboxylate (**11**): ^{1}H-NMR (300 MHz): 9.76 (*s*, CHO); 7.41 (*s*, H–C(3)); 6.20 (*dq*, $^3J = 8.13$, $^4J = 1.36$, H–C(7)); 6.06 (*dq*, $^3J = 8.52$, H–C(12)); 4.24 (*dd*, $^3J = 6.67$, H–C(8)); 3.74, 3.61 (2*s*, CO_2Me); 2.32 (*s*, Me–C(4)); 2.05 (*d*, $^4J = 1.20$, Me–C(6)); 1.52 (*d*, $^4J = 1.21$, Me–C(11)).

*Tetramethyl (2a*RS*,8a*RS*,8b*SR*,8c*RS*)-6-Formyl-2a,8a,8b,8c-tetrahydro-3,4,8c-trimethylcyclopenta[*bc*]-acenaphthylene-2,2a,7,8-tetracarboxylate* (**12**): 12 mg (2.5%). Bright-yellow crystals. M.p. 167.8–176.5°. UV/VIS (CH_2Cl_2): λ_{max} 438 (sh, 3.94), 400 (sh, 5.0), 378 (5.1), 296 (sh, 4.9), 254 (sh, 4.9); λ_{min} 322 (4.6). IR (KBr): 1736, 1723, 1671, 1268, 1205. ^{1}H-NMR (300 MHz): 9.66 (*s*, CHO); 6.56 (*d*, $^3J = 2.08$, H–C(1)); 4.04 (*dd*, $^3J = 8.71$, $^3J = 2.16$, H–C(8a)); 3.85, 3.77, 3.76, 3.72 (4*s*, CO_2Me); 2.98 (*d*, $^3J = 8.71$, H–C(8b)); 2.22, 1.29, 1.05 (3*s*, Me–C(4), Me–C(3), Me–C(8c)). ^{13}C-NMR (75 MHz): 188.1 (*d*, CHO); 172.4, 167.3, 166.1, 162.9 (*s*, 4 *C*O_2Me); 143.7, 141.2 (*s*, 2 C(sp^2)); 140.9 (*d*, CH); 139.1, 136.8, 136.2, 135.8, 134.1, 130.8 (*s*, 6 C(sp^2)); 118.9 (*d*, CH); 73.1 (C(sp^3)); 51.7 (*d*, CH); 51.5, 51.4, 50.8, 50.6 (*q*, 4 CO_2*Me*); 27.0, 19.7, 13.5 (*q*, 3 Me). EI-MS: 482 (39, $M^{+\cdot}$), 450 (28), 435 (27), 375 (100). Anal. calc. for $C_{26}H_{26}O_9$ (482.50): C 64.72, H 5.43; found: C 64.48, H 5.69. X-Ray crystal-structure of **12**; see *Fig. 2* and the *Table*.

2.1.1. *Thermal Reaction of Tricyclic Compound* **10** *with ADM*. Compound **10** (5 mg, 0.015 mmol) and ADM (7 mg, 0.05 mmol) were heated in 1 ml of decalin (1.5 h, 180°). The mixture was analyzed by anal. HPLC (*SC-04* 125 × 4 mm, *Spherisorp CN* 3.0 mm; hexane + 10% i-PrOH). Comparison of the HPLC peaks and their UV of the mixture with that of pure **12** revealed that the peak with t_R 5.65 min of the mixture represented **12**. The main component in the mixture was still the starting material **10**. A third peak with t_R 7.48 min could represent the corresponding pentacyclic carbaldehyde of type **18**, which was not isolated from the original mixture of **5** and ADM.

2.2. *Carbaldehyde* **6**. Compound **6** (0.150 g, 0.70 mmol) and ADM (0.4 g, 2.8 mmol) were heated in 5 ml of decalin. CC of the residue on silica gel (Et_2O/hexane 9:1) gave three fractions (R_f 0.35, 0.27, 0.20). First fraction contained compounds **16**, **18**, and **19**, which could be separated by fractional crystallization from Et_2O at −20°. The last two fractions were combined and purified by prep. HPLC (hexane + 15% i-PrOH) to obtain two further compounds, **15** and **17**, in pure form as oils.

Tetramethyl 8-Formyl-2,6,11,13-tetramethyltetracyclo[6.2.2.2^{2,5}.0^{1,7}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate (**16**): 4 mg (1.3%). In two modifications: colorless needles, m.p. 109°; colorless cubes, m.p.

