Formation of Unusual Products from the Acid-Catalyzed Reaction of Azulenes with Dimethyl Acetylenedicarboxylate

by **Paul Brügger**[1]**, Peter Uebelhart**, **Roland W. Kunz**, **Rolf Sigrist**, and **Hans-Jürgen Hansen***

Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

The reaction of guaiazulene (**4**) and dimethyl acetylenedicarboxylate (ADM) in tetralin or toluene, catalyzed by 5 mol-% of trifluoroacetic acid (TFA) at ambient temperature, leads to the formation of the corresponding heptalene-4,5-dicarboxylate **6** and a guaiazulenyl-substituted 2,2a,4a,8b-tetrahydrocyclopent-[*cd*]azulene derivative **7** beside the expected guaiazulenyl-substituted ethenedicarboxylates (*E*)-**5** and (*Z*)-**5** as main products (*Scheme 2*). The structure of **7** was unequivocally established by an X-ray crystal-structure analysis (*Fig. 1*). Precursor of **7** must be the 2a,4a-dihydrocyclopent[*cd*]azulene-3,4-dicarboxylate **9** which reacts, under TFA catalysis, with a second molecule of **4** (*Scheme 3*). No formation of products of type **7** has been observed in the TFA-catalyzed reaction of 4,6,8-trimethyl- and 1,4,6,8-tetramethylazulene (**13** and **16**, respectively) and ADM (*Scheme 4*). On the other hand, the TFA-catalyzed reaction of azulene (**18**) itself and ADM at ambient temperature gives rise to a whole variety of new products (*Scheme 5*), the major part of which is derived from dimethyl 2a,4a-dihydrocyclopent[*cd*]azulene-3,4-dicarboxylate (**25**) as the main intermediate (*Scheme 6*). Nevertheless, for the formation of the 2a,4a,6,8b-tetrahydrocyclobut[*a*]azulene derivatives (*E*)-**24a** and (*E*)-**24b**, a corresponding 2a,8b-dihydro precursor **29** has to be postulated as crucial intermediate (*Scheme 8*).

Introduction. – It is well-established that the reaction of dialkyl acetylenedicarboxylates (ADR) and azulenes **1**, unsubstituted at C(1) and/or C(3), leads, in the presence of *Brønsted* or *Lewis* acids, to the formation of the corresponding (*E*)- and (*Z*)-configured 1-(azulen-1-yl)ethene-1,2-dicarboxylates **2** [1–3]. It is assumed that an ADR-acid complex attacks electrophilically C(1) or C(3) of the azulenes under generation of a corresponding azulenium ion **3** which then gives rise to the formation of the observed products by prototropic rearrangement (*Scheme 1*). In the present paper as well as in the ensuing publications [4–6], we want to demonstrate that the fate of **3** depends on the reaction medium determining the prototropic mobility of H–C(1) in **3** which is finally reponsible for the formation of **2**.

Results and Discussions. – Already 20 years ago, *Hafner et al.* reported that the reaction of azulene or 4,6,8-trimethylazulene, and dimethyl acetylenedicarboxylate (ADM), in boiling tetralin in the presence of 5% CF_3COOH (TFA), leads to the formation of a 1:1 mixture of the corresponding (*E*)- and (*Z*)-1-(azulen-1-yl)ethene-1,2-dicarboxylates [2]. In the latter case, a small amount of dimethyl 4,6,8-trimethylazulene-1,2-dicarboxylate was also isolated.

In our experiments with guaiazulene (**4**) and ADM, we found that the corresponding ethene-1,2-dicarboxylates, (*E*)- and (*Z*)-**5**, are already formed during

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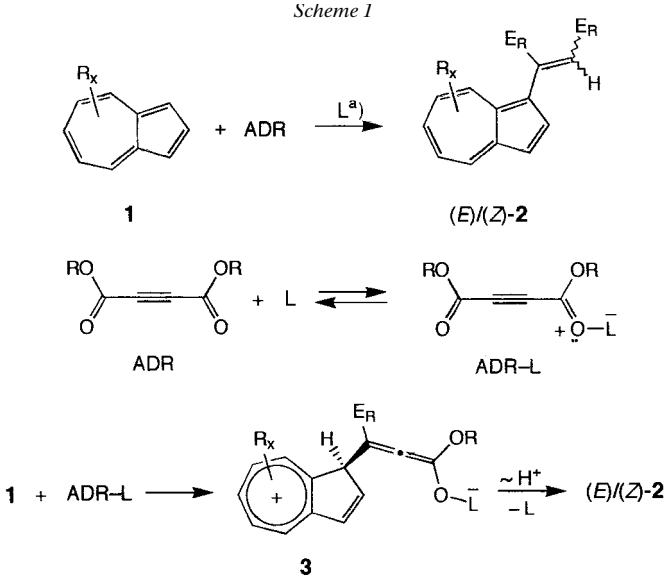
[1] Present address: *Roche Carolina Inc.*, 6173 E. Old Marion Hwy, Florence, SC 29506-9330, USA.

Scheme 1



[a]) L = *Brønsted* or *Lewis* acids.

the chromatography of these reactants on silica gel (see *Exper. Part*). Indeed, stirring **4** and 1.9 mol-equiv. of ADM in hexane at ambient temperature in the presence of silica gel for chromatography led, in a yield of 86%, to (*E*)-**5** and (*Z*)-**5**[2])[3]) in a ratio of 9.8:1. No other products were detected. Further control experiments showed that, quite generally, (*E*)- and (*Z*)-**5** are formed in protic solvents, also in the absence of silica gel. For example, the reaction of **4** and 2 mol-equiv. of ADM in pure MeOH or in $MeOH/CHCl_3$ (2:1, *v*/*v*) gives in >90% yield (*E*)- and (*Z*)-**5** in ratios of 6–7:1 (see *Exper. Part*). These experiments are in keeping with the intervention of a reversibly formed charge-transfer (CT) complex of **4** and ADM. On protonation by the protic solvent or the H_2O layer on silica gel, the CT complex breaks down to an azulenium ion of type **3** as precursor for (*E*)- and (*Z*)-**5**[4]). However, the situation changes when a strong H^+ source such as TFA is present. Catalytic amounts of TFA (*e.g.*, 5 mol-% with respect to ADM), when added to a solution of **4** and ADM, which is kept at ambient temperature for 95 h, induce also the formation of (*E*)- and (*Z*)-**5** (*Scheme 2*). The corresponding heptalene-4,5-dicarboxylate **6** [7] and a blue compound, **7**, representing a [2+1] adduct of **4** and ADM, are also found in the reaction mixture. Since a guaiazulenyl moiety, substituted at C(3), could easily be identified spectroscopically in **7**, we originally assumed that (*E*)- or (*Z*)-**5** had reacted in a [2+2] fashion with the [*b*]-side of **4** (*cf.* [3a])[5]). Similar dipolar addition modes had been observed by *Hafner et*

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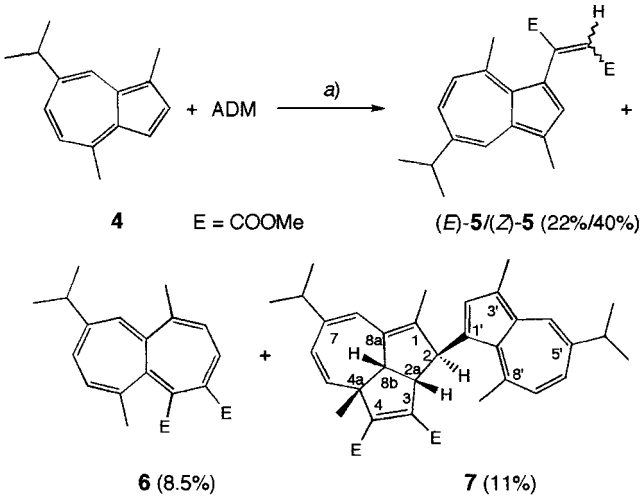
[2]) Without silica gel, no reaction at all takes places. Also irradiation, which has been found to be effective in other cases [1b], does not promote the formation of (*E*)- and (*Z*)-**5**.

[3]) The thermal equilibrium ratio of (*E*)- and (*Z*)-**5** in $CHCl_3$ at room temperature amounts to *ca.* 1.5:1.

[4]) For a more detailed investigation and discussion, see [3b].

[5]) A number of experiments reported here had already been performed 15 years ago [3a].

Scheme 2



a) A 0.5M solution of **4** in tetralin in the presence of 1.1 mol-equiv. of ADM and 4.7 mol-% of TFA with respect to ADM was kept at ambient temperature over 95 h.

al. in the uncatalyzed reaction of cyclopent[*cd*]azulene [8] with ADM at room temperature [9]. However, spectroscopic inconsistencies with the assumed guaiazulen-3-yl-substituted tricyclo[5.5.0.$0^{3,6}$]dodeca-1,7,9,11-tetraene structure prompted us to perform an X-ray crystal-structure analysis of **7** (*Fig. 1*). It revealed that the core structure of **7** represented 2,2a,4a,8b-tetrahydrocyclopent[*cd*]azulene with the guaiazulen-3-yl substituent attached at the *exo*-face of C(2). The structure of **7** clearly reflects its path of formation (*Scheme 3*). After the electrophilic attack of protonated ADM molecules at C(3) of guaiazulene (**4**) to form the corresponding azulenium ion **8**, not only deprotonation at C(3) can occur, which leads finally to (*E*)- and (*Z*)-**5**, but also ring closure by intramolecular attack of C(4) can take place, resulting in the formation of the 2a,4a-dihydrocyclopent[*cd*]azulene intermediate **9**. Protonation of **9** at C(8b) (see below) will form the tricyclic heptatrienylium ion **10**, which then can combine in an electrophilic substitution reaction with **4**, whereby bond formation takes place between the *exo*-face of C(2) of **9** and C(3) of **4**. That the decisive step in the formation of **7** from **4** and ADM under H^+ catalysis is indeed the protonation of **9** at C(8b) can be established. When the reaction of **4** and ADM is run in the presence of catalytic amounts of *O*-deuterated TFA at room temperature, and the reaction is interrupted after 16 h to avoid too much dilution of the ^2H label, it is only C(8b) of **7** that carries partially ^2H-atoms (*Scheme 3*). This fact is evidenced by the ^2H-NMR spectrum (61.4 MHz, C_6D_6) of [8b-^2H]-**7** which shows only the resonance signal of $^2H-C(8b)$ at 3.85 ppm. In the ^1H-NMR spectrum, the signal of H–C(8b) is found at 3.84 ppm as a br. *doublet* of *quintet*s with $^3J(H-C(2a),H-C(8b)) = 5.8$ Hz and further homoallylic couplings with H–C(2) and Me–C(1) of **7** (C_6D_6; see *Exper. Part*).

