# Report on an Unusual Cascade Reaction between Azulenes and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (=4,5-Dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile; DDQ)

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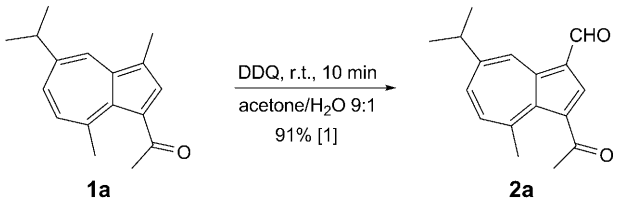
The oxidation of 1-(3,8-dimethylazulen-1-yl)alkan-1-ones **1** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (=4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile; DDQ) in acetone/$H_2O$ mixtures at room temperature does not only lead to the corresponding azulene-1-carboxaldehydes **2** but also, in small amounts, to three further products (*Tables 1* and *2*). The structures of the additional products **3**–**5** were solved spectroscopically, and that of **3a** also by an X-ray crystal-structure analysis (*Fig. 1*). It is demonstrated that the bis(azulenylmethyl)-substituted DDQ derivatives **5** yield on methanolysis or hydrolysis precursors, which in a cascade of reactions rearrange under loss of HCl into the pentacyclic compounds **3** (*Schemes 4* and *7*). The found 1,1′-[carbonylbis(8-methylazulene-3,1-diyl)]bis[ethanones] **4** are the result of further oxidation of the azulene-1-carboxaldehydes **2** to the corresponding azulene-1-carboxylic acids (*Schemes 9* and *10*).

**1. Introduction**. – More then ten years ago, we applied a procedure of *Okajima* and *Kurokawa* [1], just published at that time, to the smooth oxidation of the Me group of 1-(3-methylazulen-1-yl)alkan-1-ones with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (=4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile; DDQ) in aqueous acetone to yield the corresponding azulenecarboxaldehydes. The authors reported for the oxidation of 3-acetylguaiazulene (=1-(5-isopropyl-3,8-dimethylazulen-1-yl)-ethanone; **1a**) an attractive yield of 91% for carboxaldehyde **2a** (*Scheme 1*). In our hands, the reaction gave, in a ten times higher concentration of the reactants, also **2a** as the main product, however, in yields ranging from 40 to 60%; and to our surprise, on TLC beside the dark red spot of **2a**, at least two additional faint spots were present, a blue one, moving distinctly faster, and a red one, moving clearly slower than **2a**, which stood for two additional products of unknown structure and in estimated yields of *ca.*

*Scheme 1*

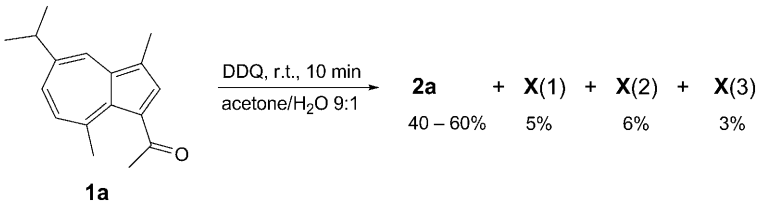



**1a** **2a**

5% or below. In the following part, we report on the elucidation of the structure of these new products and speculations about the mechanisms of their formation.

**2. Oxidation of 1-(3-Methylazulen-1-yl)alkan-1-ones with DDQ in Aqueous Acetone**[1]). – 2.1. *Reactions of 1-(5-Isopropyl-3,8-dimethylazulen-1-yl)alkan-1-ones* (= *3-Acylguaiazulenes*). In a number of oxidation experiments with DDQ and 3-acetylguaiazulene (**1a**) we got, after laborious chromatographic separations, consolidated yields of 5 and 6% of pure material of the unknown blue component **X**(1) and the unknown brick-red component **X**(2), respectively. Moreover, we found a third, relatively unstable, purple compound **X**(3) in an average yield of 3% (*Scheme 2*).

*Scheme 2*




The UV/VIS spectrum ($CH_2Cl_2$) of **X**(1) with the azulene band at 586 nm, flanked by shoulders at 550, 618, and 686 nm, confirmed the azulene nature of the compound. The IR spectrum ($CHCl_3$) showed a weak band at 2222 $cm^{-1}$, indicating the presence of at least one CN group in conjugation with a $\pi$-system, and a very strong absorption at 1792 $cm^{-1}$ only compatible, in principle, with a C=O group as part of a strained ring system, possibly a $\gamma$-lactone, but not at all with a benzoquinone ring system, which absorbs at frequencies more than 100 $cm^{-1}$ lower and shows normally two bands. Most informative was the mass spectrum of **X**(1), which showed the molecular mass at *m*/*z* 432 and 430 (EI mode) and 433 and 431 (CI mode), respectively, and in both cases in a peak ratio of 1:3, a fact that allowed us to formulate the mass balance as follows:

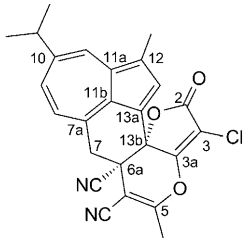
$$\mathbf{1a} + \mathrm{DDQ} = \mathbf{X}(1) + \mathrm{HCl}$$

Further information on the structure of **X**(1) came from the NMR spectra. The $^1$H-NMR spectrum ($CDCl_3$) of **X**(1) was very similar to that of the starting material **1a** with the exception that one of the three *s*s of the Me groups, namely the *s* for Me–C(8) of **1a**, was missing. Instead of this signal appeared in the spectrum of **X**(1) signals of a $CH_2$ group as *AB* system at $\delta$ 4.10 and 3.90 with $J(A,B) = 16.6$ Hz. Since only $H_B$ at $\delta$ 3.90 showed a strong reciprocal $^1$H-NOE effect with the neighbored azulene H-atom at $\delta$ 7.24, we concluded that the structure of **X**(1) must be rigid and that it must contain elements of chirality. The $^{13}$C-NMR spectrum ($CDCl_3$) revealed undoubtedly the presence of two CN groups with signals at $\delta$ 115.3 and 113.1 – in a shift range quite typical for CN groups. Most informative were HMBC measurements since they indicated a structural neighborhood of the $CH_2$ group and the CN group whose signal appeared at $\delta$ 115.3. Moreover, this CN group showed also a long-range coupling with

[1]) See *Exper. Part* for the acylation of the corresponding azulenes.

the Me signal, which appeared in the $^1$H-NMR spectrum as a sharp *s* at $\delta$ 2.10 and could be identified as the former Me group of MeCO–C(1) of **1a**, since it was not related with the H-atoms of the azulene ring. The second CN group at $\delta$ 113.1 was also related with the Me group at $\delta$ 2.10 by long-range coupling. This fact indicated that the two CN groups were still located at neighbored C-atoms of **X**(1). On the other hand, most confusing was the observation that three $^{13}$C-signals of **X**(1) were located in the region above $\delta$ 160, where normally C=O resonances are found, and only one of these signals at lowest field ($\delta$ 164.5) showed a coupling relation with the Me group at $\delta$ 2.10.

Since all further structure elucidation would have been based on assumptions without final certainty, we prepared suitable crystals of **X**(1) for an X-ray crystal-structure determination, which disclosed the full structure as (6a*RS*,13b*SR*)-3-chloro-10-isopropyl-5,12-dimethyl-2-oxo-2*H*-cyclohept[1,7]indeno[4,5-*c*]furo[3,2-*b*]pyran-6,6a-(7*H*)-dicarbonitrile (**3a**).




**3a**

The X-ray structure of **3a** (*Fig. 1*) indicated a rupture of the benzoquinone moiety of DDQ in the course of its reaction with **1a**, whereby the Me group of the Ac residue of **1a** re-appeared as Me–C(5) of the new pentacyclus. This in turn would mean that C(5) must then be the former C=O C-atom of the Ac group of **1a**. To clarify undoubtedly the Ac migration in the course of the formation of **3a**, we synthesized **1a** with a doubly $^{13}$C-labeled Ac group, *i.e.*, **1a***, and subjected it to oxidation with DDQ. The result was unambiguous (*Scheme 3*). It was indeed C(5) and its Me substituent that carried in **3a*** the double $^{13}$C-label.

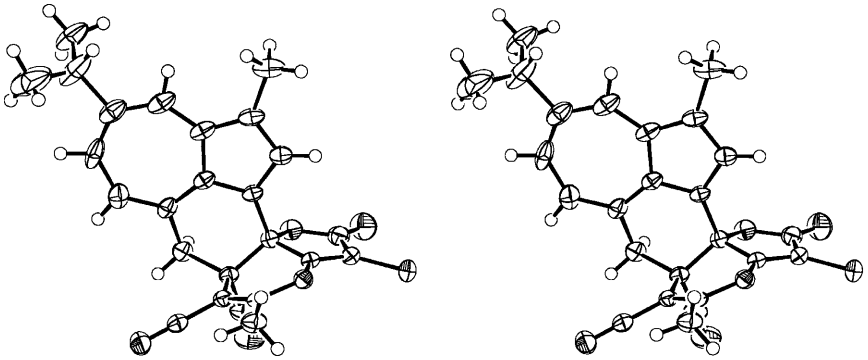
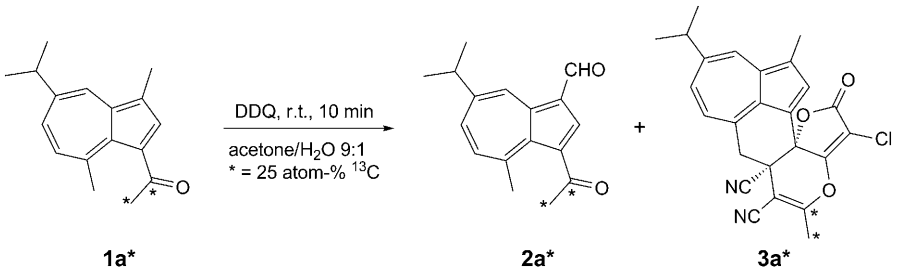
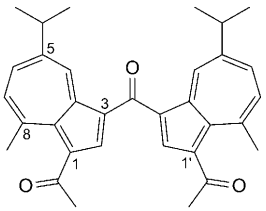


Fig. 1. *Stereoscopic view of the X-ray crystal structure of* **3a** (50% probability ellipsoids)

*Scheme 3*




The structure elucidation of **X**(2) was much easier. It showed in the IR spectrum ($CHCl_3$) a broad and strong C=O absorption band at 1652 $cm^{-1}$ (1659 $cm^{-1}$ (KBr)), slightly different in position in comparison with **2a** (1649 $cm^{-1}$ ($CHCl_3$)). On the other hand, the $^1$H-NMR spectrum ($CDCl_3$) was almost identical with that of **2a**, however, the $^{13}$C-NMR spectra ($CDCl_3$) of **2a** and **X**(2) revealed a characteristic difference in the C=O region. In contrast to **2a**, where the signal showed up at $\delta$ 196.3, the spectrum of **X**(2) revealed two signals, one at $\delta$ 196.9, close to the position of that of **2a**, and the other at $\delta$ 189.0, and both C=O signals in a ratio of intensity of *ca.* 2 : 1. Compound **X**(2) could therefore only represent 1,1′-[carbonylbis(5-isopropyl-8-methylazulene-3,1-diyl)]bis[ethanone] (**4a**). This structural assignment was fully confirmed by the mass spectrum (EI) of **4a**, which exhibited the peak of the molecular mass at *m*/*z* 478, with prominent fragment ions at *m*/*z* 463 ($[M-Me]^+$) and 435 ($[M-Ac]^+$).

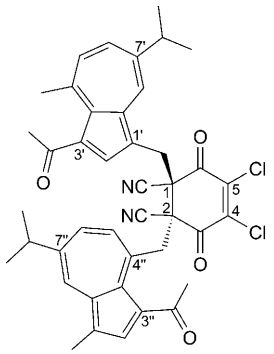



**4a**

The third unknown, **X**(3), appeared intermediately in the reaction of **1a** and DDQ and later on, with the progress of the reaction, it vanished again. So it needed some experiments to optimize its actual amount and isolate it at this point in a maximum yield of 3%. The IR spectrum ($CHCl_3$) was of interest because we observed three C=O absorption bands at 1707, 1649, and 1625 $cm^{-1}$. These observations spoke for a chemical interaction of **1a** and DDQ, whereby essential parts of the quinone skeleton with $\tilde{\nu}_{C=O}$ at 1649 and 1625 $cm^{-1}$ were still present. Indeed, the mass spectrum (ESI; MeOH/$CH_2Cl_2$ 1:1, NaI) of **X**(3) showed *m*/*z* at 727 and 729 for $[M+Na]^+$[2]), in agreement with the addition of two residues of **1a** to DDQ. Last certainty brought the full analysis of the $^1$H- and $^{13}$C-NMR spectra of **X**(3) with the unambiguous assignment of the

[2]) A detailed analysis of the $[M+Na]^+$ region revealed that it reflected a superposition of two molecular ions in a ratio of *ca.* 1:1, namely that of $[\mathbf{5a}+Na]^+$ and that of $[(\mathbf{5a}+2\,H)+Na]^+$, due to partial hydrogenation of **5a** under the ESI conditions.

position of all atoms. The compound was identified as (1*RS*,2*RS*)-1-[(3-acetyl-7-isopropyl-4-methylazulen-1-yl)methyl]-2-[(3-acetyl-7-isopropyl-1-methylazulen-4-yl)-methyl]-4,5-dichloro-3,6-dioxocyclohex-4-ene-1,2-dicarbonitrile (**5a**).