162.1–164.9°. UV/VIS (CH_2Cl_2): λ_{max} 363(3.7); λ_{min} 309(3.3). IR(KBr): 1722, 1434, 1340, 1319, 1257, 1227. ^{1}H-NMR (300 MHz): 10.05(*s*, CHO); 6.70(*q*-like, ^4J = 1.42, H–C(12)); 5.60(*q*-like, ^4J = 1.41, H–C(14)); 3.81, 3.72, 3.66, 3.64(4*s*, CO_2Me); 3.32(*q*-like, ^4J = 1.47, H–C(5)); 2.02(*d*, ^4J = 1.38, Me); 1.80(*d*, ^4J = 1.1, Me); 1.65(*s*, Me–C(12)); 1.47(*s*, Me–C(8)). ^{13}C-NMR (75 MHz): 195.6(*d*, CHO); 169.2, 168.4, 166.2, 165.2 (*s*, 4 *C*O_2Me); 162.8, 154.3, 146.8, 143.0, 140.4 (*s*, 5(C(sp^2)); 136.7, 129.9(*d*, 2 CH); 129.1, 107.2(*s*, 2 C(sp^2)); 70.2, 66.2(*s*, C(sp^3)); 52.9, 52.8, 52.5, 48.0(*q*, 4 CO_2*Me*); 46.2(*d*, CH); 45.2, 43.2(*s*, 2 C(sp^3)); 21.4, 20.5, 18.3, 14.0 (*q*, 4Me). EI-MS: 496($M^{+\cdot}$, 56), 464(100), 404(44).

Tetramethyl 4-Formyl-2,8,11,12-tetramethylpentacyclo[6.3.3.0^{1,5}.0^{9,11}.0^{10,13}.0^{12,14}]tetradeca-2,4,6-triene-6,7,10,13-tetracarboxylate (**18**): 12 mg (3.6%). Yellow-orange crystals. M.p. 168.0–168.6°. UV/VIS (CH_2Cl_2): λ_{max} 363(4.1), 263(sh, 3.8); λ_{min} 307(4.1). IR (KBr): 1740, 1731, 1672, 1435, 1318, 1245, 1201, 1174. ^{1}H-NMR (300 MHz): 9.81(*s*, CHO); 6.74(*q*, ^4J = 1.82, H–C(3)); 3.82, 3.80, 3.76(3*s*, 1:1:2, CO_2Me); 2.10(*d*, ^4J = 1.42, Me–C(2)); 1.77(*s*, H–C(9,12)); 1.48(*s*, Me–C(8)); 0.70(*s*, Me–C(11,12)). ^{13}C-NMR (75 MHz): 185.2(*d*, CHO); 168.4(*s*, *C*O_2Me); 167.5(*s*, *C*O_2Me); 151.8, 146.5, 142.6, 140.3, 128.3(*s*, 5 C(sp^2)); 126.8(*d*, CH); 72.9, 65.3 (*s*, 2 C(sp^3)); 52.4, 51.9, 51.7(*q*, 3 CO_2*Me*); 47.2(*s*, C(sp^3)); 46.2(*d*, CH); 45.4, 44.4(*s*, 2 C(sp^3)); 23.6, 14.7, 13.2 (*q*, 3 Me). EI-MS: 496(43, $M^{+\cdot}$), 464(100), 432(36), 404(51). Anal. calc. for $C_{27}H_{28}O_9$ (496.51): C 67.49, H 5.87; found: C 67.31, H 6.13. X-Ray crystal structure of **18**: see *Fig. 3* and the *Table*.

Tetramethyl (2aRS,8aRS,8bSR,8cRS)-6-Formyl-2a,8a,8b,8c-tetrahydro-3,4,8a,8c-tetramethylcyclopenta[bc]*acenaphthylene-2,2a,7,8-tetracarboxylate* (**19**): 6 mg (1.8%). Bright-yellow crystals. M.p. 222.0–222.3°. UV/VIS (CH_2Cl_2): λ_{max} 399(3.7), 278(4.1), 244(sh, 4.2); λ_{min} 334(3.2), 265.9(4.1). IR (KBr): 1727, 1673, 1260, 1172. ^{1}H-NMR (300 MHz): 9.52(*s*, CHO); 6.67(*s*, H–C(1)); 6.35(*q*-like, ^4J = 1.1, H–C(5)); 3.86, 3.79, 3.73, 3.71 (4*s*, CO_2Me); 2.59(*s*, H–C(8b)); 2.23(*d*, ^4J = 1.1, Me–C(4)); 2.02, 1.34, 1.28(3*s*, Me–C(3), Me–C(8a), Me–C(8c)). ^{1}H-NOE (400 MHz): 1.28(Me–C(8c)) → 2.59(s, H–C(8b)); 1.34(Me–C(8a)) → 2.59 (s, H–C(8b)); 6.67(s, H–C(1)); 2.02(Me–C(3)) → 2.23(s, Me–C(4)); 2.23(Me–C(4)) → 6.35(s, H–C(5)), 2.02(Me–C(3)); 2.59(H – C(8b)) → 1.28(s, Me → C(8c)), 1.34(s, Me–C(8a)). ^{13}C-NMR (75 MHz): 188.9 (*d*, CHO); 174.2, 167.8, 167.6, 164.1(*s*, 4 *C*O_2Me); 146.6(*d*, CH); 145.3, 143.8, 142.1, 137.1, 136.5, 136.4, 130.5, 129.5 (*s*, 8 C(sp^2)); 119.9(*d*, CH); 74.1, 61.3(*s*, 2 C(sp^3)); 52.7, 52.6, 52.4, 51.8 (*q*, 4 CO_2*Me*); 51.6(*d*, CH); 47.7(*s*, C(sp^3)); 27.9, 25.8, 20.7, 14.7(*q*, 4 Me). EI-MS: 496(62, $M^{+\cdot}$), 449(38), 421(100). Anal. calc. for $C_{27}H_{28}O_9$ (496.51): C 67.49, H 5.87; found: C 67.81, H 5.21.