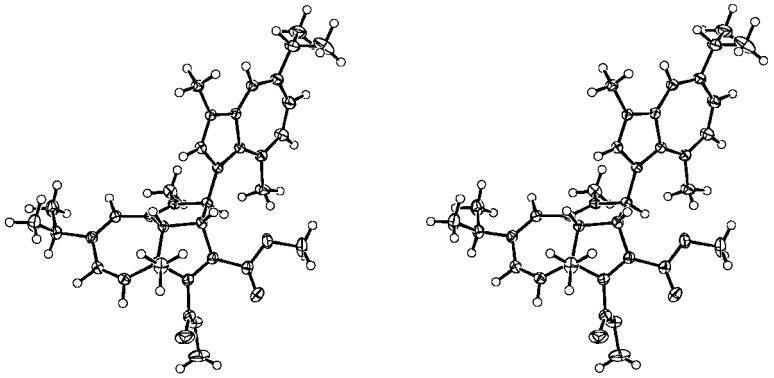
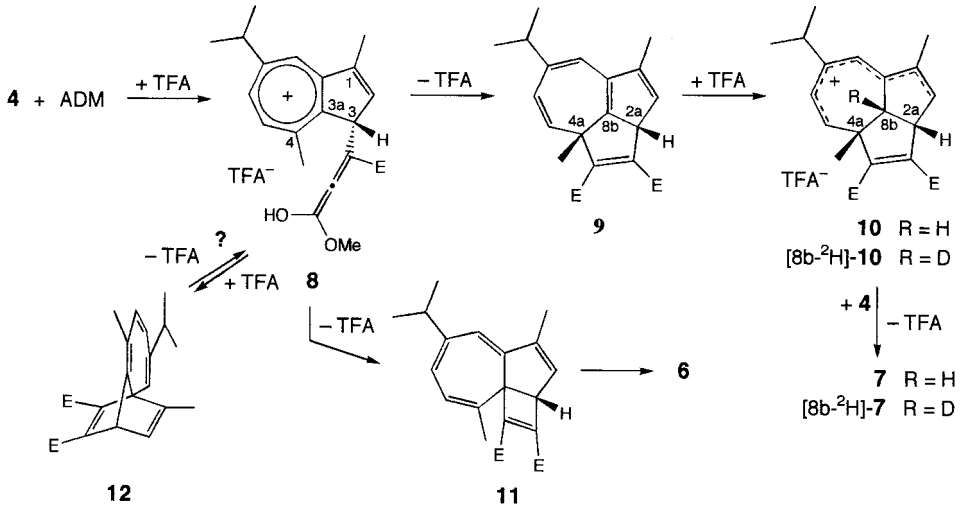


Fig. 1. *Stereoscopic view of the X-ray crystal structure of compound* **7**

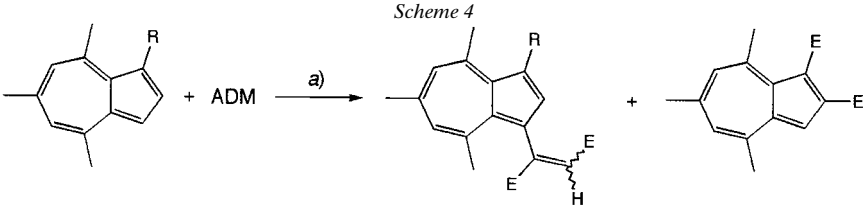
Scheme 3



The formation of a certain amount of the heptalene-4,5-dicarboxylate **6** indicates that obviously also C(3a) of the azulenium ion **8** can attack the ester-enol side chain, thus leading to the tricyclic intermediate **11** which is known to form thermally **6** (*cf.* [10]). It might be that the tricycle **12**, which is the primary intermediate and the precursor of **11** in the purely thermal reaction of **4** and ADM [10], is also formed in the catalyzed reaction by intramolecular electrophilic attack of C(8a) on the ester-enol side chain of **8** (*cf. Scheme 3*). This possibility is indicated at least by the fact that the TFA-catalyzed reaction of 4,6,8-trimethylazulene (**13**) and ADM at room temperature gives, beside the expected (*E*)-**14** and (*Z*)-**14**, also a small amount of dimethyl 4,6,8-trimethylazulene-1,2-dicarboxylate (**15**; *Scheme 4*). All three products had already been observed, as mentioned above, by *Hafner et al.* in boiling tetralin in the presence of 5% TFA. The smooth formation of **15** in our experiment is best explained by a

– possibly TFA-catalyzed – *retro-Diels-Alder* reaction of a tricyclic intermediate analogous to **12** (*Scheme 3*). The TFA-catalyzed reaction of 1,4,6,8-tetramethylazulene (**16**) and ADM at room temperature led only to the formation of (*E*)-**17** and (*Z*)-**17** (*Scheme 4*). In none of the two latter cases, we observed the formation of products of the heptalene type **6** or the tricycle type **7**[6]).

Scheme 4



R = H **13**
R = Me **16**

(*E*)-**14**/(*Z*)-**14** (14%/19%)
(*E*)-**17**/(*Z*)-**17** (22%/11%)

15 (3%)
15 (n.o.)

a) Same conditions as in *Scheme 2*. Azulene **13**, reaction time: 15 d; azulene **16**, reaction time: 9 d. In both cases, azulenes were partly recovered.

Most astonishing was the result of the TFA-catalyzed reaction of azulene (**18**) itself with a 50% molar excess of ADM in diluted tetralin solution at room temperature (*Scheme 5*). The transformation took place very slowly, and, after 14 d, only 25% of **18** had reacted. Nevertheless, the product pattern was very exciting since it comprised a whole number of new types of compounds beside the expected (*E*)- and (*Z*)-isomers of dimethyl 1-(azulen-1-yl)ethene-1,2-dicarboxylate (**19**) which were by far the main components. The structures of the various compounds, established by ^{1}H- and ^{13}C-NMR spectroscopy (see later), clearly revealed that two different acid-catalyzed processes are involved in product formation. The origin of compounds **20** to **23** must be the 2a,4a-dihydrocyclopent[*cd*]azulene-3,4-dicarboxylate **25**, formed from **18** and protonated ADM as already described for **4** and ADM (*Scheme 4*). There are several pathways open for subsequent transformations of **25** (*Scheme 6*). An intramolecular redox process, most probably TFA-catalyzed, leads *via* prototropic shifts to **20**. Compounds of this type have often been found as by-products of the thermal reaction of azulenes and ADM (*cf.* [2][12]) or of the thermal rearrangement of the primary tricyclic intermediates of type **12** in polar solvents (*cf.* [10b]). Thermal reactions of azulenes and ADM may also lead to compounds of type **21** (*cf.* [13]). Their precursors are intermediates of type **25** which react with ADM in a bisvinylogous ene reaction. We assume that this reaction takes place also in a TFA-catalyzed variant between **25** and ADM to give (*Z*)-**21**. A concerted ene process is thereby indicated by the (*Z*)-configuration of the formed ethenyl side chain.

Compounds of type **21** belong to the still rare class of 2a,8b-dihydrocyclopent-[*cd*]azulenes (*cf.* [14]) which had been named 'elassovalenes' by *Paquette et al.* [15] to indicate a lower energy content than expected according to their valence structure[7]).

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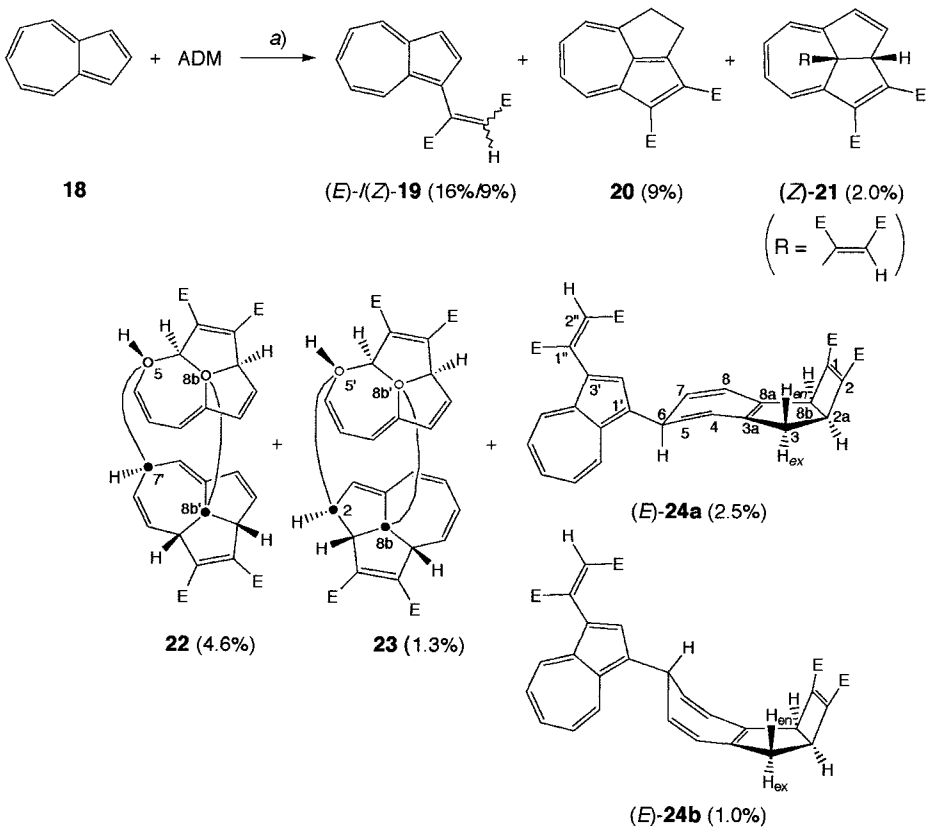
[6]) Compound **7** is also found as a by-product in the [Pd(II)Cl_2(cod)]-catalyzed reaction of **4** and ADM at 50° in MeCN [11].