**5a**

The $CH_2$ groups at C(1) and C(2) of **5a** appear in the $^1$H-NMR spectrum ($CD_2Cl_2$) as two *AB* systems at $\delta$ 4.08 and 3.79 and $\delta$ 5.10 and 4.34, respectively, with $J(A,B) =$ 15.1 and 13.9 Hz, respectively. Since we observed no $^1$H-NOE between the two *AB* systems, we assigned the *trans*-configuration to **5a**. This view is supported by AM1 calculations of the two possible conformations of *trans*- and *cis*-1-[(3-acetyl-4,7-dimethylazulen-1-yl)methyl]-2-[(3-acetyl-1,7-dimethylazulen-4-yl)methyl]cyclohex-4-ene-1,2-dicarbonitrile, where the i-Pr groups of **5a** were substituted by Me groups on grounds of simplicity. The *trans*-form with both azulenylmethyl substituents in axial positions ($\Delta H_f^\circ = 104.7$ kcal mol$^{-1}$) displays shortest distances of the H-atoms of the two $CH_2$ groups of 4.4 Å, in other words, beyond the distances of measurable $^1$H-NOE effects (*Fig. 2*). Its conformer with the azulenylmethyl substituents in diequatorial orientations ($\Delta H_f^\circ = 107.8$ kcal mol$^{-1}$) as well as the two conformations of the *cis*-form ($\Delta H_f^\circ = 102.1$ and 107.8 kcal mol$^{-1}$ for the 1-ax,2-eq and 1-eq,2-ax conformation, resp.) show shortest H distances of 2.3 Å each, *i.e.*, well in the range of observable $^1$H-NOE effects.

Further interesting information came from an attempt to record the $^1$H-NMR spectrum of **5a** in $CD_3OD$. Compound **5a** underwent in this solvent at room temperature a clean reaction to **3a** without any incorporation of D and to 1-[5-isopropyl-3-([$^2H_3$]methoxymethyl)-8-methylazulen-1-yl]ethanone (**6**) (*Scheme 4*). The same reaction was observed in MeOH, resulting in **3a** and the protio form of **6**.

The $^{13}$C-experiment had demonstrated that, in the course of the formation of **3a** from **1a**, a migration of the Ac group under abolition of the structural integrity of the quinone system of DDQ takes place. Therefore, we were interested in changing the Ac group with other acyl residues and subject these modified compounds to the treatment with DDQ. The results are summarized in *Table 1*. The product pattern is principally not changed. The pivaloyl-substituted azulene **1d** yielded, beside **2d**, still a distinctly larger amount of triketone **4d**, and also the 1,4-diketone **5d** could be isolated. However, there was no indication for the formation of pentacyclic **3d**. The oxidation of the benzoylated azulene **1e** gave only the corresponding aldehyde **2e** and an increasing

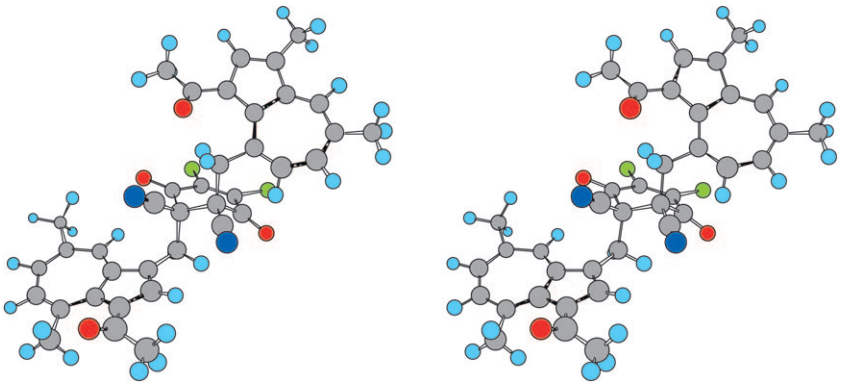
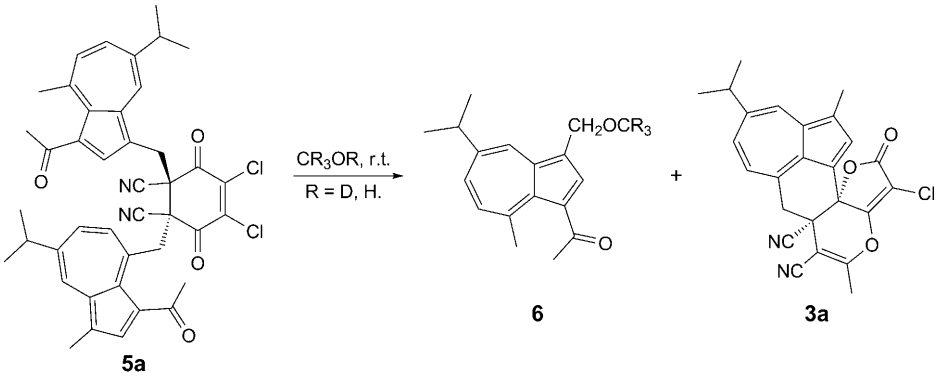


Fig. 2. *Stereoscopic view of the AM1-calculated structure of* **5a**

*Scheme 4*

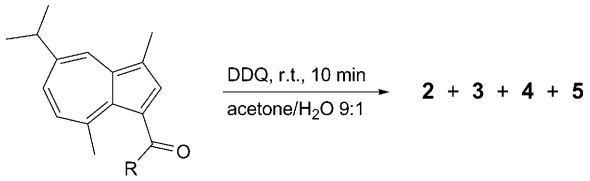



amount of triketone **4e** but neither **3e** nor **5e**. The latter two experiments illustrate that most probably steric and electronic factors of the acyl group play a decisive role in the formation of the cascade products **3**.

2.2. *Reactions of 1-(5-Alkyl-3,8-dimethylazulen-1-yl)ethanones.* In a further series of experiments, we tested a possible steric influence of the i-Pr group at C(5) of **1a** on product formation. The results are listed in *Table 2* together with those of our standard compound **1a**. They clearly indicate that a substituent at C(5) of **1** has no influence on the product pattern.

For the formation of the bis-azulenylated products **5**, which easily rearrange to the pentacycles **3** (*Scheme 4*), it is obligatory that the 1-(azulene-1-yl)alkan-1-ones **1**, subjected to the oxidation with DDQ, carry Me groups at C(8) and C(3). On the other hand, the structure of the pentacycles **3** shows only Me–C(8) engaged in the construction of the pentacycles. For this reason, we subjected also the 3-unsubstituted azulene **1j**, readily available by decarbonylation of **2a** with *Wilkinson*'s catalyst, to the

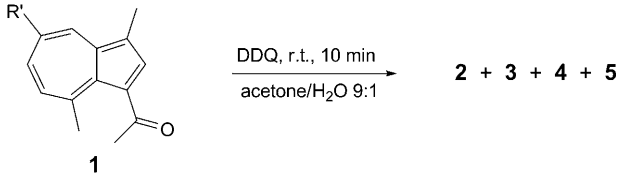
Table 1. *Oxidation of 1-(5-Isopropyl-3,8-dimethylazulen-1-yl)alkan-1-ones* **1** *with DDQ*




**1**

| | R | Yield of product [%] | | | |
|---|---|---|---|---|---|
| | | **2** | **3** | **4** | **5** |
| **1a** | Me | 40–60 | 5 | 6 | 3 |
| **1b** | Et | 38 | 7–9 | 1–2 | *ca.* 1 |
| **1c** | i-Pr | 41 | 1–2 | 6–9 | 1 |
| **1d** | *t*-Bu | *ca.* 30 | – | *ca.* 16 | 2–3 |
| **1e** | Ph | 49 | – | 22 | – |
| **1f** | $CF_3$ | 50–60 | – | – | |

Table 2. *Oxidation of 1-(5-Alkyl-3,8-dimethylazulen-1-yl)ethanones* **1a** *and* **1h** *and of 5-Unsubstituted* **1g** *with DDQ*

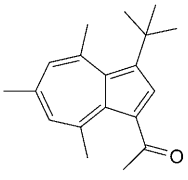



**1**

| | R′ | Yield of product [%] | | | |
|---|---|---|---|---|---|
| | | **2** | **3** | **4** | **5** |
| **1a** | i-Pr | 40–60 | 5 | 6 | 3 |
| **1h** | Et | 49 | 5 | 4 | 1 |
| **1g** | H | 52 | 5 | 14 | <1 |

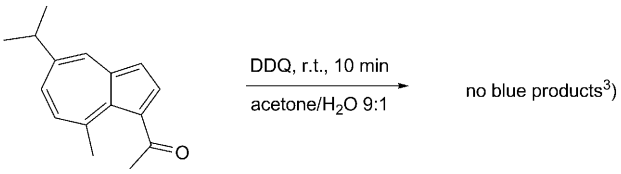
described oxidation protocol (*Scheme 5*). Indeed, this 1-(azulen-1-yl)ethanone stayed almost untouched, and no product formation was observed. The same behavior was observed for **1k** with a *t*-Bu group at C(3)[3]).

[3]) Also no blue-product formation was observed with **1k**.




**1k**

*Scheme 5*




**1j**

2.3. *Mechanistic Considerations.* There is little doubt that the bis(azulenylmethyl)-substituted compounds **5** are the pivotal key in the events of the oxidation of 1-(3,8-dimethylazulen-1-yl)alkan-1-ones with DDQ since on methanolysis they undergo, without the appearance of any further intermediates, rearrangement to the pentacyclic compounds type **3**.

The oxidation of 1-methylazulenes and comparable azulenes with DDQ to the corresponding azulenyl-1-methyl[4]) cations is a well established procedure (*cf.* [2] and lit. cit. there), whereby, in a first step, an electron is transferred from the azulene to DDQ (see *Scheme 6*), followed by deprotonation to yield the corresponding azulenyl-1-methyl radical, which then is further oxidized to the azulenyl-1-methyl cation. The present investigation teaches us that at least 1-acylazulene radical cations with Me groups at C(3) and C(8) can lose a H-atom at Me–C(3) as well as Me–C(8) to form the corresponding radicals (*Scheme 6*)[4]). The product yields realized by oxidation of the 1-(3,8-dimethylazulen-1-yl)alkan-1-ones **1a**, **1f**, and **1g** allow to estimate for these cases a product ratio of *ca.* 10:1 for the corresponding azulenyl-3-methyl[4]) and azulenyl-8-methyl[4]) radicals. Since we observed no further oxidation products of the 8-methyl group, we conclude that the azulenyl-8-methyl radicals as such are trapped by DDQ or DDQ radical anions, resulting by single-electron transfer (SET) from the azulenes to DDQ. It means that there are two imaginable reaction paths for the formation of the key intermediates of type **5**. Either the intermediate radical **1g**(8)$^{\bullet}$ is captured by DDQ or combines with the radical anion of DDQ. In the first case, the formed addition radical **8g**$^{\bullet}$ can then trap **1g**(3)$^{\bullet}$ to yield **5g** or the other way around (not shown in *Scheme 6*), *i.e.*, DDQ captures the radical **1g**(3)$^{\bullet}$, followed by recombination with **1g**(8)$^{\bullet}$. In the second case, the first step yields the anion **8g**$^{-}$, which then leads to the formation of **5g** by C-alkylation with **1g**(3)$^{+}$. As a summary, it can be said that the formation of the 3-(hydroxymethyl)azulene derivatives **7** in the presence of DDQ and $H_2O$ does not require necessarily the occurrence of azulenyl-3-methyl cations of type **1g**(3)$^{+}$, generated by SET between the corresponding radicals and DDQ. Azulene derivatives **7** can also be formed by hydrolysis of the mono- or bis-adducts of 3-acylazulenyl-1-methyl[4]) radicals and DDQ according to *Scheme 6*.