Tetramethyl 11-Formyl-2,6,8,13-tetramethyltetracyclo[6.2.2.2^{2,5}0^{1,7}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate (**15**): t_R 7.5 min. ^{1}H-NMR (300 MHz): 9.52(*s*, CHO); 7.66(*s*, H–C(12)); 5.67(*q*-like, ^4J = 1.4, H–C(13)); 3.35(*q*-like, ^4J = 2.01, H–C(5)); 3.81, 3.73, 3.71, 3.70(4*s*, CO_2Me); 1.89(*s*, Me); 1.87(*d*, ^4J = 1.29, Me–C(13)); 1.86(*s*, Me); 1.77(*s*, Me).

Dimethyl 2-Formyl-4,6,8,11-tetramethyltricyclo[6.2.2.0^{1,5}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate (**17**): yellow oil. t_R 8.5 min. ^{1}H-NMR (300 MHz): 9.85(*s*, CHO); 7.19(*s*, H–C(3)); 5.6(*q*-like, ^4J = 1.44, H–C(12)); 3.70, 3.48(2*s*, CO_2Me); 5.58(*q*-like, ^4J = 1.42, H–C(7)); 2.26(*s*, Me–C(4)); 1.98(*d*, ^4J = 1.29, Me–C(6)); 1.40(*s*, Me–C(8)); 1.36(*d*, ^4J = 1.38, Me–C(11).

2.3. *Carbaldehyde* **7**. Compound **7** (0.63 g, 0.32 mmol) and ADM (0.184 g, 1.3 mmol) were heated in 2 ml of decalin. The residue was subjected to CC on silica gel (hexane/Et_2O 9:1) and collected in two fractions. The first fraction had to be further purified on HPLC (hexane + 10% i-PrOH) to get *'anti'*-**26** (t_R 17 min), which could be crystallized from Et_2O at –20°. The second fraction contained *'anti'*-**27**, which could be also crystallized from Et_2O at r.t.

Tetramethyl 2-Formyl-7,9-dimethyltetracyclo[6.2.2.2^{2,5}.0^{1,5}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate (*'anti'*-**26**): 2 mg (1.3%). Colorless crystal powder. M.p. 118–119.5°. UV/VIS (MeOH): λ_{max} 250.6(sh, 3.5). IR (KBr): 2360, 1733, 1716, 1684, 1653, 1288. ^{1}H-NMR (300 MHz): 10.05(*s*, CHO); 6.93(*d*, ^3J = 5.1, H–C(14)); 6.47(*d*, ^3J = 5.2, H–C(13)); 6.27(*quint.*-like, ^4J = 1.5, H–C(11)); 5.40(*s*, H–C(6)); 3.71, 3.86, 3.67, 3.61(4*s*, CO_2Me); 3.21(*s*, H–C(8)); 1.93(*d*, ^4J = 1.2, Me); 1.80(*d*, ^4J = 1.3, Me).

Tetramethyl 13-Formyl-7,12-dimethyltetracyclo[6.2.2.2^{2,5}.0^{1,5}]tetradeca-3,4,9,10-pentaene-11,12,13,14-tetracarboxylate (*'anti'*-**27**): 12 mg (8%). Colorless crystals. M.p. 155.7–157.9°. UV/VIS (MeOH): λ_{max} 230.6 (sh, 3.8). IR (KBr): 1721, 1684, 1432, 1314, 1266, 1219, 1112. ^{1}H-NMR (300 MHz): 9.68(*s*, CHO); 7.61 (*d*, ^3J = 3.59, H–C(14)); 5.84(*q*-like, ^4J = 1.49, H–C(6), H–C(11)); 4.52(*d*, ^3J = 3.63, H–C(2)); 3.78, 3.75, 3.74, (3*s*, CO_2Me); 3.32(*t*-like, ^4J = 1.2, H–C(8)); 1.99(*d*, ^4J = 1.2, Me); 1.86(*d*, ^4J = 1.3, Me). ^{13}C-NMR (75 MHz): 185.8(*d*, CHO); 167.3, 165.3, 164.4, 163.2(*s*, 4 *C*O_2Me); 160.2 (*d*, CH); 154.4, 154.3, 147.7, 144.3, 143.2, 141.1, 139.8(*s*, 7 C(sp^2)); 123.6, 115.3(*d*, 2 CH); 89.7, 66.4(*s*, 2 C(sp^3)); 56.6(*d*, CH); 52.3, 52.25, 52.19, 52.13 (*q*, 4 CO_2*Me*); 48.6(*d*, CH); 27.2, 21.0(*q*, 2 Me). X-Ray crystal structure of *'anti'*-**27**: see the *Table*.