[7]) For a theoretical treatment of 'elassovalene' and other structures with through-space (homoaromatic) interactions, see [16][17] and literature cited therein.

Scheme 5



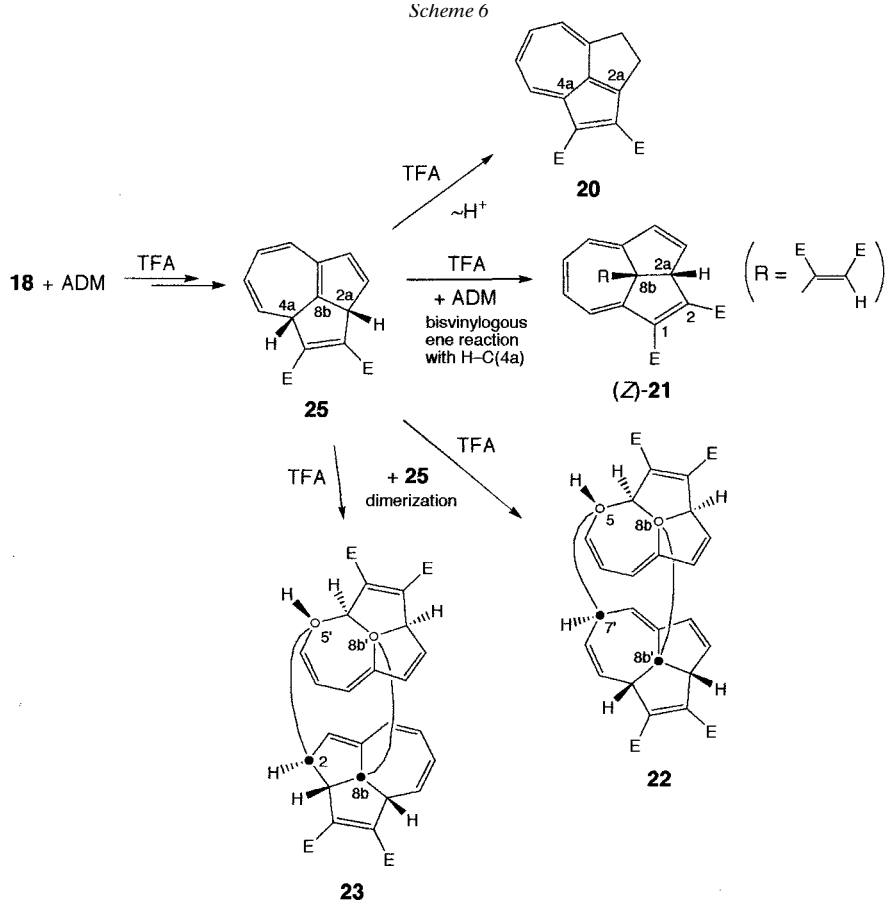
a) A 0.39M solution of **18** in tetralin in the presence of 1.5 mol-equiv. of ADM and *ca.* 5 mol-% of TFA with respect to ADM was kept at ambient temperature over 14 d. Recovery of **18**: 75%.

2a,8b-Dihydrocyclopent[*cd*]azulene itself was synthesized independently by *Paquette et al.* [18] as well as by *Vogel et al.* [19] just 25 years ago (for further syntheses of derivatives, *cf.*, *e.g.*, [20]).

The structure of **22** and **23**, which will be discussed in the context of X-ray crystal-structure analyses of this type of compounds in a forthcoming report [5], indicates, without any doubt, that these unusual (2 + 2) adducts result from a TFA-catalyzed dimerization reaction of **25** (*Scheme 6*).

Since the acid-catalysis experiments with the azulenes **4** or **18** and ADM showed that the formation of 2a,4a-dihydrocyclopent[*cd*]azulene-3,4-dicarboxylates as reactive intermediates determines the product pattern, we studied the behavior of their parent structure **26** under H^+ catalysis in more detail by calculations with the AMPAC program package [21]. The most relevant protonated forms of **26** and their relative ΔH_f values are depicted in *Scheme 7*. As expected, the protonation of C(8b) of **26** leads to the most stable cation **27a**, followed by protonation at C(2) and C(5), resulting in the formation of the tricyclic allyl and pentadienyl cations **27b** and **27c**, respectively. The

Scheme 6

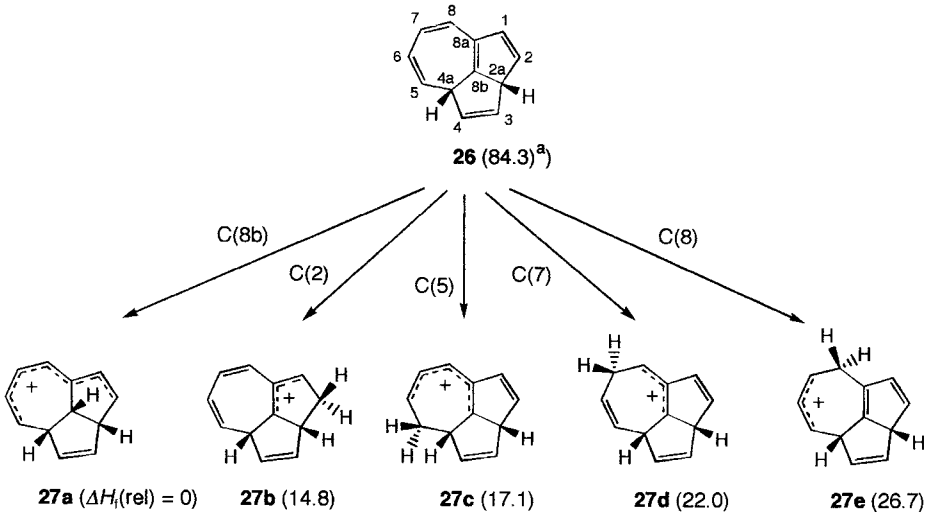


other two possible tricyclic cations, **27d** and **27e**, with allylic stabilization of the charge lie much higher with their relative ΔH_f values. An inspection of the structure of the products, so far discussed, suggests that indeed only protonated forms in analogy to **27a**–**c** play a role in product formation, whereby cations derived from **27a** as the most stable ones control the scene. However, responsible for the formation of the dimers **22** and **23** from **25** (see *Scheme 6*) seem to be the cations of type **27b** and **27c**, respectively. Electrophilic attack of cations of this type on **25** will establish the formation of the central C(8b)–C(8b′) bond of the dimers, since this will give again the most stable cationic forms of type **27a**[8]). The dimeric cations, which are derived from cations of type **27b**, can then produce **22** by bond formation between C(5) and C(7′), followed by

[8]) For the sake of clarity and simplicity, we regard the complex heptacyclic structures **22** and **23** as dimeric structures of dimethyl 2a,4a-dihydrocyclopent[*cd*]azulene-3,4-dicarboxylate (**25**) and indicate the transannular bonding locants in brackets, whereby the higher locants are primed. In this way, **22** is the [5, 7′:8b, 8b′] dimer and **23** the [2, 5′:8b, 8b′] dimer of **25**.

loss of a proton from C(2) (*cf. Scheme 6*). On the other hand, the dimeric cations, which are generated from cations of type **27c**, must be the precursors of **23**, since the second bond formation can take place between C(2) and C(5′), followed by loss of a proton from C(8). We will reconsider these aspects in a more detailed study on the acid-catalyzed formation of (2 + 2) products from azulenes and ADR [5], since there are more questions behind the proposed mechanisms than discussed here.

Scheme 7



a) MM3-Calculated ΔH_f values [kcal mol^{-1}] relative to that of **27a**.