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[4]) For convenience, the locant in the names azulenyl-1-methyl, azulenyl-3-methyl, and azulenyl-8-methyl refers to the position of the Me group in the starting azulene derivative. The discussed reaction paths in *Schemes 6* and *7* are formulated with **1g**, which bears the necessary substituents at C(1), C(3), and C(8) for the observed product patterns (*cf. Scheme 2*).

Hydrolysis of the azulenyl-1-methyl substituent at C(1) of the 3,6-dioxocyclohex-4-ene-1,2-dicarbonitriles **5** yields the 1,1-disubstituted 6-oxocyclohexa-2,4-dien-1,2-dicarbonitriles **8** with a CN group as strong $\pi$-acceptor substituent at C(2) (*Scheme 7*). It seems that these intermediates are the starting point of the subsequent cascade reactions, initiated by a most probably reversible intramolecular electrophilic addition of C(6)=O at C(3) of the azulen-4-ylmethyl substituent *via* a six-membered transition state, leading to the zwitterionic intermediate **9g**[5]). This intermediate carries at neighbored C-atoms an acyl and an oxido group, so that the acyl group can easily migrate under charge compensation and ester formation to the oxido group. Thus, formed **10g** is structurally perfectly disposed for a transannular *C*-acylation of the former C(2) of **8g** under formation of **11g**. Intermediate **11g** represents a 1,3-diketone, which generally can undergo the so-called acid cleavage under base catalysis. The catalyst in the present case can only be $H_2O$, which forms reversibly with **11g** the hydrate **12g**. The latter undergoes the acid cleavage, most probably by an intramolecular $H^+$ transfer from the hydrate to the neighbored acyl group, thus leading to cleavage and formation of enol **13g**. The new structure is again ideally arranged for an intramolecular *Michael* addition–elimination reaction, whereby the pyran ring of **14g** is formed. The rigid structure of **14g** induces finally a facile intramolecular ester formation to **3g**. The experiment with **5a** and $CD_3OD$ (*Scheme 4*) shows that the described cascade of reactions can also be induced and kept running in this solvent, which indicates that also corresponding ketals of type **12g** undergo the ring cleavage reaction to intermediates of type **13g**[6])[7]).

The obtained yields of the pentacycles **5** are low and may depend on the production rates of the azulenyl-4-methyl radicals in comparison to those of the azulenyl-1-methyl radicals, which are responsible for the formation of the carboxaldehydes **2** and also for the triketones **4**. It seems that from a stererochemical viewpoint the intramolecular electrophilic addition reaction to the zwitterionic intermediates of type **9g** is the most critical one since the alkyl residues of the acyl group determine the addition step. The established row of increasing steric demands in the series Me, Et, i-Pr, and *t*-Bu is *grosso modo* followed, since the pentacyclic compounds **3** are formed up to the i-Pr

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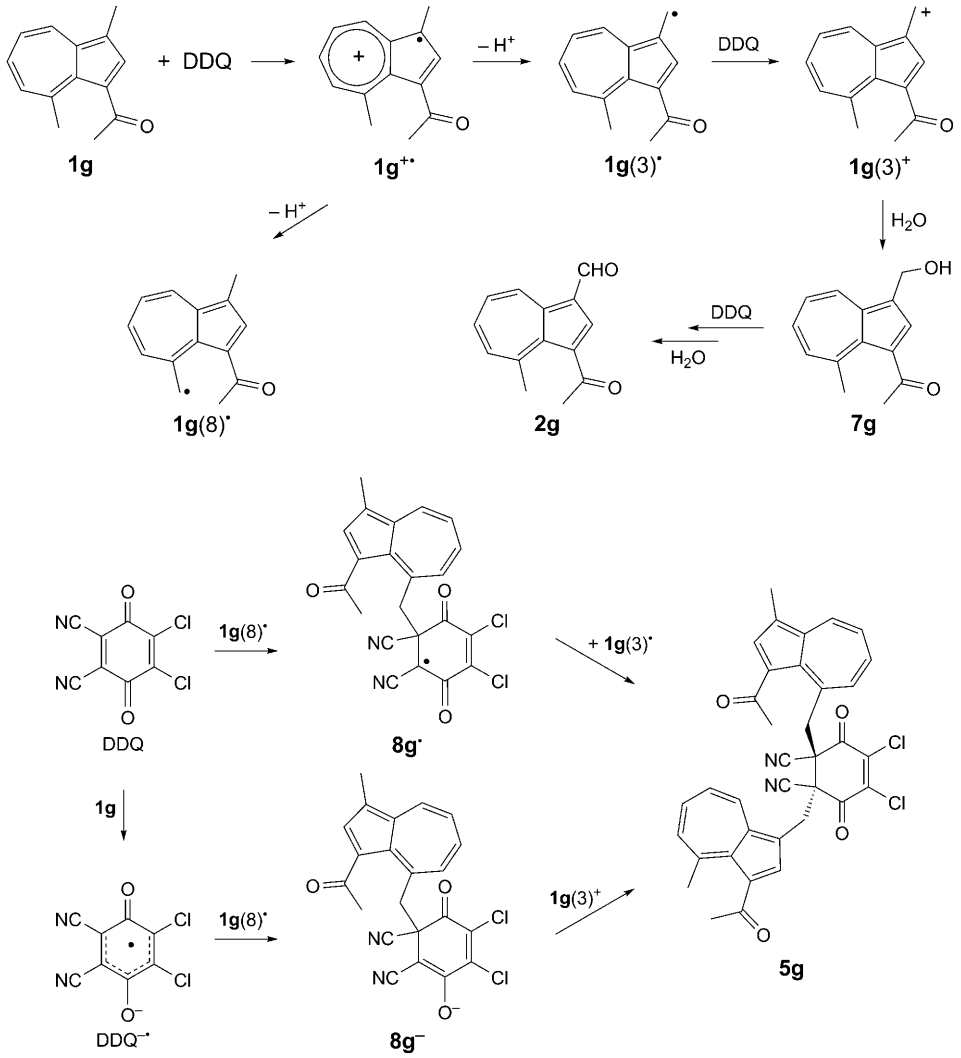
5) There are principally two stereochemically different intramolecular addition modes, one, which is sterically favored, leads to a *trans* arrangement of the neighbored Ac and oxido groups, a spatial situation that would not allow an intramolecular migration of the Ac group, and the other one, which places the Ac and oxido group in *cis* relation, ideally positioned for a migration of the Ac group concomitantly with the formation of **9g**, a driving force that may counterbalance the sterically less favorable interactions in the transition state of bond-formation to **9g**, which just slips in **10g**. The AM1-calculated $\Delta H_f^\circ$ values of **8g** and **10g** show a difference of 10 kcal mol$^{-1}$ in favor of the latter.

6) It should be noted that HCl is formed in the course of the formation of the pyran ring. In other words, the reaction cascade is most probably autocatalyzed by HCl.

7) It is of interest to note that all AM1-calculated structures of the reaction cascade **8g** → **14g** exhibit distances of the involved reactive centers of $< 3.5$ Å, which seems to be a necessary spatial requirement for a smoothly ongoing step-by-step reaction without interference with the surrounding milieu. *G. M. J. Schmidt* and co-workers realized some time ago a similar empirical rule for [2+2] cycloaddition reactions of cinnamic acids and related compounds in solid-state photochemistry, where the crystallographically controlled, critical intermolecular distance of the reacting centers was found to have to be $< 4.1$ Å, otherwise no cyclobutane-ring formation occurred on irradiation of the crystals [3] (see also [4]).

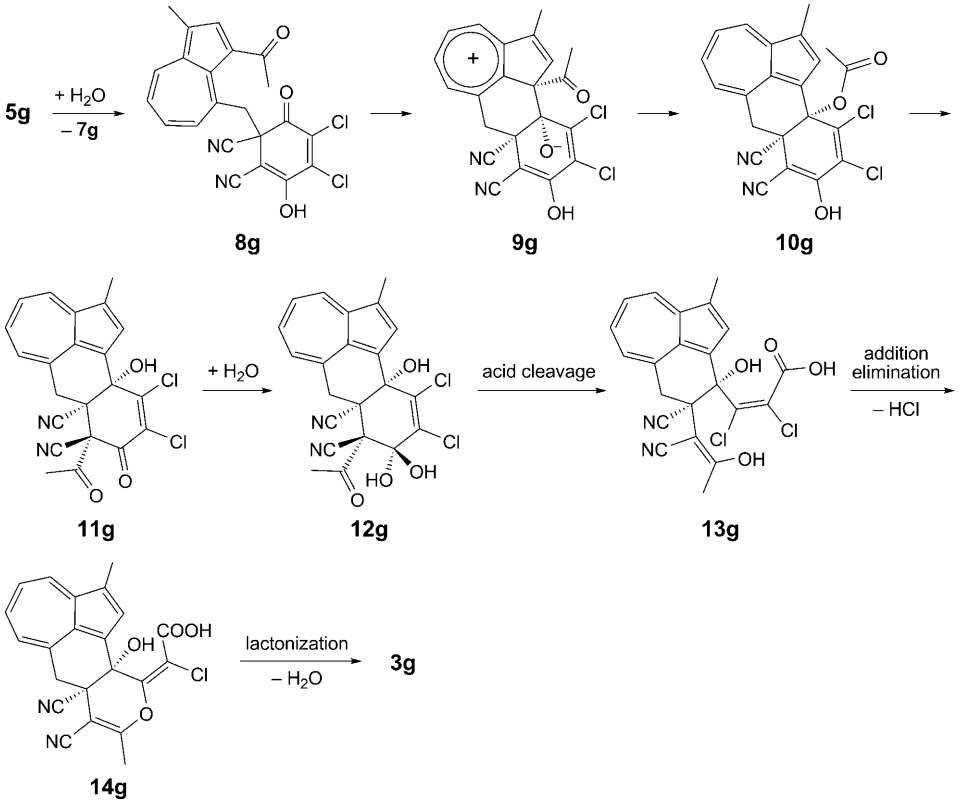
*Scheme 6*




group (*Tables 1* and *2*). The pivaloyl residue of **1d** still allows the formation of **5d**, but not any more that of the cascade product **3d**. It is also of interest to note that with increasing steric hindrance of the acyl groups, also the amount of triketones **4** is growing (*Tables 1* and *2*).

To explain the formation of the triketones **4**, we first thought that they might arise from the dimerization of the azulenyl-1-methyl radicals **1**(3)•, followed by oxidative decarbonylation (*Scheme 8*). Indeed, when separately synthesized **15a** (see *Exper. Part*) was subjected to the standard oxidative procedure with DDQ, triketone **4a**,

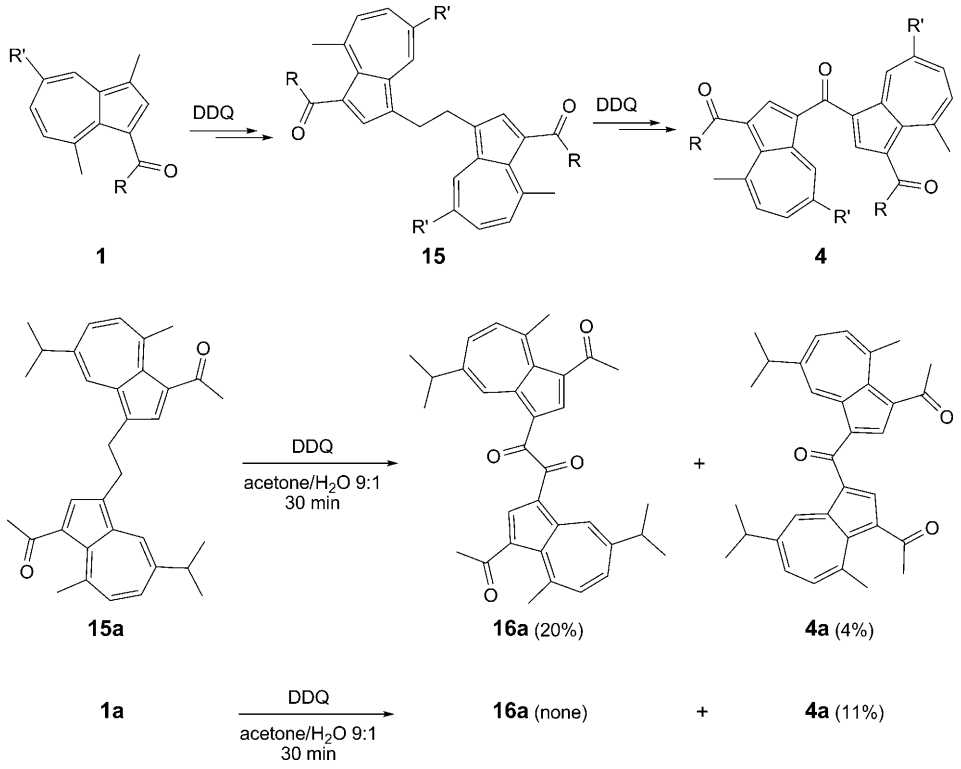
*Scheme 7*




accompanied by major amounts of the tetraketone **16a**, could be isolated in minor amounts (*cf.* [5] for similar results). However, since the oxidation of **1a** with DDQ under the same conditions gave nearly three-times the amount of **4a** but no tetraketone **16a** at all, the postulated pathway for the formation of **4a** could not be a main route to **4a** in the course of the oxidation of **1a**.