2.4. *Carbaldehyde* **8**. Compound **8**(0.203 g, 1.03 mmol) and ADM (0.7 g, 4.9 mmol) were heated in 10 ml of decalin. After the reaction, CC of the mixture on silica gel with Et_2O/hexane 9:1 gave two fractions. The first

fraction yielded compound *'anti'*-**28** as light-yellow crystals after recrystallization from EtOH. The second fraction contained a mixture of both isomers *'anti'*-**28** and *'anti'*-**29**. Further purification with HPLC (hexane + 10% i-PrOH) led to *'anti'*-**29** as a light-yellow crystal powder.

Tetramethyl 2-Formyl-7,12,13-trimethyltetracyclo[6.2.2.2^{2,5}.0^{1,5}]tetradeca-3,6,9,11,13-pentaene-3,4,9,10-tetracarboxylate (*'anti'*-**28**): 110 mg (23%). Light-yellow crystals. M.p. 163.2–165.4°. UV/VIS (MeOH): λ_{max} 249.7(sh, 3.5). IR (KBr): 2911, 1720, 1633, 1614, 1437, 1294, 1270, 1249, 1199, 1065. ^{1}H-NMR (300 MHz): 10.10(*s*, CHO); 6.47(*q*-like, ^4J = 1.87, H–C(14)); 6.23(*quint.*-like, ^4J = 1.43, H–C(11)); 5.29(*quint.*-like, H–C(6)); 3.77; 3.74, 3.75, 3,65(4*s*, CO_2Me); 3.32(*t*-like, H–C(8)); 2.01(*d*, ^4J = 1.0, Me); 1.87(*d*-like, Me); 1.78(*d*, ^4j = 1.74, Me). ^{13}C-NMR (75 MHz): 194.7(*d*, CHO); 166.2, 164.1, 162.9, 161.9(*s*, 4 CO_2Me); 151.8, 151.1, 145.8, 144.2, 141.7, 139.9, 138.9(*s*, 7 C(sp^2)); 129.2, 121.9, 113.1(*d*, 3 CH); 88.9, 71.8, 65.9(*s*, 3 C(sp^3)); 50.6, 50.4, 50.3, 50.1(4 *q*, CO_2*Me*); 46.6(*d*, CH); 25.4, 19.4, 13.1(3*q*, Me). EI-MS: 482($M^{+\cdot}$ not visible), 451([M – OMe], < 10); 423([M – CO_2Me], 100). Anal. calc. for $C_{26}H_{26}O_9 \cdot 0.5\,H_2O$ (491.49): C 63.54, H 5.54; found: C 63.45, H 5.64. X-Ray crystal structure of *'anti'*-**28**: see the *Table*.

Tetramethyl 13-Formyl,2,7,12-trimethyltetracyclo[6.2.2.2^{2,5}.0^{1,5}]tetradeca-3,6,9,11,13-pentaen-3,4,9,10-tetracarboxylate (*'anti'*-**29**): IR (KBr): 1727, 1712, 16.02, 1580, 1430, 1323. ^{1}H-NMR (300 MHz): 9.68(*s*, CHO); 7.43(*s*, H–C(14)); 6.02(*s*, H–C(11)), 5.81(*q*-like, ^4J = 1.25, H–C(6)); 3.81, 3.73, 3.72, 3.65(4*s*, CO_2Me); 3.42 (*s*, H–C(8)); 1.98(*d*, ^4J = 1.1, Me); 1.88(*d*, ^4J = 0.85, Me); 1.69(*s*, Me).

2.5. *Azulene* **9**. A mixture of **9** (0.32 g, 174 mmol) and ADM (1.16 g, 8.2 mmol) was heated at 180° in 5 ml of decalin. CC on silica gel with Et_2O/hexane 4:1 gave three fractions (R_f 0.32, 0.27, 0.20). First fraction contained compound **30** which was obtained from Et_2O as a colorless crystal powder. The second fraction was further purified by HPLC (hexane + 10% i-PrOH, t_R 15 min) to give colorless crystals (Et_2O, r.t.) of **31**. The last fraction yielded orange-colored crystals **32** which were also crystallized from Et_2O at r.t.