The formation of the pair of diastereoisomers (*E*)-**24a** and (*E*)-**24b** cannot be attributed to the occurrence of the central intermediate **25** which explains the appearance of all other products in the reaction mixture (*Scheme 6*). On the other hand, the structures of (*E*)-**24a** and (*E*)-**24b** have been unambiguously derived from their ^{1}H- and ^{13}C-NMR spectra as well as COSY measurements. Their relative configuration at C(6) follows from ^{1}H-NOESY experiments. The olefinic H-atoms at C(4), C(5), and C(7), C(8) form two independent *ABX* systems with a common X part (H–C(6)) in both diastereoisomers. The 1,2-bis(methoxycarbonyl)ethenyl-substituted azulenyl part must be linked with C(1′) to C(6) of the main body, since strong reciprocal ^{1}H-NOE effects are observed between H–C(8′) and H–C(6) in (*E*)-**24a** as well as between H–C(2′) and H–C(6) in (*E*)-**24b**. Vicinal ^{1}H,^{1}H-coupling constants in the order of 5.1 to 5.5 Hz are observed for H–C(5), H–C(6), and H–C(6), H–C(7), respectivey, for both isomers. They indicate that the cycloheptatrienyl ring adopts a boat-like conformation with the bulky azulenyl moiety at C(6) in a pseudo-equatorial position in both forms. However, this conformational behavior requires an *anti*- or a *syn*-orientation of C(6) of the seven-membered ring with respect to the cyclobuta-anellated five-membered ring in the two molecules. This overall situation has consequences with respect to the relative spatial orientation of the H-atoms at the

parent skeleton of the molecules. *Fig. 2* presents a stereoscopic view of the two MM3-calculated conformations of the parent skeleton which correspond to (*E*)-**24a** with an *anti*-orientation of C(6) with respect to C(1)=C(2) (*Fig. 2*,*a*) and (*E*)-**24b** with a *syn*-orientation of C(6) with respect to C(1)=C(2) (*Fig. 2*,*b*). They possess very similar ΔH_f° values of 86.7 and 87.0 kcal mol^{-1}, respectively. Therefore, it can be expected that a sterically demanding substituent at C(6) will indeed occupy preferentially the pseudo-equatorial position and force the seven-membered ring into the corresponding boat-like conformation according to the configuration at C(6). The relevant structural parameters of the calculated *anti*- and *syn*-conformations are collected in *Table 1*. As expected, the torsion angles are very similar for both conformations in full agreement with the observed vicinal coupling constants for both diastereoisomers, (*E*)-**24a** and (*E*)-**24b** (see also *Exper. Part*). On the other hand, both conformations show significant differences in the H,H distances around the central C(3a)=(8a) bond, and, indeed, the two diastereoisomers, (*E*)-**24a** and (*E*)-**24b**, exhibit corresponding reciprocal intensities between these H-atoms in ^{1}H-NOE experiments. For example, (*E*)-**24a** shows a strong effect between H_{endo}–C(3) ↔ H–C(4) and only weak effects between H_{exo}–C(3) ↔ H–C(4) and H–C(8) ↔ H–C(8b). The reverse is true for (*E*)-**24b** which gives rise to strong effects between H_{exo}–C(3) ↔ H–C(4) and H–C(8) ↔ H–C(8b), but only a weak effect between H_{endo}–C(3) ↔ H–C(4). The signals of H_{exo}–C(3) and H_{endo}–C(3) can be unequivocally assigned according to the observed vicinal coupling constants with H–C(2a), which possesses, due to the rigidity of this part of the molecules, defined torsion angles Θ with H_{exo}–C(3) and H_{endo}–C(3) (*cf. Table 1*). Therefore, the preferred boat-like conformation of the seven-membered ring in (*E*)-**24a** and (*E*)-**24b** determines also the relative configuration at C(6) with respect to those at C(2a) and C(8b). Finally, the configuration at the C(1″)=C(2″) bond follows from the fact that H–C(2″) shows no ^{1}H-NOE effects with the H-atoms at the azulene core of the molecules.

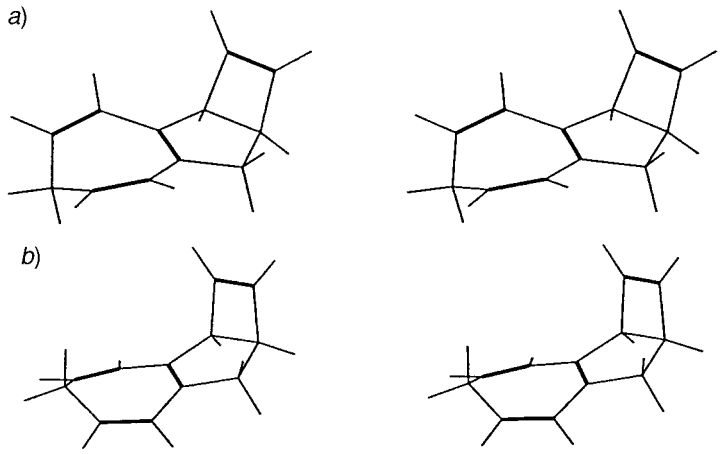


Fig. 2. *MM3-Calculated conformations of the core structure of* (E)-**24a** *and* (E)-**24b** (*cf. Scheme 5*). *a*) *anti*-Conformation. *b*) *syn*-Conformation (the bold lines represent the C=C bonds).

Table 1. *Calculated Interatomic H,H Distances* (*d*) *and H,H Torsion Angles* (Θ) *of the* syn- *and* anti-*Conformation of 2a,3,6,8b-Tetrahydrocyclobut[*a*]azulene*[a])

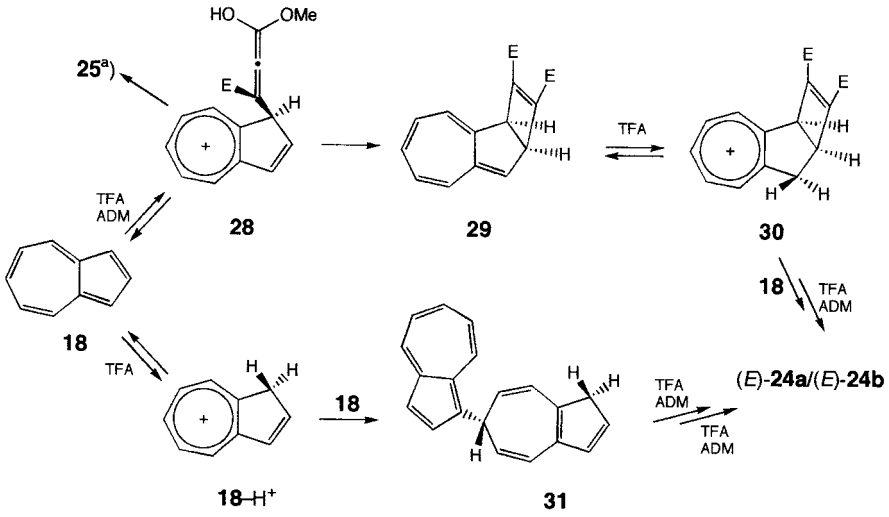
d [pm]	*syn*-Conformation[b])	*anti*-Conformation[c])
$H_{endo}-C(3) \leftrightarrow H-C(4)$	294.1	263.6
$H_{exo}-C(3) \leftrightarrow H-C(4)$	270.4	305.7
$H-C(8) \leftrightarrow H-C(8b)$	267.8	295.9
Θ [°]	*syn*-Conformation[b])	*anti*-Conformation[c])
$H-C(2a)-C(3)-H_{endo}$	107.5	106.8
$H-C(2a)-C(3)-H_{exo}$	– 13.1	– 13.7
$H-C(2a)-C(8b)-H$	4.0	4.3
$H-C(4)-C(5)-H$	1.0	– 0.8
$H-C(5)-C(6)-H_{ax}$	99.4	– 100.7
$H-C(5)-C(6)-H_{eq}$	– 15.5	14.4
$H_{ax}-C(6)-C(7)-H$	– 98.9	101.0
$H_{eq}-C(6)-C(7)-H$	16.0	– 14.1
$H-C(7)-C(8)-H$	– 0.9	0.9

[a]) MM3-Calculated. [b]) See *Fig. 2,b*; $\Delta H_f^\circ = 87.0$ kcal mol^{-1}. [c]) See *Fig. 2,a*; $\Delta H_f^\circ = 86.7$ kcal mol^{-1}.

The structures of (*E*)-**24a** and (*E*)-**24b** suggest two possible pathways for their formation (*Scheme 8*). The azulenium ion **28**, which results from the electrophilic attack of protonated ADM on azulene (**18**), may not only cyclize to give the central tricyclic intermediate **25** (*cf. Scheme 6*), but also, at least to a certain extent (*ca.* 10:1), to yield **29**. Indeed, in the purely thermal reaction of azulenes with ADM in apolar solvents, the formation of heptalene-2,3-dicarboxylates as ring-opening products of postulated intermediates of type **29**, has been observed beside that of heptalene-4,5-dicarboxylates as major products (*cf.* [12][22]; for an X-ray crystal-structure analysis of a heptalene-2,3-dicarboxylate, see [22][23]). At ambient temperature, compounds of type **29**, should be stable (*cf.* [24]). Therefore, protonation of the heptafulvene substructure at C(3) may occur leading to the tropylium ions **30** which, as electrophiles, should react with azulene (**18**) under formation of the C(6)–C(1′) bond, since tropylation of azulenes with the tropylium ion has been realized in several cases (*cf.* [25][26]). The thus produced azulene derivative of **29** may further react with protonated ADM to yield finally (*E*)-**24a** and (*E*)-**24b**. In principle, the tropylium ion **30** could also combine in an electrophilic substitution reaction with already formed (*E*)-**19** to give the mixture (*E*)-**24a**/(*E*)-**24b**. However, it can be argued that the electron-withdrawing properties of the 1,2-bis(methoxycarbonyl)ethenyl substituent at C(1′) deactivates (*E*)-**19** as well as (*Z*)-**19** for an electrophilic attack at C(3′) with the 'smooth' cation **30**. Nevertheless, *Nozoe et al.* [26] reported on the almost quantitative tropylation of azulene-1-carboxylates with ethyl tropyl ether and ditropyl ether, respectively, under acid catalysis. However, it has to be explained why only (*E*)-configured **24** is found in the reaction mixture, whereas acid-catalyzed reactions of

ADM with azulenes always lead to the formation of (*E*)/(*Z*)-mixtures of the corresponding dimethyl ethene-1,2-dicarboxylates, mostly with the (*Z*)-isomer in excess (*cf. Schemes 2* and *4* as well as [3b])[9]).

Scheme 8



[a]) See *Scheme 6*.