A second possibility for the formation of **4**, which we envisaged, was the occurrence of the corresponding 3-acylazulene-1-carboxylic acid as precursor, after we had found trace amounts of 1,1′-(methylenediazulene-3,1-diyl)bis[ethanones] in the original reaction mixtures. We prepared therefore the azulenecarboxylic acid **17a** by oxidation of **2a** with $KMnO_4$ (*Scheme 9*). Indeed, when we oxidized **1a** with DDQ in acetone/$H_2O$ in the presence of the acid, we obtained the triketone **4a** in a yield of 26%, accompanied by 55% of **2a**, and 6% of the 1,1′-(methylenediazulene-3,1-diyl)bis-[ethanone] **18a** (*Scheme 9*). The latter could be converted quantitatively into **4a** by treatment with DDQ in acetone/$H_2O$. This experiment convinced us that $CH_2$-bridged bis-azulenes of type **18** are key intermediates for the formation of the triketones **4**, following the pathways depicted in *Scheme 10*.

*Scheme 8*




Later on, we learned that *Scheme 10* reflects only one half of the mechanistic reality[8]).

**3. Concluding Remarks.** – We think that beside the disclosure of an unusual cascade reaction, it is of importance to realize that soft azulen-1-ylmethyl cations may serve as mobile protecting groups, *e.g.*, to trap reactive enols in their keto form, which can easily be removed again in protic solvents such as $H_2O$ or MeOH by formation of azulene-1-methanols or their methyl ethers.

We are thankful to *Rolf Schindler*, *Christoph Oberli*, and *Petra Wolint* for experimental assistance, to our NMR laboratory for specific NMR measurements, our MS laboratory for mass spectra, and our laboratory for microanalysis for elemental analyses. Great thanks go also to *Anthony Linden*, who solved for us the X-ray crystal structure of compound **3a**. Financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

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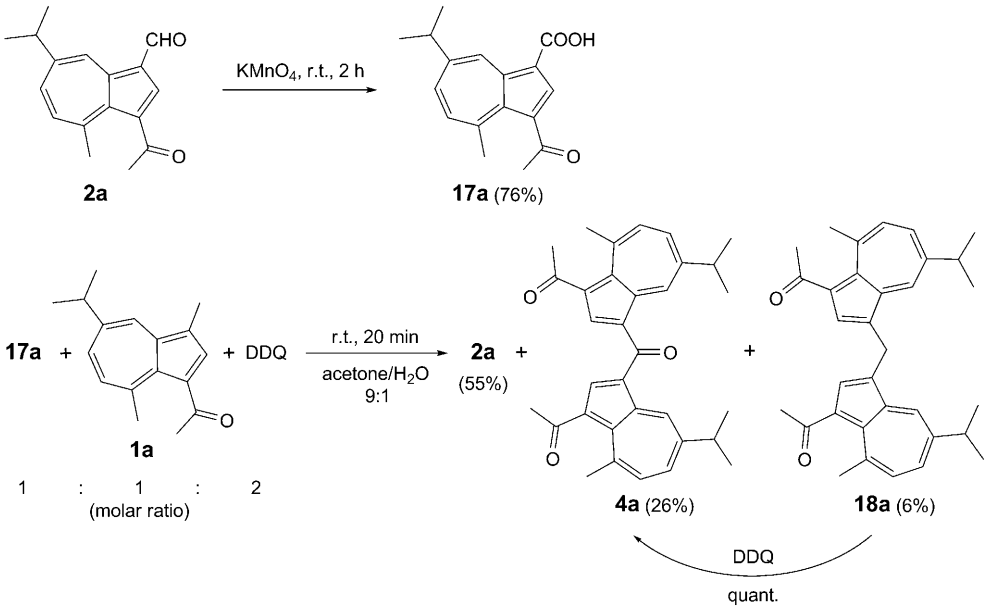
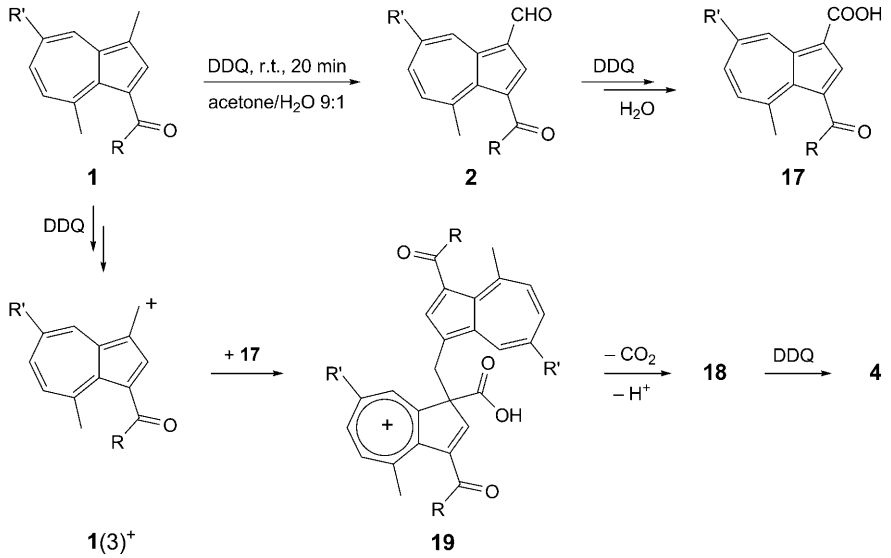
[8]) See the subsequent communication on the synthesis of nonsymmetrically substituted bis(azulen-1-yl) ketones [6].

*Scheme 9*




*Scheme 10*




## Experimental Part

*General*. All solvents were distilled before use, or when necessary dried over Na/benzophenone and then distilled, with the exception of solvents of *p.a.* quality from *Merck*, toluene, acetone, and AcOH. Dioxane was filtered through *Alox* (act. I; *ICN*) prior to distillation. [$^{13}C_2$]AcCl (99%; *Cambridge*

*Isotope Lab.*) was diluted with AcCl to 25 mol-% $^{13}C$. M.p.: *FP-52* and *FP-5* with microscope (*Mettler*); not corrected. TLC: *Polygram®* sheets (*Macherey-Nagel*) covered with silica gel ($SiO_2$) *N-HR/UV*$_{254}$[9]) or alumina *N/UV*$_{254}$. Column chromatography (CC): basic *Alox* (act. III, *ICN*; method *A*) and $SiO_2$ *60* (40–63 and 60–200 μm; *Merck*; method *B*). Low-pressure LC (method *C*): $SiO_2$ columns (*Merck*; *Lichroprep Si 60*) equipped with a He tank (5 bar max.) and a differential refractometer *R 401* (*Waters Associates*). UV/VIS Spectra: *Lambda-19* instrument (*Perkin-Elmer*); $\lambda_{max}$ and $\lambda_{min}$ in nm, log $\varepsilon$ in parentheses. IR Spectra: *Perkin-Elmer* spectrophotometers FT-IR *1600* and *Spectrum One*; $\tilde{\nu}$ in $cm^{-1}$. NMR Spectra: *Bruker* instruments *AC-300*, *ARX-300*, and *AMX-600*; assignments of the signals by $^1H$,$^{13}C$ correlations (HSQC and HMBC), and in addition by COSY, NOESY, and INADEQUATE measurements; $\delta$ ($CHCl_3$) 7.26, $\delta$ ($CHCl_3$) 77.0, $\delta$ ($C_6HD_5$) 7.16, and $\delta$ ($C_6D_6$) 128.0. MS (70 eV): *MAT-SSQ-700* (*Finnigan*) instrument (EI) and *MAT 112S* (*Varian*) instrument (CI); in *m/z* (rel. %).

1. *1-(3,8-Dimethylazulen-1-yl)alkan-1-ones.* 1.1. *Acylation of Guaiazulene.* To a stirred soln. of guaiazulene and the corresponding anhydride was added dropwise the *Lewis* acid (see *Table 3*). After the reaction, hydrolysis was performed by addition of EtOH and $H_2O$. The products were then extracted with several portions of *t*-butyl methyl ether (*t*-BuOMe). The combined *t*-BuOMe extracts were washed with $H_2O$ or aq. $NaHCO_3$ soln. and with sat. NaCl soln. and then dried ($Na_2SO_4$). The residue was purified by CC (method *B*) and then subjected to bulb-to-bulb distillation under high vacuum.

1.2. *Acetylation of Guaiazulene Analogs.* Half of the used amount of $Et_2O$ was cooled to $-60°$ or $-70°$. At this temp., $SnCl_4$ and $Ac_2O$ were added dropwise. To the resulting milky suspension, the corresponding azulene dissolved in the second half of $Et_2O$, was added dropwise. The workup procedure was the same as described under 1.1. The results are summarized in *Table 4*.

2. *Oxidation of the 1-(Azulen-1-yl)alkan-1-ones with DDQ in Aqueous Acetone: General Procedure.* As reported in [1], however, in ten times higher concentration and mostly with 5–10 mmol of the azulenes. The products **2**–**5** were isolated and purified by chromatographic methods as described under *General*; for average yields of pure material, see *Tables 1* and *2*.

2.1. *1-(5-Isopropyl-3,8-dimethylazulen-1-yl)ethanone* (**1a**). Products **2a**, **3a**, **4a**, and **5a**. *3-Acetyl-7-isopropyl-4-methylazulene-1-carboxaldehyde* (**2a**): Dark red crystals. M.p. 84–85° (hexane). $R_f$ (toluene/*t*-BuOMe 4:1) 0.38. IR ($CHCl_3$): 3008*m*, 2967*m*, 1649v*s*, 1509*s*, 1447*s*, 1421*s*, 1391*s*, 1373*s*, 960*w*, 880*m*. $^1H$-NMR (600 MHz, $C_6D_6$): 10.25 (*d*, $^4J(6,8) = 2.2$, H–C(8)); 10.24 (*s*, CHO); 7.85 (*s*, H–C(2)); 7.09 (*dd*, $^3J(5,6) = 10.9$, $^4J(6,8) = 2.2$, H–C(6)); 6.95 (*d*, $^3J(5,6) = 10.9$, H–C(5)); 2.78 (*s*, Me–C(4)); 2.73 (*sept.*, $J = 6.9$, $Me_2CH$–C(7)); 2.38 (*s*, MeCO–C(3)); 1.09 (*d*, $J = 6.8$, $Me_2CH$–C(7)). EI-MS: 254 (29, $M^{+\cdot}$), 239 (100, $[M - Me]^+$), 224 (8), 211 (8), 165 (18), 152 (21).

*(6a*RS,*13b*SR*)-3-Chloro-10-isopropyl-5,12-dimethyl-2-oxo-2*H*-cyclohept[1,7]indeno[4,5-*c*]furo[3,2-*b*]pyran-6,6a(7*H*)-dicarbonitrile* (**3a** = **X**(1)): Blue prisms (toluene/hexane). M.p. *ca.* 215° (dec.). $R_f$ (toluene/*t*-BuOMe 4:1) 0.76. UV/VIS (hexane): max. 588 (2.75), 374 (3.82), 355 (3.75), 363 (sh, 3.69), 306 (sh, 4.32), 299 (4.47), 294 (4.47), 246 (4.54), 208 (4.32); min. *ca.* 419 (2.11), 363 (3.67), 320 (3.40), 274 (4.20), 223 (4.23). IR ($CHCl_3$): 2964*m*, 2222*w* (C≡N), 1792v*s* (C=O), 1691*s*, 1631*m*, 1452*m*, 1428*w*, 1387*m*, 1322*s*, 1302*w*, 1169*w*, 1129*w*, 998*s*, 971*s*. $^1H$-NMR (300 MHz, $CDCl_3$): 8.29 (*d*, $^4J(9,11) = 1.5$, H–C(11)); 7.69 (*dd*, $^3J(8,9) = 11.3$, $^4J(9,11) = 1.3$, H–C(9)); 7.44 (*s*, H–C(13)); 7.24 (*d*, $^3J = 10.4$, H–C(8)); 4.11, 3.91 (*AB*, $^2J(A,B) = 16.6$, $CH_2$(7)); 3.17 (*sept.*, $J = 6.9$, $Me_2CH$–C(10)); 2.62 (*s*, Me–C(12)); 2.10 (*s*, Me–C(5)); 1.41 (*d*, $J = 6.9$, $Me_2CH$–C(10)). $^{13}C$-NMR (150 MHz, $CDCl_3$): 164.54 (C(5)); 163.72 (C(2)=O); 161.45 (C(3a)); 144.93 (C(10)); 137.37 (C(9)); 137.29 (C(11a)); 135.89 (C(7a)); 135.77 (C(11)); 133.78 (C(11b)); 133.20 (C(13)); 126.55 (C(12)); 125.78 (C(8)); 115.40 (N≡*C*–C(6a)); 113.13 (N≡*C*–C(6)); 109.24 (C(13a)); 102.57 (C(3)); 89.64 (C(6)); 74.33 (C(13b)); 40.19 (C(6a)); 38.90 ($Me_2CH$–C(10)); 37.02 (C(7)); 24.69, 24.67 ($Me_2CH$–C(10)); 19.22 (Me–C(5)); 12.53 (Me–C(12)). CI-MS: 433.1 and 431.1 (33 and 100, $[M + H]^+$). Anal. calc. for $C_{25}H_{19}ClN_2O_3$ (430.89): C 69.69, H 4.44, N 6.50, Cl 8.23; found C 69.79, H 4.51, N 6.12, Cl 9.04.