*Dimethyl (2*RS,*8*SR,*9*SR,*12*SR*)-2,4,12,13-Tetramethyltetracyclo[6.4.2.0^{1,5}.0^{9,12}]tetradeca-2,4,6,10,13-pentaene-6,7,10,11-tetracarboxylate* (**30**): 55 mg (6.5%). Colorless crystal powder. M.p. 171.1–172.7°. UV/VIS (CH_2Cl_2): λ_{max} 361.1(4.2); λ_{min} 280.9(3.1). IR (KBr): 1734, 1718, 1705, 1640, 1435, 1251. ^{1}H-NMR (300 MHz): 6.17(*q*-like, ^4J = 1.46, H–C(3)); 5.68(*dd*, ^3J = 7.05, ^4J = 0.6, H–C(14)); 4.18(*dd*, ^3J = 7.65, ^4J = 2.3, H–C(8)); 3.84, 3.80, 3.77, 3.76(4*s*, CO_2Me); 2.64(*d*, ^4J = 2.05, H–C(9)); 1.98(*s*, Me–C(4)); 1.92(*d*, ^4J = 1.27, Me–C(2)); 1.55(*d*, ^4J = 1.55, Me–C(13)); 1.03(*s*, Me–C(12)). COSY (^{1}H,^{1}H, 300 MHz): 1.03(Me–C(12) → 2.64 (w, H–C(9)); 1.55(Me–C(13)) → 5.68(s, H–C(14)); 1.92(Me–C(2)) → 6.17(s, H–C(3)); 1.98(Me–C(4)) → 6.17(s, H–C(3)); 2.64(H–C(9)) → 4.18(s, H–C(8)); 2.64(H–C(9)) → 5.68(s, H–C(14)). NOESY (300 MHz): 1.03(Me–C(12)) → 1.92(w, Me–C(2)), 2.64(s, H–C(9)), 6.17(w, H–C(3)); 1.55(Me–C(13)) → 1.92 (s, Me–C(2)), 5.68(s, H–C(14)); 1.92(Me–C(2)) → 1.03(w, Me–C(12)), 1.55(s, Me–C(13)), 3.77(s, MeO), 6.17(s, H–C(3)); 1.98(Me) → 3.80(s, MeO), 6.17(s, H–C(3)); 2.64(H–C(9)) → 1.03(s, Me–C(12)), 4.18 (s, H–C(8)); 4.18(H–C(8)) → 2.64(s, H–C(9)), 5.68(s, H–C(14)). COSY (^{1}H,^{13}C, 150 MHz): 6.17(H–C(3)) → 138.6(C(3)); 5.68(H–C(14))119.9(C(14)); 4.18(H–C(8)) → 35.8(C(8)); 2.64(H–C(9)) → 46.9(C(9)). ^{13}C-NMR (150 MHz): 169.5, 166.9, 164.5, 161.3(*s*, 4 CO_2Me); 155.7(C(4)); 149.5(C(11)); 146.8(C(2)); 138.6(*d*, *C*(3)); 136.7(C(10)); 136.4 C(5)); 136.3(C(7)); 132.6(C(13)); 123.9(C(6)); 119.9(*d*, C(14)), 69.9(*s*, C(12)); 52.4, 52.2, 51.9, 51.8(*q*, 4 CO_2*Me*); 51.3(*s*, C(1)); 46.9(*d*, C(9)); 35.8(*d*, C(8)); 19.8, 16.8, 16.1, 14.7(*q*, 4 Me). EI-MS: 468(96, $M^{+\cdot}$), 241(100). Anal. calc. for $C_{26}H_{28}O_8$ (468.18): C 66.64, H 6.03; found C 65.87, H 5.80.

Tetramethyl 2,4,11,12-Tetramethylpentacyclo[6.3.3.0^{1,5}.0^{9,11}.0^{10,13}.0^{12,14}]tetradeca-2,4,6-triene-6,7,10,13-tetracarboxylate (**31**): 25 mg (3%). Colorless crystals. M.p. 137.2–150.1°. UV/VIS (CH_2Cl_2): λ_{max} 355.9(4.4) λ_{min} 288.8(3.3). IR (KBr): 1727, 1701, 1547, 1432, 1317, 1285, 1252, 1283, 1137. ^{1}H-NMR (400 MHz): 6.20(*q*-like, ^4J = 1.48, H–C(3)); 4.20(*t*, ^3J = 5.48, H–C(8)); 3.88, 3.75, 3.73(3*s*, CO_2Me); 2.07(*s*, Me–C(4)); 2.06 (*d*, ^4J = 1.24, Me–C(2)); 1.84(*d*, ^3J = 5.47, H–C(9,14)); 0.66(*s*, Me–C(11,12)). ^{13}C-NMR (75 MHz): 170.7 (*s*, 2 CO_2Me); 170.5(*s*, CO_2Me); 168.2(*s*, CO_2Me); 155.9, 147.9, 139.9(*s*, 3 C(sp^2)); 137.2(*d*, CH); 133.1, 124.1 (*s*, 2 C(sp^2)); 72.2(*s*, C(sp^3)), 53.2, 52.1, 52.8(*q*, 3 CO_2Me); 47.0, 44.5(*s*, 2 C(sp^3)); 40.7, 39.3(*d*, 2 CH); 15.7, 15.1(*q*, 2 Me); 14.5(*q*, 2 Me). CI-MS (NH_3): 469.5(100, $M^{+\cdot}$), 437.5(14). X-Ray crystal structure of **31**: see the *Table*.