We believe that we can exclude the second pathway for the formation of (*E*)-**24a** and (*E*)-**24b** (*Scheme 8*). It would require that the azulenium ions **18**-H$^+$ react in an electrophilic substitution reaction with azulene (**18**) to the biazulene **31**. An acid-catalyzed [2 + 2]-addition reaction of ADM to the C(2)=C(3) bond would lead to the parent skeleton of the final products. The reaction sequence is then terminated by the acid-catalyzed addition of ADM at C(3′) of the azulenyl part of the cyclobuta-anellated intermediate. The last two reaction steps may also take place in the reverse mode. However, the crucial intermediate would be **31**. All our attempts to generate this intermediate by treatment of azulene (**18**) in tetralin at ambient temperature with

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[9]) X-Ray crystal-structure analyses of (*E*)- and (*Z*)-isomers of 1-(azulen-1-yl)-substituted dimethyl ethene-1,2-dicarboxylates show, in most cases studied by us [3b], larger s-*cis* torsion angles for the (*E*)-configured structures as compared to their (*Z*)-counterparts along C(1′)–C(2′) of the azulene and C(1)–C(2) of the ethene part. Moreover, a stronger π-conjugative interaction of the azulenyl substituent and the ethene part in the (*Z*)-isomers is also evidenced in solution by a much stronger broad absorption band around 400 nm of these isomers as compared to the corresponding (*E*)-forms (*cf. Exper. Part* and [3b]). Responsible for these findings is the fact that the (*E*)-isomers bear the bulky azulenyl substituent at C(1) and the MeOCO group at C(2) in *cis*-relation to each other, whereas, in the (*Z*)-isomers, the azulenyl substituent at C(1) is confronted by an H-atom at C(2). As a consequence, the strong π-acceptor effect on the MeOCO-substituted ethene part should be more pronounced in the (*Z*)-isomers than in the (*E*)-forms. The almost exclusive formation of (*E*)-configured **24** may, therefore, be the result of a kinetic differentiation between (*E*)-**19** and (*Z*)-**19** in the electrophilic substitution reaction with the tropylium ion **30**. Unfortunately, the mixture (*E*)-**19**/(*Z*)-**19** (see *Scheme 5*) does not react with tropylium tetrafluoroborate in toluene at ambient temperature to support the hypothesis discussed above. Nevertheless, cations **30** may be stronger electrophiles than tropylium ions themselves.

catalytic amounts of TFA, followed, after a reaction time of up to 14 d, by an excess of ADM, did not lead to the formation of (*E*)-**24a** and/or (*E*)-**24b**. These observations render the lower reaction sequence in *Scheme 8* unlikely.

In conclusion, we can state that the acid-catalyzed reactions of guaiazulene (**4**) and azulene (**18**) with ADM have revealed a new reaction channel of these transformations leading to the formation of 2a,4a-dihydrocyclopent[*cd*]azulene-3,4-dicarboxylates, *e.g.*, **9** and **25**, an interesting class of reactive intermediates which are, in general, not accessible in the purely thermal reactions. They open, under the conditions of acid catalysis, a whole field of new or otherwise difficult-to-synthesize structures.

We are grateful to Dr. *A. Linden* who performed the X-ray crystal-structure analysis. We thank Prof. *M. Hesse* and his co-workers for mass spectra, our NMR department for NMR support and several COSY and NOESY measurements, and Mrs. *J. Kessler* for elemental analyses. The financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. See [10][13][27].

1. Reaction of Guaiazulene (4) with Dimethyl Acetylenedicarboxylate (ADM). – 1.1. *Upon Chromatography on Silica Gel*. A soln. of **4** (25.0 g, 0.126 mol) and ADM (30.0 ml, 0.246 mol) in tetralin (150 ml) was slowly chromatographed on silica gel (1000 g), first with hexane and then with hexane/Et_2O 4:1, which led, after a fore-run of tetralin, to four fractions. The first one contained mainly non-reacted **4** and ADM. The second one, a brown oil (31 g), consisted of residual ADM, which was removed by distillation (40–50°/0.03 Torr), and mainly (*E*)-**5** (8.1 g). Crystallizations from Et_2O/hexane gave black shining crystals (in total 7.3 g) of (*E*)-**5**. The third fraction was a green-brownish oil (2.4 g) and contained a 3:1 mixture of (*E*)- and (*Z*)-**5**. Finally, the forth fraction, obtained as a green oil (2.0 g), was almost pure (*Z*)-**5**, which was additionally purified by prep. TLC (hexane/Et_2O 1:1).

*Dimethyl (*E*)-1-(5-Isopropyl-3,8-dimethylazulen-1-yl)ethene-1,2-dicarboxylate* ((*E*)-**5**). Total yield *ca.* 21%. M.p. 80–81°. R_f (hexane/Et_2O 1:1) 0.59. VIS (hexane): λ_{max} 607 (2.65), 660 (sh, 2.54), 738 (sh, 2.02); λ_{min} 542 (2.52), 776 (1.45). UV (hexane and MeCN, resp.): λ_{max} 244.5/243 (4.43/4.43), 288/289 (4.55/4.56), 306/305 (sh, 4.08/sh, 4.13), 349/347 (3.69/3.71), 367.5/365 (3.47/3.49), 415/418 (very br. 3.52/very br. 3.43); λ_{min} 225/225 (4.28/4.28), 261/260.5 (4.15/4.13), 328/332 (flat 3.66/3.68), 362/361 (3.44/3.46), 376/376 (3.33/3.31). IR (KBr): 1719 (COOR); 1387, 1369 (Me_2CH). IR (CCl_4): 1742 (sh), 1727 (COOR); 1630 (C=C); 1390, 1375 (Me_2CH). ^{1}H-NMR (400 MHz): 8.145 (*d*, *J* = 2.0, H–C(4′)); 7.382 (br. *s*, H–C(2′)); 7.346 (*dd*, *J* = 10.7, 2.0, H–C(6′)); 7.076 (*s*, H–C(2)); 6.946 (*d*, *J* = 10.7, H–C(7′)); 3.748, 3.538 (2*s*, 2 MeOCO); 3.050 (*sept.*, Me_2CH); 2.678, 2.616 (2*s*, Me–(8′), Me–C(3′)); 1.347 (*d*, *J* = 6.9, Me_2CH). ^{13}C-NMR (100.6 MHz): 167.82 (^3J(*Me*OCO) = 3.4, ^3J(C(1)–*C*O,H–C(2)) = 6.2, MeO*C*O–C(1)); 165.76 (^3J(*Me*OCO) ≈ ^2J(C(2)–*C*O, *H*–C(2)) ≈ 3.2, MeO*C*O–C(2)); 139.33 (C(2′)); 124.23 (C(3′)); 119.02 (^2J(*H*–C(2′),C(1′)) ≈ 9, ^3J(*H*–C(2),C(1′)) ≈ 4, C(1′)). EI-MS: 340 (100, $M^{+\bullet}$), 281 (78, $[M - MeOC]^+$). Anal. calc. for $C_{21}H_{23}O_4$ (340.42): C 74.09, H 7.11; found: C 73.76, H 7.23.

*Dimethyl (*Z*)-1-(5-Isopropyl-3,8-dimethylazulen-1-yl)ethene-1,2-dicarboxylate* ((*Z*)-**5**). Total yield *ca.* 4.7%. R_f (hexane/Et_2O 1:1) 0.44. VIS (hexane): λ_{max} 576 (sh, 2.56), 599 (2.60), 650 (sh, 2.50), 723 (2.01); λ_{min} 477 (1.95), 768 (1.19). UV (hexane and MeCN, resp.): λ_{max} 244/242.5 (4.22/4.29), 260/– (sh, 4.08/–), 289/290 (4.35/4.34), 305.5/306 (4.02/sh, 4.04), 325/327 (very br. 3.96/very br. 3.97), 399/407 (br. 3.86/br. 3.89); λ_{min} 266.5/268 (4.04/4.07), 303.5/– (4.01/–), 313/315 (3.95/3.96), 358/359 (3.52/3.53). IR (film): 1736, 1718 (COOR); 1603 (C=C). ^{1}H-NMR (90 MHz): 8.18 (*d*, *J* = 2.0, H–C(4′)); 7.68 (br. *s*, H–C(2′)); 7.46 (*dd*, *J* = 11.0, 2.0, H–C(6′)); 7.12 (*d*, *J* = 11.0, H–C(7′)); 5.68 (*s*, H–C(2)); 3.80, 3.79 (2*s*, 2 MeOCO); 3.08 (*sept.*, Me_2CH); 2.86 (*s*, Me–C(8′)); 2.60 (*s* with f.s., Me–C(3′)); 1.36 (*d*, *J* = 6.9, Me_2CH). ^{13}C-NMR (100.6 MHz): 168.92 (^3J(*Me*OCO) = 3.9, ^3J(C(1)–*C*O,*H*–C(2)) = 11.9, MeO*C*O–C(1)); 165.56 (^3J(*Me*OCO) ≈ 4, ^2J(C(2)–*C*O, *H*–C(2)) = 2.4, MeO*C*O–C(2)); 138.40 (C(2′)); 124.98 (C(3′)); 120.64 (C(1′)). EI-MS: 340 (100, $M^{+\bullet}$).

1.2. *In the Presence of Silica Gel*. Azulene **4** (2.00 g, 10.1 mmol) and ADM (2.4 ml, 19 mmol) were dissolved in hexane (13 ml), and silica gel (0.04–0.063 mm, 4.01 g) was added. The mixture was stirred for 15 h at r.t. The workup (see *1.1*) yielded (*E*)-**5** (2.69 g, 78%) and (*Z*)-**5** (0.27 g, 8%) as the sole products.

1.3. *In MeOH*. Azulene **4** (0.501 g, 252 mmol) and ADM (0.73 g, 5.14 mmol) were dissolved in MeOH (9 ml; *Merck*, *p.a.*, passed over *Alox®B*, act. 1, just before use) and stirred for 21 h at r.t. Workup as before gave

81% of (*E*)-**5** and 12% of (*Z*)-**5** as the sole products. The same reaction (18 h) in a mixture of MeOH (6 ml) and $CHCl_3$ (3 ml) at r.t. gave 80% of (*E*)-**5** and 13% of (*Z*)-**5**.