The structure of **3a** was finally established by an X-ray crystal-structure analysis (*Fig. 1* and *Table 5*)[10]).

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9) Not specifically mentioned in the text.

10) CCDC-669699 contains the supplementary crystallographic data for **3a**. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

Table 3. *Formation of 1-(5-Isopropyl-3,8-dimethylazulen-1-yl)alkan-1-ones* **1** (= *3-Acylguaiazulenes*; see *Table 1* for R)

| | R | Molar ratios | | | Reaction conditions | | | | | Physical data | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | reactant | $(RCO)_2O$ | $BF_3 \cdot Et_2O$ | solvent | conc. [solv./react.][a]) | time [h] | temp. [°] | yield [%] | M.p. [°] | $\delta$(C=O) [ppm] |
| **1a** | Me | 1 | 2.4[b]) | – | octane | 2:1 | 67 | r.t. | 79 | 86–87 (88.2–88.8 [7]) | 196.33[c]) |
| **1a*** | Me* | 1.2 | 2.4[d]) | 1[e]) | hexane | 3:1 | 45 | 45 | 29 | – | 196.32 ($d$, $^1J$ = 42.3)[c]) |
| **1b** | Et | 1 | 12 | 4 | $Et_2O$ | 40:1 | 24 | r.t. | 48 | 42–43 (crude 36 [8]) | 199.26[f]) |
| **1c** | i-Pr | 1 | 12 | 4 | $Et_2O$ | 40:1 | 24 | r.t. | 57 | 58–59 | 204.30[c]) |
| **1d** | *t*-Bu | 1 | 12 | 6.4 | $Et_2O$ | 40:1 | 48 | reflux | 69 | 57–58 | 210.87[f]) |
| **1e** | Ph | 1 | 5.6 | 2.5 | $Et_2O$ | 30:1 | 192 | reflux | 60 | 119–121 (120–121 [9]) | 193.67[f]) |
| **1f** | $CF_3$ | 1 | 2.7 | – | $CH_2Cl_2$ | 10:1 | 2.3 | r.t. | 94 | 52–53 (50–51.5 [10]) | 175.03 ($q$, $^2J$ = 33.0)[c]) |

[a]) Solvent [ml], reactant [g]. [b]) AcBr instead of $Ac_2O$. [c]) In $CDCl_3$. [d]) [$^{13}C_2$]AcCl instead of $Ac_2O$. [e]) LiBr instead of $BF_3 \cdot Et_2O$. [f]) In $C_6D_6$.

Table 4. *Formation of 1-(5-Alkyl-3,8-dimethylazulen-1-yl)ethanones* (see *Table 2* for R′)

| | R′ | Molar ratios | | | Reaction conditions | | | | | Physical data | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | reactant | $(MeCO)_2O$ | $SnCl_4$ | solvent | conc. [solv./react.][a]) | time [h][b]) | temp. [°] | yield [%] | M.p. [°] | $\delta$(C=O) [ppm] |
| **1g** | H | 1 | 22 | 5.2 | $Et_2O$ | 40:1 | 1.5 | −60 → r.t. | 88 | 81–82 | 197.43[c]) |
| **1i** | Me | 1 | 35 | 7.8 | $Et_2O$ | 63:1 | 15 | −70 → r.t. | 73 | 100–101[d]) | 195.04[e]) |
| **1h** | Et | 1[f]) | 22 | 5.2 | $Et_2O$ | 35:1 | 1 | −70 → r.t. | 64 | 58–59 (crude: 36 [10]) | 196.44[c]) |

[a]) Solvent [ml], reactant [g]. [b]) Time at r.t. [c]) $CDCl_3$. [d]) From hexane. [e]) In $C_6D_6$. [f]) Chamazulene (= 7-ethyl-1,4-dimethylazulene).

Table 5. *Crystallographic Data of* **3a**

| | | | |
|---|---|---|---|
| Crystallized from | toluene/hexane | $F(000)$ | 1792 |
| Empirical formula | $C_{25}H_{19}ClN_2O_3$ | $D_x$ [g cm$^{-3}$] | 1.306 |
| $M_r$ | 430.89 | $\mu$(Mo$K_\alpha$) [mm$^{-1}$] | 0.203 |
| Crystal color, habit | blue, prism | Scan type | $\omega/2\theta$ |
| Crystal dimensions [mm] | $0.30 \times 0.30 \times 0.45$ | $2\theta_{(max)}$ [°] | 55 |
| Temperature [K] | 173 (1) | Total reflections measured | 5435 |
| Crystal system | monoclinic | Symmetry-independent reflections | 5026 |
| Lattice type | C-centered | $R_{int}$ | 0.030 |
| Space group | $C2/c$ (#15) | Reflections used ($I > 2\sigma(I)$) | 3506 |
| $Z$ | 8 | Parameters refined | 281 |
| Reflections for cell determination | 25 | Reflection/parameter ratio | 12.5 |
| $2\theta$ Range for cell determination [°] | 38–40 | Final $R$ | 0.0598 |
| Unit cell parameters | | $wR$ | 0.0547 |
| $a$ [Å] | 23.784 (3) | Weights: $p$ in $w = [\sigma^2(F_o) + (pF_o)^2]^{-1}$ | 0.005 |
| $b$ [Å] | 10.222 (2) | Goodness of fit | 2.503 |
| $c$ [Å] | 18.751 (3) | Secondary extinction coefficient | $1.9(2) \cdot 10^{-7}$ |
| $\alpha$ [°] | 90 | Final $\Delta_{max}/\sigma$ | 0.0001 |
| $\beta$ [°] | 106.073 (9) | $\Delta\rho$ (max; min) [e Å$^{-3}$] | 0.65; −0.67[a]) |
| $\gamma$ [°] | 90 | Range of $\sigma(d_{(C-C)})$ [Å] | 0.003–0.006 |
| $V$ [Å$^3$] | 4381 (1) | | |

[a]) Near-disordered i-Pr group.

*1,1′-[Carbonylbis(5-isopropyl-8-methylazulene-3,1-diyl)]bis[ethanone]* (**4a** = **X**(2)): Red crystals. M.p. 186–187° (EtOH). $R_f$ (toluene/*t*-BuOMe 4:1) 0.28. UV/VIS (hexane): max. 524 (3.31), 407 (4.40), 395 (sh, 4.39), 308 (4.73), 250 (4.69); min. 455 (3.15), 355 (4.11), 270 (4.27). IR ($CCl_4$): 2964*m*, 2930*w*, 2871*w*, 1663*s*, 1597*m*, 1505*s*, 1442*s*, 1405*s*, 1368*m*, 1302*w*, 1219*w*, 1191*s*, 1158*w*, 956*w*, 887*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 9.75 (*d*, $^4J$(4,6) = 2.1, H–C(4)); 8.33 (*s*, H–C(2)); 7.81 (*dd*, $^3J$(6,7) = 10.9, $^4J$(4,6) = 2.1, H–C(6)); 7.66 (*d*, $^3J$(6,7) = 10.9, H–C(7)); 3.23 (*sept.*, $J$ = 6.9, $Me_2CH$–C(5)); 2.96 (*s*, Me–C(8)); 2.69 (*s*, MeCO–C(1)); 1.39 (*d*, $J$ = 6.9, $Me_2$CH–C(5)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 196.97 (Me*C*O–C(1)); 189.06 (C=O); 151.50–126.49 (20 azulene C)[11]); 38.35 ($Me_2$*C*H–C(5)); 30.35 (*Me*CO–C(1)); 29.10 (*Me*–C(8)); 24.35 ($Me_2$CH–C(5)). EI-MS: 478 (100, $M^{+\bullet}$), 463 (74, [$M$ – Me]$^+$), 435 (57, [$M$ – MeCO]$^+$), 393 (19), 253 (12), 239 (24), 224 (15), 211 (12), 165 (13). Anal. calc. for $C_{33}H_{34}O_3$ (478.63): C 82.81, H 7.16; found: C 82.96, H 7.10.

*(1*RS*,2*RS*)-1-[(3-Acetyl-7-isopropyl-4-methylazulen-1-yl)methyl]-2-[(3-acetyl-7-isopropyl-1-methylazulen-4-yl)methyl]-4,5-dichloro-3,6-dioxocyclohex-4-ene-1,2-dicarbonitrile* (**5a** = **X**(3)): Dark red crystals (EtOH). M.p. *ca.* 250° (dec.). $R_f$ (toluene/*t*-BuOMe 4:1) 0.48. IR ($CHCl_3$): 2966*m*, 1707*s*, 1648*m*, and 1625*m* (C=O), 1397v*s*, 1371*s*. $^1$H-NMR (500 MHz, $CD_2Cl_2$): 8.13 (*d*, $^4J$(6″,8″) = 2.1, H–C(8″)); 7.76 (*s*, H–C(2″)); 7.72 (*d*, $^4J$(6′,8′) = 2.0, H–C(8′)); 7.55 (*dd*, $^3J$(5″,6″) = 10.7, $^4J$(6″,8″) = 2.1, H–C(6″)); 7.44 (br. *d*, not resolved, $^3J$(5′,6′) = 10.8, H–C(6′)); 7.44 (*d*, $^3J$(5″,6″) = 10.8, H–C(5″)); 7.42 (*s*, H–C(2′)); 7.23 (*d*, $^3J$(5′,6′) = 10.9, H–C(5′)); 5.10, 4.34 (*AB*, $^2J$(*A*,*B*) = 13.9, $CH_2$–C(2)); 4.08, 3.79 (*AB*, $^2J$(*A*,*B*) = 15.1, $CH_2$–C(1)); 3.00 (*sept.*, $J$ = 6.9, $Me_2CH$–C(7″)); 2.87 (*sept.*, $J$ = 6.9, $Me_2CH$–C(7′)); 2.56 (*s*, Me–C(4′)); 2.35 (*s*, Me–C(1″)); 2.32 (*s*, MeCO–C(3′)); 2.32 (*s*, MeCO–C(3″)); 1.22, 1.21 (2*d*, $J$ = 6.9, $Me_2$CH–C(7″)); 1.16, 1.15 (2*d*, $J$ = 6.9, $Me_2$CH–C(7′)). $^1$H-NMR (300 MHz, $C_6D_6$): 5.71, 4.66 (*AB*, $^2J$(*A*,*B*) = 13.8, $CH_2$–C(2)); 4.00, 3.78 (*AB*, $^2J$(*A*,*B*) = 15.1, $CH_2$–C(1)). $^{13}$C-NMR (125 MHz, $CD_2Cl_2$): 196.30 (Me*C*O–C(3′)); 194.54 (Me*C*O–C(3″)); 179.26 (C(6)=O); 176.50 (C(3)=O); 151.23 (C(4′)); 149.82 (C(7″)); 147.24 (C(7′)); 145.24 (C(8a″)); 144.92

[11]) Here and in the following part, only the $^{13}$C-signals at lowest and highest field of the azulene core are given.