*Hexamethyl (4*Z,*6*E,*8*Z,*10*Z*)-2,11,13,16-Tetramethyltricyclo[10.3.1.0^{3,13}]hexadeca-2,4,6,8,10,12(16),14-heptaene-4,5,8,9,14,15-hexacarboxylate* (**32**): 9 mg (0.6%). Orange-colored crystals. M.p. 193.2–193.4°. UV/VIS (CH_2Cl_2): λ_{max} 400.5(3.1), 316(3.9), 236.6(4.2), 261.7(sh, 4.1); λ_{min} 290.1(3.8). IR (KBr): 1721, 1434, 1315, 1247, 1209, 1114. ^{1}H-NMR (300 MHz): 6.73(*d*, ^3J = 16.0, H–C(7)); 6.00(*s*, H–C(10)); 5.97(*d*, ^3J = 16.1, H–C(6)); 4.59(*s*, H–C(1)); 3.84, 3.83, 3.80, 3.79, 3.75, 3.73(6*s*, CO_2Me); 1.95, 1.90, 1.73, 1.68(4*s*, Me). ^{1}H-NOE (400 MHz): 1.68(Me–C(2)) → 4.59(*s*, H–C(1)), 5.97(w, H–C(6)); 1.73(Me–C(16)) → 4.59(s, H–C(1)); 1.90(Me–C(13)) → 6.73(s, H–C(7)); 1.95(Me–C(11)) → 6.00(s, H–C(10)); 4.59(H–C(1)) → 1.73, 1.68(m, Me–C(16), Me–C(2)); 6.00(H–C(10)) → 1.95(m, Me–C(11)). ^{13}C-NMR (75 MHz): 167.7, 167.4, 166.5, 166.4,

166.2, 163.7(*s*, 6 CO_2Me); 157.9, 144.4, 144.1, 142.9, 142.2, 141.7, 140.4, 1.36.9, 135.1(*s*, 9 C(sp^2)); 132.0(*d*, CH); 130.0(*s*, C(sp^2)); 126.9, 123.7(*d*, 2 CH); 56.9(*d*, CH); 53.2(C(sp^3)); 52.6, 52.5, 52.4, 52.1(*q*, 4 CO_2*Me*); 24.6, 17.8, 17.7, 14.2(*q*, 4 Me). EI-MS: 610(3, $M^{+\cdot}$), 578(100), 577(45), 563(20). Anal. calc. for $C_{32}H_{34}O_{12}$ (610.61): C 62.95, H 5.61; found: C 63.14, H 5.87. X-Ray crystal structure of **32**: see *Fig. 4* and the *Table*.

2.6. *1-[$^2H_3$]Methyl-3,4,8-trimethylazulene* (1-[$^2H_3$]Me-**9**). 2.6.1. The indroduction of the [$^2H_3$]Me into 1,4,8-trimethylazulene was performed in the usual manner *via Vilsmeier* formylation of the azulene with (D_7)DMF in 1,2-dichlorobenzene and subsequent reduction of the [^{2}H]carbaldehyde function with NaB[$^2H_4$]/BF_3 · Et_2O.

1-[$^2H_3$]Me-**9**. The ^{1}H-NMR data were identical with those of **9**. The *s* of Me–C(1,3) at 2.85 showed only half of the intensity compared with the *s* at 2.98(Me–C(4,8)).

2.6.2. *Thermal Reaction.* A mixture of 1-[$^2H_3$]Me-**9** (0.28 g, 1.5 mmol) and ADM (1.04 g, 7.3 mmol) was heated in 5 ml of decalin. Workup and isolation of the products as described in *Sect. 2.5*.

Hexamethyl (4Z,6E,8Z,10Z)-11,13,16-Trimethyl-2-([$^2H_3$]methyl- (2-[$^2H_3$]Me-**32**) *and 2,11,13-Trimethyl-16-([$^2H_3$]methyl)tricyclo[10.3.1.0^{3,13}]hexadeca-2,4,6,8,10,12(16),14-heptaene-4,5,8,9,14,15-hexacarboxylate* (16-[$^2H_3$]Me-**32**): ^{1}H-NMR (300 MHz): 6.75(*d*, ^3J = 15.9, H–C(7)); 6.00(*s*, H–C(10)); 5.97(*d*, ^3J = 16.1, H–C(6)); 4.59(*s*, H–C(1)); 3.84, 3.81, 3.79, 3.74, 3.73(6*s*, CO_2Me); 1.94(*s*, Me–C(11)); 1.91(*s*, Me–C(13)); 1.75, 1.68 (2*s*, Me–C(16,2)). The integration of the latter two signals gave half of the integrals compared with the signals at 1.94 and 1.91. EI-MS: 6.13($M^{+\cdot}$ not visible), 581(100, [M – MeOH]$^+$), 566(60).