1.4. *In the Presence of Cat. Amounts of CF_3COOH (TFA)*. Azulene **4** (10.0 g, 50.4 mmol) was dissolved in freshly distilled tetralin (100 ml). ADM (6.8 ml, 55.4 mmol) was added, followed by TFA (0.2 ml, 2.6 mmol; 5 mol-% with respect to ADM). The mixture was kept at r.t. for 95 h. Most of the tetralin was removed by distillation (rot. evap. 60–70°/0.05 Torr). CC (1000 g silica gel; hexane/Et_2O 4:1) of the residue led to the elution of (*E*)-**5** (3.7 g, 22%), a new compound **7** (1.35 g, 11.0%), (*Z*)-**5** (7.0 g, 40%), and, finally, **6** (1.45 g, 8.5%). The latter compound was identified by its mixed m.p. with an authentic sample [7], which showed no depression, and by its spectral data [7].

*Dimethyl (2*R*,*2a*S*,*4a*R*,*8b*S*)-2,2a,4a,8b-Tetrahydro-7-isopropyl-2-(5-isopropyl-3,8-dimethylazulen-1-yl)-1,4a-dimethylcyclopent[*cd*]azulene-3,4-dicarboxylate* (**7**). Blue crystals. M.p. 146–148° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.54. VIS (hexane): λ_{max} 574 (sh, 2.55), 618–622 (br., 2.65), 679 (sh, 2.53), 752 (sh, 2.54); λ_{min} 440 (1.42). UV (hexane): λ_{max} 246 (4.42), 287 (4.57), 293 (sh, 4.56), 308 (4.51), 342 (sh, 3.96), 355 (4.00), 373 (3.94); λ_{min} 229 (4.33), 259 (4.28), 303.5 (4.48), 350 (3.93), 367 (3.79). IR (KBr): 2956, 2932, 2868, 1726 (COOR); 1637 (C=C); 1546, 1517, 1462, 1432, 1375, 1363 (Me_2CH); 1317; 1281; 1265; 1236; 1190; 1153; 1119; 1103; 1055; 1031; 996; 916; 856; 810; 783. ^{1}H-NMR (300 MHz; C_6D_6/$CDCl_3$/C_5D_5N): 8.118/8.060/8.249 (*d*, *J* = 2.1, H–C(4′)); 7.593/7.304/7.726 (br. *s*, H–C(2′)); 7.124/7.272/7.378 (*dd*, *J* = 10.7, 2.1, H–C(6′)); 6.755/6.859/6.986 (*d*, *J* = 10.7, H–C(7′)); 6.366/6.224/6.428 (br. *s*, H–C(8)); 6.214/5.839/6.195 (*d*, *J* = 12.9, H–C(5)); 5.870/5.785/5.973 (*d*, *J* = 12.9, H–C(6)); 5.289/4.940/5.302 (br. *s*, H–C(2)); 3.901/3.695/4.051 (*dd*, *J* = 6.0, 1.2, H–C(2a)); 3.843/3.655/4.020 (br. *dquint.*, H–C(8b)); 3.406/3.801/3.794 (*s*, MeOCO–C(3)); 3.385/3.751/3.770 (*s*, MeOCO–C(4)); 3.050/2.972/3.131 (*s*, Me–C(8′)); 2.536/3.001/2.662 (*s*, Me–C(3′)); 2.793/3.025/2.991 (*sept.*, (i-Pr)–C(5′)); 2.318/2.399/2.420 (*sept.*, (i-Pr)–C(7)); 1.572/1.626/1.66 (br. *s*, Me–C(1)); 1.492/1.429/1.576 (*s*, Me–C(4a)); 1.221/1.347/1.310 (*d*, *J* = 6.9, (i-Pr)–C(5′)); 1.081 and 1.069/1.106 and 1.104/1.115 and 1.099 (2*d*, *J* = 6.8, (i-Pr)–C(7)). ^{1}H-NOE (400 MHz, $CDCl_3$): 1.429 (Me–C(4a)) → 5.839 (*s*, H–C(5)), 3.695 (*m*, H–C(2a)), 3.655 (*m*, H–C(8b)); 1.626 (Me–C(1)) → 7.304 (*w*, H–C(2′)), 6.224 (*s*, H–C(8)), 4.940 (*m*, H–C(2)); 2.972 (Me–C(8′)) → 6.859 (*m*, H–C(7′)), 4.940 (*s*, H–C(2)). ^{13}C-NMR (150.9 MHz, C_6D_6/100.6 MHz, $CDCl_3$): 166.66/166.27 (MeO*C*O–C(4)); 166.01/165.69 (MeO*C*O–C(3)); 150.51/149.46 (C(4)); 145.43/144.65 (C(8′)); 143.81/142.67 (C(1′)); 141.94/141.17 (C(7)); 140.27/139.46 (C(3′a)); 139.93/138.77 (C(5′)); 138.63/138.09 (C(3)); 138.42/137.48 (C(2′)); 136.26/134.90 (C(5)); 134.66/134.24 (C(6′)); 133.82/133.24 (C(4′)); 132.84/131.58 (C(8′a)); 132.18/131.40 (C(8a)); 131.28/130.17 (C(1)); 127.44/126.62 (C(7′)); 126.01/125.21 (C(3′)); 125.95/125.35 (C(6)); 121.99/120.96 (C(8)); 62.32/61.86 (C(8b)); 58.66/57.70 (C(2a)); 56.45/55.38 (C(4a)); 52.48/51.40 (C(2)); 51.845/51.86 (*Me*OCO–C(3)); 51.83/51.86 (*Me*OCO–C(4)); 38.31/37.61 (Me_2CH–C(5′)); 37.89/37.06 (Me_2CH–C(7)); 30.11/29.30 (*Me*–C(4a)); 28.90/28.00 (*Me*–C(8′)); 25.09 and 25.07/24.56 and 24.53 (Me_2CH–C(5′)); 23.06 and 22.55/22.52 and 22.01 (Me_2CH–C(7)); 14.53/14.12 (*Me*′C(1)); 13.65/13.09 (*Me*–C(3′)). EI-MS: 539 (40, $[M+1]^+$·), 538 (100, M^+·), 523 (17), 491 (24), 479 (6), 463 (21), 449 (5), 431 (5), 421 (5), 405 (6), 211 (11), 198 (18), 195 (12), 183 (14), 179 (11), 165 (12). Anal. calc. for $C_{36}H_{42}O_4$ (538.73): C 80.26, H 7.86; found: C 80.15, H 8.10.

1.4.1. *Catalysis with CF_3COO^2H ([^{2}H]TFA) Azulene* **4** (7.40 g, 37.5 mmol), ADM (5.0 ml, 40.8 mmol), and [^{2}H]TFA (0.15 ml, 1.95 ml) were dissolved in toluene (90 ml) under dry N_2. The soln. was kept at ambient temp. for 16 h. The chromatographic workup as described above led to a recovery of **4** (3.00 g, 41%) and a mixture (*E*)-**5**/**7**. Crystallization from hexane removed most of (*E*)-**5**. The mother liquor was rechromatographed, giving, after crystallization from hexane, pure blue crystals of **7** (0.06 g, 0.5%). ^{2}H-NMR (61.4 MHz, C_6D_6; C_6D_6 at 7.160 ppm): 3.85 (br *s*, [^{2}H]–C(8b)). No other ^{2}H signal was recognizable.

2. Reaction of 4,6,8-Trimethylazulene (13) with ADM under TFA Catalysis. – Azulene **13** (2.00 g, 11.8 mmol), ADM (1.6 ml, 12.9 mmol), and TFA (0.06 g) were dissolved in tetralin (30 ml). The mixture was kept for 15 d at ambient temp. CC (300 g of silica gel), first with hexane to remove tetralin and non-reacted **13** and ADM, then with Et_2O, gave a red-brown oil (2.9 g), which was further separated with prep. TLC (hexane/Et_2O 1:1) leading to **15** (0.10 g, 3%), and (*Z*)-**14** (0.70 g, 19%) and (*E*)-**14** (0.50 g, 14%).

Dimethyl 4,6,8-Trimethylazulene-1,2-dicarboxylate (**15**). Violet crystals, R_f (hexane/Et_2O 1:1) 0.38. Identified by comparison with an authentic sample [28].

Dimethyl (Z)-1-(4,6,8-Trimethylazulen-3-yl)ethene-1,2-dicarboxylate ((*Z*)-**14**). Red-brown crystals, m.p. 94–95° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.47. VIS (hexane): λ_{max} 544 (2.73), 584 (sh, 2.64), 640 (sh, 2.17); λ_{min} 452 (2.15), long tailing in the range of 660–730. UV (hexane and MeCN, resp.): λ_{max} 243/243.5 (4.44/4.45), 280/286 (sh, 4.37/sh, 4.45) 291/292 (4.49/4.49), 322/329 (4.18/4.16), 331/– (sh, 4.17/–), 351/353 (sh, 3.91/sh, 3.91), 386/390 (3.87/3.91); λ_{min} 265/255.5 (4.04/4.03), 308/310 (413/4.11), 362/363 (3.74/3.74). IR (KBr): 3006; 2986;

2948; 2841; 1734, 1712 (COOR); 1624 (C=C); 1605; 1577; 1561; 1521; 1498; 1435; 1416; 1394; 1374; 1346; 1331; 1305; 1245; 1297; 1163; 1107; 1077; 1021; 968; 936; 888; 857; 831; 789; 746; 726; 695. ^{1}H-NMR (270 MHz): 7.78 (*d*, *J* = 4.3, H–C(2′)); 7.27 (*d*, *J* = 4.3, H–C(1′)); 7.12 (br. *s*, H–C(5′), H–C(7′)); 5.74 (*s*, H–C(2)); 3.89, 3.78 (2*s*, 2 MeOCO); 2.91, 2.85 (2*s*, Me–C(8′), Me–C(4′)); 2.61 (*s*, Me–C(6′)). EI-MS: 312 (84, $M^{+\bullet}$), 297(7), 281(5), 265(6), 254(21), 253(100), 239(23), 238(6), 221(15), 195(9), 194(39) 193(53), 179(42), 178(20), 165(13). Anal. calc. for $C_{19}H_{20}O_4$ (312.37): C 73.06, H 6.45; found: C 72.98, H 6.31.