(C(2″)); 143.95 (C(5)); 142.97 (C(4)); 142.12 (C(2′)); 140.99 (C(8a′)); 140.23 (C(3a″)); 138.26 (C(6′)); 137.59 (C(3a′)); 137.31 (C(6″)); 137.16 (C(4″)); 136.36 (C(8″)); 134.68 (C(8′)); 134.10 (C(5″)); 133.75 (C(5′)); 128.52 (C(3′)); 127.00 (C(1″)); 125.70 (C(3″)); 115.24 (N≡*C*−C(1)); 114.96 (N≡*C*−C(2)); 114.96 (C(1′)); 61.02 (C(2)); 59.56 (C(1)); 46.69 (*C*H$_2$−C(2)); 38.54 (Me$_2$*C*H−C(7′)); 38.53 (Me$_2$*C*H−C(7″)); 37.38 (*C*H$_2$−C(1)); 30.76 (*Me*CO−C(3″)); 30.35 (*Me*CO−C(3′)); 28.84 (*Me*−C(4′)); 24.52, 24.40 (*Me*$_2$CH−C(7″)); 24.29, 23.85 (*Me*$_2$CH−C(7′)); 13.00 (*Me*−C(1″)). CI-MS ($C_{42}H_{38}Cl_2N_2NaO_4^+$/$C_{42}H_{40}Cl_2N_2NaO_4^+$): 727.4 (69), 725.4 (36), 729.4 (100), 730.4 (45), 731.3 (52), 732.4 (21), 733.3 (14), 734.4 (6); calc. rel. % for a *ca.* 1:1 ratio of $[M+Na]^+$ and $[MH_2+Na]^+$: 57:27:100:46:53:22:11:3. Anal. calc. for $C_{42}H_{38}Cl_2N_2O_4$ (705.68): C 71.49, H 5.43, N 3.97; found: C 71.66, H 5.72, N 3.88.

2.1.1. *Solvolysis of* **5a**. When **5a** (0.02 g) was dissolved in MeOH or [$^2H_3$]MeOD (0.4 ml each) at r.t., the color of the soln. changed rapidly from red to blue (**5a** → **3a**). Workup by chromatography gave pure **3a** and as a second, slower-moving component, the methyl or [$^2H_3$]methyl ether derivative **6** of 1-[3-(hydroxymethyl)-5-isopropyl-8-methylazulen-1-yl]ethanone. No D had been incorporated in **3a** in the experiment with [$^2H_3$]MeOD.

*1-[5-Isopropyl-3-(methoxymethyl)-8-methylazulen-1-yl]ethanone* (**6**, R = H; *Scheme 4*): Violet oil. $R_f$ (hexane/*t*-BuOMe 2:1) 0.30. $^1$H-NMR (300 MHz, $C_6D_6$): 8.60 (*d*, $^4J$(4,6) = 2.1, H−C(4)); 7.85 (*s*, H−C(2)); 7.12 (*dd*, partly superimp. by the signal of $C_6HD_5$, $^3J$(6,7) ≈ 11, $^4J$(4,6) = 2.1, H−C(6)); 6.94 (*d*, $^3J$(6,7) = 10.9, H−C(7)); 4.75 (*s*, CH$_2$−C(3)); 3.18 (*s*, MeO); 2.98 (*s*, Me−C(8)); 2.74 (*sept.*, *J* = 6.9, Me$_2$*CH*−C(5)); 2.52 (*s*, MeCO−C(1)); 1.13 (*d*, *J* = 6.9, *Me*$_2$CH−C(5)). EI-MS: 270 (41, $M^{+\bullet}$), 255 (34, $[M-Me]^+$), 239 (100, $[M-MeO]^+$).

*1-[5-Isopropyl-3-([$^2H_3$]methoxymethyl)-8-methylazulen-1-yl]ethanone* (**6**, R = D; *Scheme 4*). $^1$H-NMR (300 MHz, $C_6D_6$): As above, but no signal at 3.18 (MeO). EI-MS: 273 (45, $M^{+\bullet}$), 258 (34, $[M-Me]^+$), 239 (100, $[M-[^2H_3]MeO]^+$).

2.1.2. *1-(5-Isopropyl-3,8-dimethylazulen-1-yl)[$^{13}C_2$]ethanone* (**1a***)[12]. Products **2a***, **3a***, and **5a***. *3-[$^{13}C_2$]Acetyl-7-isopropyl-4-methylazulene-1-carboxaldehyde* (**2a***): $^1$H-NMR (300 MHz, $CDCl_3$): 2.77 (*dd*, $^1J(^1H,^{13}C)$ = 127.4, $^2J(^1H,^{13}C)$ = 5.8, *Me*CO−C(3)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 196.68 (*d*, $^1J(^{13}C,^{13}C)$ = 42.8, Me*C*O−C(3)); 30.19 (*d*, $^1J(^{13}C,^{13}C)$ = 42.8, *Me*CO−C(3)).

*(6a*RS,*13b*SR*)-3-Chloro-10-isopropyl-5-[$^{13}$C]methyl-12-methyl-2-oxo-[5-$^{13}$C]-2*H*-cyclohept[1,7]indeno[4,5-*c*]furo[3,2-*b*]pyran-6,6a(7*H*)-dicarbonitrile* (**3a***): $^1$H-NMR (300 MHz, $CDCl_3$): 2.12 (2.10) (*dd*, $^1J(^1H,^{13}C)$ = 130.3, $^2J(^1H,^{13}C)$ = 7.3, Me−C(5)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 19.23 (19.18) (*d*, $^1J(^{13}C,^{13}C)$ = 51.8, *Me*−C(5)); 164.60 (164.59) (*d*, $^1J(^{13}C,^{13}C)$ = 51.8, C(5)).

*(1*RS,*2*RS*)-1-[(3-[$^{13}C_2$]Acetyl-7-isopropyl-4-methylazulen-1-yl)methyl]-2-[3-[$^{13}C_2$]acetyl-7-isopropyl-1-methylazulen-4-yl)methyl]-4,5-dichloro-3,6-dioxocyclohex-4-ene-1,2-dicarbonitrile* (**5a***). Identified by $R_f$ on TLC. Not further analyzed.

2.2. *1-(5-Isopropyl-3,8-dimethyl-1-yl)propan-1-one* (**1b**). Products **2b**, **3b**, **4b**, and **5b**. 7-*Isopropyl-4-methyl-3-(1-oxopropyl)azulene-1-carboxaldehyde* (**2b**)[13]: Red crystals. M.p. 56–57° (pentane). $R_f$ ($CH_2Cl_2$/AcOEt 100:1) 0.20. IR ($CHCl_3$): 1648v*s*. $^1$H-NMR (300 MHz, $CDCl_3$): 3.12 (*q*, *J* = 7.4, MeC*H*$_2$CO−C(3)); 1.31 (*t*, *J* = 7.4, *Me*CH$_2$CO−C(3)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 35.99 (Me*C*H$_2$CO−C(3)); 9.37 (*Me*CH$_2$CO−C(3)). EI-MS: 268 (21, $M^{+\bullet}$), 239 (100). Anal. calc. for $C_{18}H_{20}O_2$ (268.35): C 80.57, H 7.51; found: C 80.53, H 7.62.

*(6a*RS,*13b*SR*)-3-Chloro-5-ethyl-10-isopropyl-12-methyl-2-oxo-2*H*-cyclohept[1,7]indeno[4,5-*c*]furo[3,2-*b*]pyran-6,6a(7*H*)-dicarbonitrile* (**3b**): Blue crystals. M.p. *ca.* 260° (dec.). $R_f$ ($CH_2Cl_2$/AcOEt 100:1) 0.54. IR ($CHCl_3$): 2222*w*, 1794v*s*, 1693*s*. $^1$H-NMR (300 MHz, $CDCl_3$): 2.42, 2.30 (2 *dq*, $^2J$ ≈ 15.0, $^3J$ = 7.5, MeC*H*$_2$−C(5)); 0.91 (*t*, $^3J$ = 7.5, *Me*CH$_2$−C(5)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 26.43 (Me*C*H$_2$−C(5)); 10.66 (*Me*CH$_2$−C(5)). CI-MS ($NH_3$): 447 and 445 (34 and 100, $[M+H]^+$). Anal. calc. for $C_{26}H_{21}ClN_2O_3$ (444.92): C 70.19, H 4.76, N 6.30; found: C 70.54, H 4.93, N 5.89.

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12) $^1$H-NMR (300 MHz, $CDCl_3$): 2.74 (2.72) (*dd*, $^1J(H,^{13}C)$ = 130.7, $^2J(H,^{13}C)$ = 6.2, MeCO−C(1)). $^{13}$C-NMR (75 MHz, $CDCl_3$): *Table 3*.

13) For the following compounds of the **1b**–**1f** series, normally only the most important changes of the spectroscopic data due to the change of the acyl group are given.

*1,1′-[Carbonylbis(5-isopropyl-8-methylazulene-3,1-diyl)]bis[propan-1-one]* (**4b**): Red crystals. M.p. 136–139° (EtOH). $R_f$ ($CH_2Cl_2$/AcOEt 100:1) 0.07. IR ($CHCl_3$): 1652*s*, 1589*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 3.02 (*q*, *J* = 7.4, MeC$H_2$CO–C(1)); 1.27 (*t*, *J* = 7.4, *Me*$CH_2$CO–C(1)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 197.07 (Et*C*O–C(1)); 189.11 (C=O); 36.12 (Me*C*$H_2$CO–C(1)); 9.58 (*Me*$CH_2$CO–C(1)). EI-MS: 506 (43, $M^{+\bullet}$), 477 (82, $[M - Et]^+$), 239 (100, $[M - C_{18}H_{19}O_2]^+$). Anal. calc. for $C_{35}H_{38}O_3$ (506.67): C 82.97, H 7.56; found: C 81.84, H 7.58.

*(1*RS,*2*RS*)-1-{[7-Isopropyl-4-methyl-3-(1-oxopropyl)azulen-1-yl]methyl}-2-{[7-isopropyl-1-methyl-3-(1-oxopropyl)azulen-4-yl]methyl}-4,5-dichloro-3,6-dioxocyclohex-4-ene-1,2-dicarbonitrile* (**5b**): Red crystals. M.p. *ca.* 250° (dec.). IR ($CHCl_3$): 1708*s*, 1647*m*, and 1624*m* (C=O). $^1$H-NMR (300 MHz, $C_6D_6$): 2.74 (br. *q*, *J* ≈ 7.0, MeC$H_2$CO–C(3′,3″)); 1.25 (*t*, $^3J$ = 7.2, *Me*$CH_2$CO–C(3′)); 1.20, 1.15 (2 *d*, *J* = 6.9, *Me*$_2$CH–C(7″)); 1.12 (*t*, $^3J$ = 7.3, *Me*$CH_2$CO–C(3″)); 0.99 (*d*, *J* = 6.9, *Me*$_2$CH–C(7′)). $^{13}$C-NMR (75 MHz, $C_6D_6$): 35.89 (Me*C*$H_2$CO–C(3′)); 35.28 (Me*C*$H_2$CO–C(3″)); 9.10 (*Me*$CH_2$CO–C(3′,3″)). ESI-MS (NaI): 759, 757, 755 ($[M + Na]^+$). Anal. calc. for $C_{44}H_{42}Cl_2N_2O_4$ (733.73): C 72.03, H 5.77, N 3.82; found: C 71.74, H 6.07, N 3.56.

2.3. *1-(5-Isopropyl-3,8-dimethylazulen-1-yl)-2-methylpropan-1-one* (**1c**). Products **2c**, **3c**, **4c**, and **5c**. *7-Isopropyl-4-methyl-3-(2-methyl-1-oxopropyl)azulene-1-carboxaldehyde* (**2c**): Red crystals. M.p. 69–72°. $R_f$ ($CH_2Cl_2$/AcOEt 100:1) 0.16. IR ($CHCl_3$): 1645v*s*. $^1$H-NMR (300 MHz, $CDCl_3$): 3.59 (*sept.*, *J* = 6.9, Me$_2$C*H*CO–C(3)); 1.31 (*d*, *J* = 6.9, *Me*$_2$CHCO–C(3)). $^{13}$C-NMR (75 MHz, $C_6D_6$): 39.83 (Me$_2$*C*HCO–C(3)); 19.52 (*Me*$_2$CHCO–C(3)). EI-MS: 282 (8, $M^{+\bullet}$), 239 (100, $[M - i\text{-}Pr]^+$). Anal. calc. for $C_{19}H_{22}O_2$ (282.38): C 80.82, H 7.85; found: C 80.52, H 7.97.

*(6a*RS,*13b*SR*)-3-Chloro-5,10-diisopropyl-12-methyl-2-oxo-2*H*-cyclohept[1,7]indeno[4,5-*c*]furo[3,2-*b*]pyran-6,6a(7*H*)-dicarbonitrile* (**3c**): Blue crystals (hexane). M.p. *ca.* 250° (dec.). IR ($CHCl_3$): 2221*w*, 1795*s*, 1693*s*. $^1$H-NMR (300 MHz, $CDCl_3$): 2.80 (*sept.*, *J* = 6.8, Me$_2$C*H*–C(5)); 1.19, 0.61 (2*d*, *J* = 6.8, *Me*$_2$CH–C(5)). $^{13}$C-NMR (300 MHz, $CDCl_3$): 32.47 (Me$_2$*C*H–C(5)); 18.90, 18.73 (*Me*$_2$CH–C(5)). EI-MS: 460 and 458 (35 and 100, $M^{+\bullet}$). Anal. calc. for $C_{27}H_{23}ClN_2O_3$ (458.94): C 70.66, H 5.05, N 6.10; found: C 70.84, H 5.16, N 6.00.