Tetramethyl 4,12,13-Trimethyl-2-([$^2H_3$]methyl)- (2-[$^2H_3$]Me-**30**) and *2,12,13-Trimethyl-4-([$^2H_3$]methyl)-tetracyclo[6.4.2.0^{1,5}.0^{9,12}]tetradeca-2,4,6,10,13-pentaene-6,7,10,11-tetracarboxylate* (4-[$^2H_3$]Me-**30**): ^{1}H-NMR (300 MHz): 6.17(*s*, H–C(3)); 5.67(*d*, ^3J = 7.6, H–C(14)); 4.17(*dd*, ^3J = 9.9, ^4J = 2.3, H–C(8)); 3.85, 3.80, 3.77, 3.76(4*s*, CO_2Me); 2.65(*d*, ^4J = 1.9, H–C(9)); 1.98(*s*, Me–C(4)); 1.92(*d*, ^4J = 1.4, Me–C(2)): The integration of the latter two signals gave half of the integrals compared with the signals at 1.50(*d*, ^4J = 1.4, Me–C(13)) and 1.03(*s*, Me–C(12)). EI-MS: 471(100, $M^{+\cdot}$).

Tetramethyl 4,11,12-Trimethyl-2-([$^2H_3$]methyl)- (2-[$^2H_3$]Me-**31**) *and 2,11,12-Trimethyl-4-([$^2H_3$]methyl-pentacyclo[6.3.3.0^{1,5}.0^{9,11}.0^{10,13}.0^{12,14}]tetradeca-2,4,6-triene-6,7,10,14-tetracarboxylate* (4-[$^2H_3$]Me-**31**): ^{1}H-NMR (300 MHz): 6.21(*s*, H–C(3)); 4.20(*t*, ^3J = 5.44, H–C(8)); 3.89, 3.76, 3.74(3*s*, CO_2Me); 2.08, 2.06(2*s*, Me–C(2,4)). The integration of the latter two signals gave half of the integrals compared to the signal at 0.70(*s*, Me–C(11,12)). EI-MS: 471(33, $M^{+\cdot}$), 439(39), 244(99), 243(100).

3. X-Ray Crystal-Structure Determination of 10, 12, 18, *'anti'*-27, *'anti'*-28, 31, and 32[6])[7]). – All measurements were conducted on a *Rigaku AFC5R* diffractometer fitted to a 12-kW rotating anode generator. The intensities were collected using $w/2q$ scans, and three standard reflections, which were measured after every 150 reflections, remained stable throughout each data collection. The intensities were corrected for *Lorentz* and polarization effects, and for **12**, a semi-empirical absorption correction [20] was applied. Each structure was solved by direct methods using SHELXS 86 [21] which revealed the positions of all non-H-atoms. All refinements were carried out on F using full-matrix least-squares procedures which minimized the function $\sum w(|F_o| - |F_c|)^2$, where $1/w = [\sigma^2(F_o) + (pF_o)^2]$. The data collection and refinement parameters for each compound are listed in the *Table*. Neutral atom scattering factors for non-H-atoms were taken from [22a] and the scattering factors for H-atoms from [23]. Anomalous dispersion effects were included in F_c [24]; the values for f' and f'' were taken from [22b]. All calculations were performed using the TEXSAN [25] crystallographic software package and the figures were produced with ORTEPII [26].

For *'anti'*-**28**, the O-atom of the CHO group is disordered with the two orientations about the C(2)–C(15) bond lying *ca.* 180° apart. The site occupation of the disordered atoms was refined and yielded an occupation factor for the major component of *ca.* 0.83. The asymmetric unit also contains two sites partially occupied by H_2O molecules. The occupation factors were set at 0.25, which yielded reasonable thermal parameters for the O-atoms of the H_2O molecules. The non-H-atoms were refined anisotropically, except for the O-atoms of the H_2O

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[6]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-10/36. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (fax: + 44(0)1 223 336033 or email: teched@chemcrys.cam.ac.uk).

[7]) The structure of dimethyl 2-formyl-7-isopropyl-4,11-dimethyltricyclo[6.2.2.0^{1,5}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate has also been determined, but is not reported here. The crystallographic data have been deposited with the CCDC.