*Dimethyl (*E*)-1-(4,6,8-Trimethylazulen-3-yl)ethene-1,2-dicarboxylate* ((*E*)-**14**). Black shining crystals. M.p. 106–107° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.58. VIS (hexane): λ_{max} 551 (2.68), 595 (sh, 2.57), 655 (sh, 2.05); λ_{min} 503 (2.58), long tailing in the range of 670–730. UV (hexane and MeCN, resp.): λ_{max} 244/244 (4.46/4.47), 287/287 (sh, 4.59/sh, 4.60), 292/292 (4.60/4.61), 334/334 (sh, 3.74/3.77), 349/349 (3.76/3.78), 392–394/*ca.* 400 (3.41/3.38); λ_{min} 260/260 (3.90/3.90), –/324 (–/3.74), 339/340 (3.73/3.76), 370/370 (3.32/3.31). IR (KBr): 3001; 2950; 2927; 2852; 1722 (COOR); 1635 (C=C); 1580; 1558; 1530; 1505; 1433; 1416; 1371; 1325; 1284; 1250; 1208; 1178; 1105; 1061; 1061; 1013; 965; 932; 890; 849; 796; 773; 724. ^{1}H-NMR (270 MHz): 7.40 (*d*, *J* = 4.1, H–C(2′)); 7.31 (*d*, *J* = 4.1, H–C(1′)); 7.08 (*s*, H–C(2)); 7.04, 7.00 (2 br. *s*, H–C(5′), H–C(7′)); 3.74, 3.53 (2*s*, 2 MeOCO); 2.85, 2.73 (2*s*, Me–C(4′), Me–C(8′)); 2.57 (*s*, Me–C(6′)). EI-MS: Identical with that of (*Z*)-**14**. Anal. calc. for $C_{19}H_{20}O_4$ (312.37): C 73.06, H 6.45; found: C 72.99, H 6.50.

3. Reaction of 1,4,6,8-Tetramethylazulene (16) with ADM under TFA-Catalysis. – Azulene **16** (2.00 g, 10.8 mmol), ADM (1.5 ml, 11.9 mmol), and TFA (0.06 g) were dissolved in tetralin (30 ml). The mixture was kept for 9 d at ambient temperature. Tetralin and residual ADM were removed by distillation (80°/0.05 Torr) and the residue separated and purified by prep. TLC (hexane/Et_2O 1:1). (*E*)- (0.80 g, 22%) and (*Z*)-**17** (0.40 g, 11%) were obtained in pure form. No other product was present in the mixture.

*Dimethyl (*E*)-1-(1,4,6,8-Tetramethylazulen-3-yl)ethene-1,2-dicarboxylate* ((*E*)-**17**). Black shining crystals. M.p. 112–113° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.60. VIS (hexane): λ_{max} 575 (2.64), 628 (sh, 2.51), 696 (sh, 2.02); λ_{min} 532 (2.59), long tailing in the range of 670–730. UV (hexane and MeCN, resp.): λ_{max} 247/245.5 (4.45/4.42), 291/290 (sh, 4.60/4.55), 295.5/294–297 (4.61/4.55), 340/340 (3.75/3.73), 354/356 (3.76/sh, 3.72), 404–406/412–418 (3.40/3.30); λ_{min} 264.5/264 (4.00/3.97), –/292 (–/354), 332/332 (3.73/3.71), 380/385 (3.32/3.27). IR (KBr): 3005; 2991; 2952; 2919; 2874; 2842; 1733, 1717 (COOR); 1631 (C=C); 1574; 1555; 1511; 1457; 1434; 1394; 1374; 1315; 1298; 1242; 1211; 1182; 1154; 1106; 1069; 1016; 991; 979; 959; 892; 868; 834; 793; 774; 717; 683. ^{1}H-NMR (90 MHz): 7.25 (br. *s*, H–C(2′)); 7.10 (*s*, H–C(2)); 6.87 (br. *s* with f.s., H–C(5′), H–C(7′)); 3.78, 3.56 (2*s*, 2 MeOCO); 3.00, 2.85 (2*s*, Me–C(4′), Me–C(8′)); 2.70 (*s*, Me–C(3′)); 2.52 (*s*, Me–C(6′)). EI-MS: 326 (87, $M^{+\bullet}$), 311(21), 279(6), 267(100), 253(31), 252(13), 251(7), 237(5), 236(5), 235(21), 209(8), 208(38), 207(50), 194(17), 193(65), 192(14), 191(12), 189(8), 179(9), 178(15), 165(16). Anal. calc. for $C_{20}H_{22}O_4$ (326.39): C 73.60, H 6.79; found: C 73.58, H 6.91.

*Dimethyl (*Z*)-1-(1,4,6,8-Tetramethylazulen-1-yl)ethene-1,2-dicarboxylate* ((*Z*)-**17**). Greenish brown oil. R_f (hexane/Et_2O 1:1) 0.51. VIS (hexane): λ_{max} 571 (2.58), 617 (sh, 2.47), 678 (sh, 1.99); λ_{min} 473 (2.11), long tailing in the range of 670–730. UV (hexane and MeCN, resp.): λ_{max} 247/247 (4.35/4.36), 289/289 (sh, 4.37/sh, 4.34), 294.5/296 (4.41/4.38), 338/334 (sh, 4.07/4.03), 400/405 (3.78/3.78); λ_{min} 270.5/271 (4.04/4.04), 313/316 (4.03/4.01), 368/370 (3.58/3.58). IR (film): 2925; 2874; 1735, 1717 (COOR); 1607 (C=C); 1579; 1553; 1511; 1436; 1407; 1375; 1334; 1305; 1250; 1194; 1159; 1111; 1083; 1051; 1023; 981; 928; 871; 839; 785; 754. ^{1}H-NMR (90 MHz): 7.49 (br. *s*, H–C(2′)); 6.92 (br. *s*, H–C(5′), H–C(7′)); 5.64 (*s*, H–C(2)); 3.90, 3.77 (2*s*, 2 MeOCO); 2.96, 2.82 (2*s*, Me–C(8′), Me–C(4′)); 2.76 (*s*, Me–C(3′)); 2.52 (*s*, Me–C(6′)). EI-MS: Identical with that of (*E*)-**17**.

4. Reaction of Azulene (18) with ADM under TFA Catalysis. – Azulene (**18**; 1.00 g, 7.80 mmol), ADM (1.5 ml, 11.9 mmol), and TFA (0.027 g) were dissolved in tetralin (20 ml). The soln. was kept at ambient temp. over 14 d and then subjected to CC (300 g silica gel; hexane) to remove tetralin and non-reacted ADM and **18** (0.75 g recovered, 75%). Continuation of CC with hexane and increasing amounts of Et_2O eluted a mixture of at least five compounds (TLC), which was further seperated by CC with hexane/Et_2O 1:1 to give five fractions *a*–*e* (*a:* 0.087 g, *b:* 0.047 g, *c:* 0.010 g, *d:* 0.035 g, and *e:* 0.064). Fraction *a* contained mainly (*E*)-**19** (16%), fraction *b* mainly (*Z*)-**19** (9%), and fraction *c* the [5–7′;8b–8b′] dimer **22** (2%). ^{1}H-NMR of fraction *d* indicated the presence of at least four additional compounds. It was, therefore, further separated by prep. HPLC (*Spherisorb CN*, 20 × 250 nm; hexane/10% i-PrOH, 10 ml/min) into fractions d_1–d_4. Fraction d_1 was identical with **20** (9%), but still contained small amounts of **22**. Fraction d_2 provided the bisvinylogous ene product (*Z*)-**21** (2%), fraction d_3 the novel product type (*E*)-**24a** (2.5%), and d_4 its stereoisomer (*E*)-**24b** (1%). Fraction *e* contained a 2:1 mixture of **22** (2.6%) and its constitutional [2,5′:8b,8b′] dimer **23** (1.3%). The latter mixture was not further separated, since crystallization from E_2O/hexane led again to a 2:1 mixture of both compounds.

*Dimethyl (*E*)-1-(Azulen-3-yl)ethene-1,2-dicarboxylate* ((*E*)-**19**). Greenish-brown oil. R_f (hexane/Et_2O 1:1) 0.44. ^{1}H-NMR (270 MHz): 8.36 (*d*, *J* = 10.0, H–C(4′)); 8.07 (*d*, *J* = 10.0, H–C(8′)); 7.93 (*d*, *J* = 4.0, H–C(2′)); 7.63 (*t*, *J* = 10, H–C(6′)); 7.42 (*d*, *J* = 4.0, H–C(1′)); 7.20, 7.24 (2*t*, *J* = 10, H–C(5), H–C(7′)); 7.16 (*s*, H–C(2)); 3.81, 3.49 (2*s*, 2 MeOCO). EI-MS: 270 (82, $M^{+\cdot}$), 239(7), 211(100), 210(28), 196(12), 181(7), 179(18), 168(10), 167(12), 165(9), 155(28), 153(20), 152(96), 151(27), 150(12), 128(6).

*Dimethyl (*Z*)-1-(Azulen-3-yl)ethene-1,2-dicarboxylate* ((*Z*)-**19**). Green oil. R_f (hexane/Et_2O 1:1) 0.25. ^{1}H-NMR (270 MHz): 8.65 (*d*, *J* = 10.0, H–C(4′)); 8.36 (*d*, *J* = 10.0, H–C(8′)); 7.96 (*d*, *J* = 4.5, H–C(2′)); 7.70 (*t*, *J* = 10, H–C(6′)); 7.36 (*d*, *J* = 4.5, H–C(1′)); 7.31, 7.34 (2*t*, *J* = 10, H–C(5′), H–C(7′)); 6.31 (*s*, H–C(2)); 3.82, 3.98 (2*s*, 2 MeOCO). EI-MS: Identical with that of (*E*)-**19**.