*1,1′-[Carbonylbis(5-isopropyl-8-methylazulene-3,1-diyl)]bis[2-methylpropan-1-one]* (**4c**): Red crystals. M.p. 190.0–190.5° (heptane). $R_f$ (toluene/*t*-BuOMe 4:1) 0.59. IR ($CHCl_3$): 1657*s*, 1588*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 3.46 (*sept.*, *J* = 6.9, Me$_2$C*H*CO–C(1)); 1.26 (*d*, *J* = 6.9, *Me*$_2$CHCO–C(1)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 39.88 (Me$_2$*C*HCO–C(1)); 19.47 (*Me*$_2$CHCO–C(1)). CI-MS ($NH_3$): 535 (100, $[M + H]^+$). Anal. calc. for $C_{37}H_{42}O_3$ (534.73): C 83.11, H 7.92; found: C 82.70, H 8.01.

*(1*RS,*2*RS*)-1-{[7-Isopropyl-4-methyl-3-(2-methyl-1-oxopropyl)azulen-1-yl]methyl}-2-{[7-isopropyl-1-methyl-3-(2-methyl-1-oxopropyl)azulen-4-yl]methyl}-4,5-dichloro-3,6-dioxocyclohex-4-ene-1,2-dicarbonitrile* (**5c**): Red crystals. M.p. *ca.* 160° (dec.). IR ($CHCl_3$): 1709*m*, 1641*m*, and 1622*m* (C=O). $^1$H-NMR (300 MHz, $C_6D_6$): 3.30 (br. *m*, 2 Me$_2$C*H*CO–C(3′,3″)); 2.77, 2.58 (*sept.*, Me$_2$C*H*–C(7′,7″)); 1.34 (*d*, *J* = 6.8, 3 H, *Me*$_2$CH); 1.27–1.13 (*m*, 15 H, *Me*$_2$CH); 1.02, 1.01 (2*d*, *J* = 6.8, 6 H, *Me*$_2$CH). $^{13}$C-NMR (75 MHz, $C_6D_6$): 39.92, 39.24 (4 Me$_2$*C*H); 20.62, 20.55, 19.90, 19.13 (4 *Me*$_2$CH). ESI-MS (NaI): 787, 785, 783 ($[M + Na]^+$). Anal. calc. for $C_{46}H_{46}Cl_2N_2O_4$ (761.77): C 72.53, H 6.09, N 3.68; found: C 71.28, H 6.13, N 3.59.

2.4. *1-(5-Isopropyl-3,8-dimethylazulen-1-yl)-2,2-dimethylpropan-1-one* (**1d**). Products **2d**, **4d**, and **5d**. *3-(2,2-Dimethyl-1-oxopropyl)-7-isopropyl-4-methylazulene-1-carboxaldehyde* (**2d**): Red crystals. M.p. 100–101°. $R_f$ (toluene/*t*-BuOMe 6:1) 0.48. IR ($CHCl_3$): 1647v*s*. $^1$H-NMR (300 MHz, $CDCl_3$): 1.42 (*s*, Me$_3$CCO–C(3)). $^{13}$C-NMR (75 MHz, $C_6D_6$): 45.09 (Me$_3$*C*CO–C(3)); 28.62 (*Me*$_3$CCO–C(3)). EI-MS: 296 (5, $M^{+\bullet}$), 239 (100, $[M - t\text{-}Bu]^+$). Anal. calc. for $C_{20}H_{24}O_2$ (296.40): C 81.04, H 8.16; found: C 81.05, H 8.16.

*1,1′-[Carbonylbis(5-isopropyl-8-methylazulene-3,1-diyl)]bis[2,2-dimethylpropan-1-one]* (**4d**): Red crystals. M.p. 223–224° (EtOH). $R_f$ (toluene/*t*-BuOMe 6:1) 0.56. IR ($CHCl_3$): 1664*s*, 1584*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 1.41 (*d*, *J* = 6.9, *Me*$_2$CH–C(5)); 1.39 (*s*, Me$_3$CCO–C(1)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 45.17 (Me$_3$*C*CO–C(1)); 28.80 (*Me*$_3$CCO–C(1)); 28.72 (*Me*–C(8)); 24.42 (*Me*$_2$CH–C(5)). EI-MS: 562 (8, $M^{+\bullet}$), 505 (100, $[M - t\text{-}Bu]^+$), 239 (99). Anal. calc. for $C_{39}H_{46}O_3$ (562.78): C 83.23, H 8.24; found: C 83.18, H 8.25.

*(1*RS,*2*RS*)-1-{[3-(2,2-Dimethyl-1-oxopropyl)-7-isopropyl-4-methylazulen-1-yl]methyl}-2-{[3-(2,2-dimethyl-1-oxopropyl)-7-isopropyl-1-methylazulen-4-yl]methyl}-4,5-dichloro-3,6-dioxocyclohex-4-ene-*

*1,2-dicarbonitrile* (**5d**): $^1$H-NMR (300 MHz, $C_6D_6$): 2.80, 2.56 (2 *sept.*, $Me_2CH-C(7',7'')$); 1.38, 1.34 (2 *s*, $Me_3CCO-C(3',3'')$); 1.25, 1.20 (2 *d*, $J = 6.9$, $Me_2CH-C(7'')$); 1.02 (*t*-like, $J \approx 6.9$, $Me_2CH-C(7')$).

2.5. *(5-Isopropyl-3,8-dimethylazulen-1-yl)phenylmethanone* (**1e**). Products **2e** and **4e**. *3-Benzoyl-7-isopropyl-4-methylazulene-1-carboxaldehyde* (**2e**): Red crystals. M.p. 99–101° (hexane/AcOEt 10:1). $R_f$ (hexane/AcOEt 2:1) 0.37. IR ($CHCl_3$): 1647v*s*. $^1$H-NMR (300 MHz, $CDCl_3$): 7.96 (*dd* with f.s., $^3J \approx 8.0$, $^4J \approx 1.3$, $H_o$ of Ph); 7.62 (*tt*, $^3J \approx 7.4$, $^4J \approx 1.3$, $H_p$ of Ph); 7.51 (*t* with f.s., $^3J \approx 7.9$, $H_m$ of Ph). $^{13}$C-NMR (75 MHz, $CDCl_3$): 132.30 ($C_p$ of Ph); 130.50 ($C_m$ of Ph); 128.45 ($C_o$ of Ph). CI-MS ($NH_3$): 317 (100, $[M+H]^+$). Anal. calc. for $C_{22}H_{20}O_2$ (316.39): C 83.51, H 6.37; found: C 83.66, H 6.33.

*Bis(3-benzoyl-7-isopropyl-4-methylazulen-1-yl)methanone* (**4e**): Red crystals. M.p. 220–221° (EtOH). $R_f$ (hexane/AcOEt 3:1) 0.30. IR ($CHCl_3$): 2966*m*, 2931*w*, 2872*w*, 1638*m*, 1597*m*, 1579*m*, 1506*s*, 1448*s*, 1409*s*, 1386*m*, 1372*m*, 1303*w*, 1164*m*, 1132*w*, 1062*w*, 1047*w*, 1025*w*, 1002*w*, 959*m*, 941*w*, 898*w*, 845*s*, 828*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 9.85 (*d*, $^4J(6,8) = 2.1$, H–C(8)); 8.03 (*s*, H–C(2)); 7.88 (*dd* with f.s., $J_o \approx 8.0$, $J_m \approx 1.3$, $H_o$ of Ph); 7.80 (*dd*, $^3J(5,6) = 10.8$, $^4J(6,8) = 2.1$, H–C(6)); 7.58 (*d*, $^3J(5,6) = 10.9$, H–C(5)); 7.51 (*tt*, $J_o \approx 7.4$, $J_m \approx 1.3$, $H_p$ of Ph); 7.35 (*t* with f.s., $J_o \approx 7.9$, $H_m$ of Ph); 3.26 (*sept.*, $J = 6.9$, $Me_2CH-C(7)$); 2.82 (*s*, Me–C(4)); 1.42 (*d*, $J = 6.9$, $Me_2CH-C(7)$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 194.29 (Ph*C*O–C(3)); 189.12 (C=O); 150.44–126.44 (20 azulene C, 8 benzene C), 38.45 ($Me_2CH-C(7)$); 28.70 (*Me*–C(4)); 24.43 ($Me_2CH-C(7)$). CI-MS ($NH_3$): 603 (100, $[M+H]^+$). Anal. calc. for $C_{43}H_{38}O_3$ (602.77): C 85.68, H 6.35; found: C 85.45, H 6.53.

2.6. *2,2,2-Trifluoro-1-(5-isopropyl-3,8-dimethylazulen-1-yl)ethanone* (**1f**). Product **2f**. *7-Isopropyl-4-methyl-3-(2,2,2-trifluoroacetyl)azulene-1-carboxaldehyde* (**2f**). Red crystals. M.p. 73–74° (hexane). $R_f$ (toluene/*t*-BuOMe 4:1) 0.60. IR ($CHCl_3$): 1685*m*, 1659*s*. $^1$H-NMR (300 MHz, $CDCl_3$): 10.27 (*s*, CHO); 10.05 (*d*, $^4J(6,8) = 2.1$, H–C(8)); 8.63 (*q*, $^5J(2,F) = 2.0$, H–C(2)); 7.98 (*dd*, $^3J(5,6) = 10.9$, $^4J(6,8) = 2.2$, H–C(6)); 7.89 (*d*, $^3J(5,6) = 10.9$, H–C(5)); 3.31 (*sept.*, $Me_2CH-C(7)$); 2.94 (*s*, Me–C(4)); 1.45 (*d*, $Me_2CH-C(7)$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 187.16 (CHO); 176.44 (*q*, $^2J(F,C=O) = 33.9$. $CF_3CO$); 156.15–119.95 (10 azulene C with C(2) at 147.74 (*q*, $^4J(F,C(2)) = 3.4$)); 117.30 (*q*, $^1J(C,F) = 289$, $CF_3CO$); 38.53 ($Me_2CH-C(7)$); 29.18 (*Me*–C(4)); 24.36 ($Me_2CH-C(7)$). EI-MS: 308 (29, $M^{+\cdot}$), 239 (100, $[M-CF_3]^+$). Anal. calc. for $C_{17}H_{15}F_3O_2$ (308.30): C 66.23, H 4.90; found: C 66.17, H 4.97.

2.7. *1-(3,8-Dimethylazulen-1-yl)ethanone* (**1g**). Products **2g**, **3g**, **4g**, and **5g**. *3-Acetyl-4-methylazulene-1-carboxaldehyde* (**2g**): Red crystals. M.p. 149–150° (EtOH). $R_f$ (toluene/*t*-BuOMe 4:1) 0.53. IR ($CHCl_3$): 1652v*s*. $^1$H-NMR (300 MHz, $CDCl_3$): 10.31 (*s*, CHO); 9.84 (*dd*, $^3J(7,8) = 9.7$, $^4J(6,8) = 1.2$, H–C(8)); 8.49 (*s*, H–C(2)); 7.92 (*t* with f.s., $^3J(5,6) \approx {}^3J(6,7) = 9.6$, H–C(6)); 7.77 (*d*, $^3J(5,6) = 10.1$, H–C(5)); 7.73 (*t*, $^3J(6,7) \approx {}^3J(7,8) = 9.6$, H–C(7)); 2.96 (*s*, Me–C(4)); 2.79 (*s*, MeCO–C(3)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 197.40 (CHO); 186.66 (Me*C*O–C(3)); 154.18–124.09 (10 azulene C); 30.50 (*Me*CO–C(3)); 29.37 (*Me*–C(4)). EI-MS: 212 (24, $M^{+\cdot}$), 198 (55, $[M-CH_2]^+$), 197 (100, $[M-Me]^+$). Anal. calc. for $C_{14}H_{12}O_2$ (212.25): C 79.22, H 5.70; found: C 79.24, H 5.96.