Table. *X-Ray Crystal-Structure Data*

	10	**12**	**18**	*'anti'*-**27**	*'anti'*-**28**	**31**	**32**
Crystallized from	Et_2O	Et_2O	Et_2O	Et_2O	Et_2O	Et_2O	Et_2O
Empirical formula	$C_{20}H_{20}O_5$	$C_{26}H_{26}O_9$	$C_{27}H_{28}O_9$	$C_{25}H_{24}O_9$	$C_{26}H_{26}O_9 \cdot \frac{1}{2}H_2O$	$C_{26}H_{28}O_8$	$C_{32}H_{34}O_{12}$
Formula weight	340.37	482.49	496.51	468.46	491.49	468.50	610.61
Crystal color, habit	yellow, prism	bright-yellow, prism	yellow-orange, prism	colorless, prism	colorless, prism	colorless, irregular prism	orange, prism
Crystall dimensions [mm]	0.35 · 0.40 · 0.40	0.10 · 0.20 · 0.34	0.23 · 0.25 · 0.43	0.18 · 0.38 · 0.38	0.25 · 0.35 · 0.40	0.27 · 0.32 · 0.45	0.10 · 0.18 · 0.33
Crystal temp. [K]	173(1)	297(1)	173(1)	173(1)	173(1)	173(1)	173(1)
Radiation	MoK_α	CuK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α
Wavelength [Å]	0.17106	1.54179	0.17106	0.17106	0.17106	0.17106	0.17106
Crystal system	orthorhombic	triclinic	monoclinic	triclinic	monoclinic	triclinic	triclinic
Space group	$Pca2_1$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	4	2	4	2	4	2	2
Reflections for cell determination	25	25	23	25	25	25	19
2θ Range for cell determination [°]	38–40	81–91	37–40	24–26	38–40	39–40	37–39
Unit cell parameters							
a [Å]	13.060(1)	8.4172(5)	10.890(2)	10.591(2)	7.741(2)	11.737(2)	11.225(3)
b [Å]	9.781(1)	17.838(1)	18.839(5)	12.864(3)	17.114(2)	13.572(3)	15.611(4)
c [Å]	13.433(1)	8.150(1)	11.683(2)	8.942(2)	20.142(2)	7.897(1)	9.319(3)
α [°]	90	91.959(8)	90	98.03(2)	90	91.75(2)	93.47(3)
β [°]	90	93.301(9)	91.34(1)	107.34(1)	100.20(1)	103.75(1)	113.02(2)
γ [°]	90	80.975(5)	90	78.25(2)	90	110.86(2)	89.42(2)
V [Å^3]	1715.9(3)	1206.1(2)	2408.8(7)	1134.5(4)	2626.1(8)	1132.5(4)	1500.1(8)
D_x [g cm^{-3}]	1.317	1.328	1.369	1.371	1.243	1.374	1.352
μ [mm^{-1}]	0.0942	0.847	0.103	0.105	0.095	0.102	0.104
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{(max)}$ [°]	60	120	60	55	60	60	46
Total reflections mesasured	3366	3881	7567	5507	8420	6895	4432
Symmetry independent refl.	2603	3596	7023	5223	7651	6601	4180

Table (cont.)

	10	**12**	**18**	*'anti'*-**27**	*'anti'*-**28**	**31**	**32**
Refl. used $[I > 2\sigma(I)]$	2236	2979	4610	3774	5200	4821	2736
Variables	306	342	437	403	434	419	398
Reflection/parameter ratio	7.31	8.71	10.5	9.36	12.0	11.5	6.87
Final R	0.0389	0.0423	0.0486	0.0419	0.0548	0.0455	0.0515
R_w	0.0347	0.0443	0.0422	0.0362	0.0589	0.0397	0.0490
p for $Y_w = \sigma^2(F_o) + (pF_o)^2$	0.005	0.005	0.005	0.005	0.005	0.005	0.0075
Goodness of fit	1.803	2.415	1.643	2.066	2.401	1.907	1.873
Final Δ_{max}/σ	0.0002	0.0003	0.0003	0.0005	0.0003	0.0004	0.0001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.27; −0.19	0.18; −0.16	0.32; −0.20	0.33; −0.19	0.45; −0.41	0.33; −0.23	0.26; −0.23

molecules, which were refined only isotropically. The disordered aldehyde H-atoms were fixed in geometrically calculated positions and were assigned fixed isotropic displacement parameters with a value equal to 1.2 U_{eq} of the parent C-atom. The H-atoms of the H_2O molecules were omitted from the model. All of the other H-atoms were placed in the positions indicated by a difference electron density map and their positions were allowed to refine together with individual isotropic displacement parameters.

For all other compounds, the non-H-atoms were refined anisotropically. For **10**, **18**, *'anti'*-**27**, and **31**, the H-atoms were located in difference-electron-density maps and their positions were refined together with individual isotropic displacement parameters. For **12** and **32**, the H-atoms were fixed in geometrically idealized positions (d(C–H) = 0.95 Å), and for **12** their isotropic displacement parameters were allowed to refine, while for **32** the H-atoms were assigned fixed isotropic displacement parameters with the value equal to 1.2 U_{eq} of the parent C-atom. A correction for secondary extinction was applied for **10** and **32**.

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