*Dimethyl 1,2-Dihdrocyclopent[*cd*]azulene-3,4-dicarboxylate* (**20**). Dark-blue crystals. t_R 5.38 min[10]). ^{1}H-NMR (300 MHz, $CDCl_3$ and C_6D_6, resp.): 8.866/9.031 (*d*, *J* = 10.1, H–C(5)); 7.626/6.907 (*t*, *J* = 10, H–C(6)); 7.260/6.663 (*t*, *J* = 10.2, H–C(7)); 7.216/6.437 (*d*, *J* = 10.1, H–C(8)); 3.958 and 3.948/3.731 and 3.727 (2*s*, 2 MeOCO); 3.80–3.76/3.07–3.04 (*m*, 2 H–C(1)); 3.46–3.43/2.93–2.89 (*m*, 2 H–C(2)).

*Dimethyl 2a,8b-Dihydro-8b-[(*Z*)-1,2-bis(methoxycarbonyl)ethenyl]cyclopent[*cd*]azulene-1,2-dicarboxylate* ((*Z*)-**21**). t_R 6.74 min[10]). ^{1}H-NMR (600 MHz, $CDCl_3$): C*H*Cl_3 at 7.260): 6.871 (*ddd*, *J* = 10.9, 6.8, 0.7, H–C(6)); 6.804 (*d*, *J* = 6.9, H–C(8)); 6.743 (*dd*, *J* = 10.9, 6.9, H–C(7)); 6.727 (*d*, *J* = 6.7, H–C(5)); 6.636 (*dd*, *J* = 5.4, 1.6, H–C(4)); 6.106 (*dd*, *J* = 5.4, 2.6, H–C(3)); 5.381 (*s*, H–C(2′)); 4.321 (*dd*, *J* = 2.5, 1.8, H–C(2a)); 3.889, 3.835, 3.688, 3.598 (4*s*, 4 MeOCO).

Data of the [5,7′:8b,8b′] dimer **22** of *dimethyl cyclopent[*cd*]azulene-3,4-dicarboxylate* (**25**) will be reported later in the context with its derivatives [5] (see also [22]).

Data of the [2,5′:8b,8b′] dimer **23** of **25** will be reported later in the context with its derivatives in [5] (see also [22]).

*Dimethyl (2a*R**,6*S**,8b*S**)-2a,3,6,8b-Tetrahydro-6-{3-[(*E*)-1,2-bis(methoxycarbonyl)ethenyl]azulen-1-yl}-cyclobut[a]azulene-1,2-dicarboxylate* ((*E*)-**24a**). t_R 6.98 min[10]). ^{1}H-NMR (600 MHz, $CDCl_3$; C*H*Cl_3 at 7.260): 8.227 (*d*, *J* = 9.5, H–C(8′)); 8.041 (*s*, H–C(2′)); 8.037 (*d*, *J* = 9.5, H–C(4′)); 7.587 (*t*, *J* = 9.8, H–C(6′)); 7.151 (*s*, H–C(2″)); 7.146 (*t*, *J* = 9.9, H–C(7′)); 7.141 (*t*, *J* = 9.8, H–C(5′)); 6.638 (*d*, *J* = 9.4, H–C(8)); 6.120 (*d*, *J* = 9.4, H–C(4)); 5.572 (*dd*, *J* = 9.7, 5.3, H–C(5)); 5.557 (*dd*, *J* = 10.0, 5.1, H–C(7)); 4.249 (*q*-like, *J* ≈ 3.5, 2.2, H–C(8b)); 3.847 (*s*, MeOCO–C(1)); 3.838 (*s*, MeOCO–C(2)); 3.828 (*s*, MeOCO–C(1″)); 3.505 (*s*, MeOCO–C(2″)); 3.598 (*ddd*, *J* = 10.2, 3.7, 2.9, H–C(2a)); 3.483 (*t*, *J* = 5.2, H–C(6)); 3.061 (br. *dd*, *J* = 18.6, 10.2, H_{exo}–C(3)); 2.908 (*dq*-like, *J* ≈ 18, H_{endo}–C(3)). ^{13}C-NMR (150.9 MHz, $CDCl_3$; C*D*Cl_3 at 77.00): 167.75 (O*C*–C(1″)); 165.96 (O*C*–C(2″)); 161.83 (O*C*–C(2)); 161.49 (O*C*–C(1)); 148.49 (C(1)); 145.16 (C(2)); 142.91 (C(3a)); 139.72 (C(8a)); 139.52 (C(1″)); 138.21 (C(8a′)); 137.89 (C(3a′)); 131.26 (C(1′)); 120.61 (C(3′)); 138.26 (C(6′)); 137.02 (C(2′)); 134.77 (C(4′)); 134.23 (C(8′)); 127.64 (C(2″)); 126.25 (C(7)); 125.24 (C(5)); 124.30 (C(4)); 123.74 (C(5′)); 123.52 (C(8)); 123.47 (C(7′)); 52.92 (*Me*OCO–C(2)); 52.01 (*Me*OCO–C(1)); 51.95 (*Me*OCO–C(1″)); 51.80 (*Me*OCO–C(2″)); 54.83 (C(8b)); 40.56 (C(2a)); 38.49 (C(6)); 34.81 (C(3)).

*Dimethyl (2a*R**,6*R**,8b*S**)-2a,3,6,8b-Tetrahydro-6-{3-[(*E*)-1,2-bis(methoxycarbonyl)ethenyl]azulen-1-yl}-cyclobut[a]azulene-1,2-dicarboxylate* ((*E*)-**24b**). t_R 7.32 min[10]). ^{1}H-NMR (300 and 600 MHz, $CDCl_3$ and C_6D_6, resp.; C*H*Cl_3 at 7.260/C_6D_5H at 7.160): 8.194/7.974 (*d*, *J* = 9.5, H–C(8′)); 8.027/7.040 (*d*, *J* = 9.5, H–C(4′)); 8.030/7.381 (*s*, H–C(2″)); 7.590/7.058 (*t*, *J* = 9.8, H–C(6′)); 7.159/6.571 (*t*, *J* = 9.7, H–C(7′)); 7.138/6.703 (*t*, *J* = 10.0/9.6, H–C(5′)); 7.151/8.120 (*s*, H–C(2′)); 6.338/6.300 (*d*, *J* = 9.5/9.3, H–C(8)); 6.188/5.978 (*d*, *J* = 9.3, H–C(4)); 5.583/5.555 (*dd*, *J* = 9.2/9.3, 5.5, H–C(7)); 5.505/5.479 (*dd*, *J* = 9.3, 5.6/5.7, H–C(5)); 4.219/3.893 (*q*-like/br. *quint*.-like, *J* ≈ 3.5, 2.2, H–C(8b)); –[11])/3.659 (*t*, *J* = 5.6, H–C(6)); –/3.271 (*ddd*, *J* = 10.7, 3.9, 2.7, H–C(2a)); –/2.969 (*dt*, *J* = 17.8, 3.2, H_{endo}–C(3)); –/2.640 (*dd*, *J* = 17.9, 10.8, H_{exo}–C(3)); 3.842 and 3.826/3.381 and 3.363 (2*s*, MeOCO–C(1), MeOCO–C(2)); 3.789/3.310 (*s*, MeOCO–C(1″)); 3.502/3.086 (*s*, MeOCO–C(2″)).

5. X-Ray Crystal-Structure Analysis of Compound 7[12]). – All measurements were conducted on a *Rigaku AFC5R* diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71069 Å) and a 12-kW rotating

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[10]) Anal. column: *Spherisorb CN*, 4 × 125 mm; hexane/10% i-PrOH, 0.7 ml/min.

[11]) Signals not unequivocally assignable in $CDCl_3$.

[12]) 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-102878. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-(0)1223-336033 or email. deposit@ccdc.cam.ac.uk).

Table 2. *Crystallographic Data for Compound* **7**

Crystallized from		hexane
Empirical formula		$C_{36}H_{42}O_4$
Formula weight [g mol^{-1}]		538.73
Crystal color, habit		dark blue, prism
Crystal dimensions [mm]		$0.18 \times 0.23 \times 0.38$
Temp. [K]		173(1)
Crystal system		triclinic
Space group		$P\bar{1}$
Z		2
Reflections for cell determination		21
2θ Range for cell determination [°]		24 – 26
Unit cell parameters	a [Å]	12.667(4)
	b [Å]	12.919(4)
	c [Å]	10.771(4)
	α [°]	96.73(3)
	β [°]	108.68(3)
	γ [°]	63.47(2)
	V [Å^3]	1493(1)
$D_{calc.}$ [g cm^{-3}]		1.198
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]		0.0713
$2\theta_{(max)}$ [°]		60
Total reflections measured		9069
Symmetry-independent reflections		8702
Reflections used [$I > 3\sigma(I)$]		5832
Parameters refined		361
R		0.0501
wR		0.0454
Goodness of fit s		1.776
Final D_{max}/σ		0.003
$D\rho$(max; min) [eÅ^{-3}]		0.29; – 0.26
$\sigma(d(\mathrm{C-C}))$ [Å]		0.002 – 0.003

anode generator. The intensities were collected using $\omega/2\theta$ scans. 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, but not for absorption. The structure was solved using SHELXS86 [29], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were fixed in geometrically calculated positions ($d(\mathrm{C-H}) = 0.95$ Å), and each was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of the parent C-atom. A correction for secondary extinction was not applied. Refinement of the structure was carried out on F using full-matrix least-squares procedures which minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + (0.005F_0)^2]^{-1}$. The data collection and refinement parameters are listed in *Table 2*. Neutral atom scattering factors for non-H-atoms were taken from [30a] and the scattering factors for H-atoms from [31]. Anomalous dispersion effects were included in F [32]; the values for f' and f'' were taken from [30b]. All calculations were performed using the TEXAN [33] crystallographic software package and the figure was produced with ORTEPII [34].

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