*(6a*RS,*13b*SR*)-3-Chloro-5,12-dimethyl-2-oxo-2*H*-cyclohept[1,7]indeno[4,5-*c*]furo[3,2-*b*]pyran-6,6a(7*H*)-dicarbonitrile* (**3g**): Blue crystals (toluene/hexane). M.p. >100° (dec.). $R_f$ (toluene/*t*-BuOMe 4:1) 0.73. IR ($CHCl_3$): 2223*w* (C≡N), 1796v*s* (C=O), 1691*s*, 1632*m*, 1361*s*, 987*s*. $^1$H-NMR (600 MHz, $CDCl_3$): 8.35 (*d*, $^3J(10,11) = 9.2$, H–C(11)); 7.74 (*t*, $^3J(10,11) \approx {}^3J(9,10) = 10.0$, H–C(10)); 7.48 (*s*, H–C(13)); 7.35 (*t*, $^3J(9,10) \approx {}^3J(8,9) = 9.8$, H–C(9)); 7.27 (*d*, $^3J(8.9) = 10.1$, H–C(8)); 4.13, 3.93 (*AB*, $^2J(A,B) = 16.8$, $CH_2$(7)); 2.62 (*s*, Me–C(12)); 2.09 (*s*, Me–C(5)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 164.68 (C(5)); 163.70 (C(2)=O); 161.45 (C(3a)); 138.67–124.24 (9 C); 115.34 (N≡*C*–C(6a)); 113.06 (N≡*C*–C(6)); 110.77 (C(13a)); 102.72 (C(3)); 89.61 (C(6)); 74.18 (C(13b)); 40.20 (C(6a)); 37.24 (C(7)); 19.19 (*Me*–C(5)); 12.54 (*Me*–C(12)). EI-MS: 390 and 388 (34 and 100, $M^{+\cdot}$), 257 (39). Anal. calc. for $C_{22}H_{13}ClN_2O_3$ (388.81): C 67.96, H 3.37, Cl 9.12, N 7.20; found: C 68.04, H 3.40, Cl 9.08, N 7.08.

*1,1'-[Carbonylbis(8-methylazulene-3,1-diyl)]bis[ethanone]* (**4g**): Dark red crystals. M.p. 236–238° (AcOEt). $R_f$ (toluene/*t*-BuOMe 4:1) 0.21. IR ($CHCl_3$): 1660*s*, 1595*m*, 1563*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 9.84 (*dd*, $^3J(4,5) = 9.9$, $^4J(4,6) = 1.3$, H–C(4)); 8.32 (*s*, H–C(2)); 7.92 (*td*, $^3J(5,6) \approx {}^3J(6,7) = 10.2$, H–C(6)); 7.69 (*d*, $^3J(6,7) = 10.4$, H–C(7)); 7.61 (*t*, $^3J(5,6) \approx {}^3J(4,5) = 9.6$, H–C(5)); 2.98 (*s*, Me–C(8)); 2.71 (*s*, MeCO–C(1)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 197.78 (Me*C*O–C(1)); 189.01 (C=O); 153.26–126.99 (20 azulene C); 30.70 (*Me*CO–C(1)); 29.41 (*Me*–C(8)). EI-MS: 394 (100, $M^{+\cdot}$), 379 (74, $[M-Me]^+$), 351 (54, $[M-MeCO]^+$), 268 (31), 253 (66). Anal. calc. for $C_{27}H_{22}O_3$ (394.47): C 82.21, H 5.62; found: C 81.23, H 5.45.

*(1*RS,*2*RS*)-1-[(3-Acetyl-4-methylazulen-1-yl)methyl]-2-[(3-acetyl-1-methylazulen-4-yl)methyl]-4,5-dichloro-3,6-dioxocyclohex-4-ene-1,2-dicarbonitrile* (**5g**): Dark red powder. M.p. >300°. $R_f$ (toluene/*t*-BuOMe 4:1) 0.37. $^1$H-NMR (300 MHz, $C_6D_6$): 7.70 (*d* with f.s., $^3J(7'',8'')=9.7$, H–C(8'')); 7.55 (*d* with f.s., $^3J(7',8')=9.7$, H–C(8')); 7.52 (*s*, H–C(2'')); 7.50 (*s*, H–C(2')); 7.11–6.62 (H–C(5',5''), H–C(6',6''), H–C(7',7'')); 5.66, 4.50 (*AB*, $^2J(A,B)=13.7$, $CH_2$–C(2)); 3.85, 3.65 (*AB*, $^2J(A,B)=15.1$, $CH_2$–C(1)); 2.63 (*s*, Me–C(4')); 2.34 (*s*, MeCO–C(3')); 2.33 (*s*, MeCO–C(3'')); 2.09 (*s*, Me–C(1'')). $^{13}$C-NMR (150 MHz, $C_6D_6$): 195.54 (Me*C*O–C(3'')); 193.62 (Me*C*O–C(3')); 179.38 (C(6)=O); 176.09 (C(3)=O); 46.81 (*C*$H_2$–C(2)); 36.65 (*C*$H_2$–C(1)); 30.72 (*Me*CO–C(3'')); 30.23 (*Me*CO–C(3')); 29.16 (*Me*–C(4')); 12.60 (*Me*–C(1'')).

2.8. *1-(5-Ethyl-3,8-dimethylazulen-1-yl)ethanone* (**1h**). Products **2h**, **3h**, **4h**, and **5h**. *3-Acetyl-7-ethyl-4-methylazulene-1-carboxaldehyde* (**2h**): Red crystals. M.p. 80.5–82.5° (EtOH). $R_f$ (toluene/*t*-BuOMe 4:1) 0.37. IR ($CHCl_3$): 1649v*s*. $^1$H-NMR (300 MHz, $CDCl_3$): 10.25 (*s*, CHO); 9.81 (*d*, $^4J(6,8)=2.0$, H–C(8)); 8.58 (*s*, H–C(2)); 7.86 (*dd*, $^3J(5,6)=10.8$, $^4J(6,8)=2.0$, H–C(6)); 7.72 (*d*, $^3J(5,6)=10.8$, H–C(5)); 2.97 (*q*, $J=6.8$, MeC$H_2$–C(7)); 2.88 (*s*, Me–C(4)); 2.74 (*s*, MeCO–C(3)); 1.40 (*t*, $J=7.1$, *Me*$CH_2$–C(7)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 196.74 (CHO); 186.59 (Me*C*O–C(3)); 33.61 (Me*C*$H_2$–C(7)); 30.23 (*Me*CO–C(3)); 29.08 (*Me*–C(4)); 16.67 (*Me*$CH_2$–C(7)). EI-MS: 240 (29, $M^{+\cdot}$), 225 (100, $[M-Me]^+$). Anal. calc. for $C_{16}H_{16}O_2$ (240.30): C 79.97, H 6.71; found: C 79.65, H 6.64.

*(6a*RS,*13b*SR*)-3-Chloro-10-ethyl-5,12-dimethyl-2-oxo-2*H*-cyclohept[1,7]indeno[4,5-*c*]furo[3,2-*b*]pyran-6,6a(7*H*)-dicarbonitrile* (**3h**): Blue crystals (toluene). M.p. 111.0–111.5°. $R_f$ (toluene/*t*-BuOMe 4:1) 0.82. IR ($CHCl_3$): 2222*w* (C≡N), 1793v*s* (C=O), 1710*m*, 1691*s*, 1631*m*. $^1$H-NMR (600 MHz, $CDCl_3$): 2.94 (*q*, $J=7.0$, MeC$H_2$–C(10)); 2.62 (*s*, Me–C(12)); 2.11 (*s*, Me–C(5)); 1.40 (*t*, $J=7.0$, *Me*$CH_2$–C(10)). $^{13}$C-NMR (150 MHz, $CDCl_3$): 164.59 (C(5)); 163.77 (C(2)=O); 161.49 (C(3a)); 115.41 (N≡*C*–C(6a)); 113.15 (N≡*C*–C(6)); 109.30 (C(13a)); 102.60 (C(3)); 89.65 (C(6)); 74.32 (C(13b)); 40.17 (C(6a)); 37.02 (C(7)); 34.37 (Me*C*$H_2$–C(10)); 19.18 (Me–C(5)); 17.18 (*Me*$CH_2$–C(10)); 12.51 (*Me*–C(12)). CI-MS ($NH_3$): 419 and 417 (36 and 100, $[M+H]^+$). Anal. calc. for $C_{24}H_{17}ClN_2O_3$ (416.86): C 69.15, H 4.11, N 6.72; found: C 69.00, H 4.12, N 6.55.

*1,1'-[Carbonylbis(5-ethyl-8-methylazulene-3,1-diyl)]bis[ethanone]* (**4h**): Red crystals. M.p. 177–178° (EtOH). $R_f$ (toluene/*t*-BuOMe 4:1) 0.27. IR ($CHCl_3$): 1663*s*, 1596*m*, 1506*s*. $^1$H-NMR (300 MHz, $CDCl_3$): 3.07 (*q*, $J=7.5$, MeC$H_2$–C(5)); 2.93 (*s*, Me–C(8)); 2.64 (*s*, MeCO–C(1)); 1.36 (*t*, $J=7.5$, *Me*$CH_2$–C(5)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 196.97 (Me*C*O–C(1)); 189.11 (C=O); 33.72 (Me*C*$H_2$–C(5)); 30.41 (*Me*CO–C(1)); 29.15 (Me–C(8)); 16.73 (*Me*$CH_2$–C(5)). EI-MS: 450 (66, $M^{+\cdot}$), 435 (61, $[M-Me]^+$), 241 (100), 240 (74), 221 (34). Anal. calc. for $C_{31}H_{30}O_3$ (450.58): C 82.64, H 6.71; found: C 81.38, H 6.56.

*(1*RS,*2*RS*)-1-[(3-Acetyl-7-ethyl-4-methylazulen-1-yl)methyl]-2-[(3-acetyl-7-ethyl-1-methylazulen-4-yl)methyl]-4,5-dichloro-3,6-dioxocyclohex-4-ene-1,2-dicarbonitrile* (**5h**): Dark red crystals (AcOEt). M.p. 165.5–166.0°. $R_f$ (toluene/*t*-BuOMe 4:1) 0.55. IR ($CHCl_3$): 1708*s*, 1649*m*, and 1626*m* (C=O). $^1$H-NMR (300 MHz, $C_6D_6$): 5.62, 4.53 (*AB*, $^2J(A,B)=13.8$, $CH_2$–C(2)); 3.93, 3.78 (*AB*, $^2J(A,B)=15.0$, $CH_2$–C(1)); 2.69 (*s*, Me–C(4')); 2.49 (*q* with f.s., $J\approx7.5$, MeC$H_2$–C(7'')); 2.36 (*q*, partially covered by the two signals of MeCO, $J\approx7.5$, MeC$H_2$–C(7')); 2.36 (2*s*, separated by <0.01 ppm, MeCO–C(3',3'')); 2.19 (*s*, Me–C(1'')); 1.15 (*t*, $J\approx7.5$, *Me*$CH_2$–C(7'')); 0.98 (*t*, $J\approx7.5$, *Me*$CH_2$–C(7')). $^{13}$C-NMR (75 MHz, $C_6D_6$): 195.33 (Me*C*O–C(3'')); 193.53 (Me*C*O–C(3')); 179.31 (C(6)=O); 175.99 (C(3)=O); 115.35 (N≡*C*–C(1)); 114.87 (N≡*C*–C(2)); 46.83 (*C*$H_2$–C(2)); 37.10 (*C*$H_2$–C(1)); 33.38 (Me*C*$H_2$–C(7')); 33.19 (Me*C*$H_2$–C(7'')); 30.54 (*Me*CO–C(3'')); 30.00 (*Me*CO–C(3')); 28.87 (*Me*–C(4')); 16.22 (*Me*$CH_2$–C(7'')); 16.06 (*Me*$CH_2$–C(7')); 12.69 (*Me*–C(1'')). ESI-MS: 703, 701, and 699 ($[M+Na]^+$), 475 ($[(M-C_{16}H_{17}O)+Na]^+$). Anal. calc. for $C_{40}H_{34}Cl_2N_2O_4$ (677.63): C 70.90, H 5.06, N 4.13; found: C 70.21, H 5.04, N 4.07.

3. *Mechanistic Investigations on Triketone* **4** *Formation.* 3.1. *Oxidation of 1,1'-[Ethane-1,2-diylbis(5-isopropyl-8-methylazulene-3,1-diyl)]bis[ethanone]* (**15a**) *with DDQ in Aqueous Acetone.* 3.1.1. *Synthesis of* **15a** (*cf.* [11]). 3.1.1.1. *1-[3-(Dimethylamino)-5-isopropyl-8-methylazulen-1-yl)ethanone.* A mixture of AcOH (4 ml), paraformaldehyde (0.84 g, 2.80 mmol), and *N*,*N*,*N'*,*N'*-tetramethylmethanediamine (0.28 ml, 3.77 mmol) was heated at 80° until a clear soln. was formed (*ca.* 20 min). This soln. was added with a syringe to a soln. of 1-(5-isopropyl-8-methylazulen-1-yl)ethanone (1.022 g, 4.47 mmol; m.p. 74.5–75.5°; formed on decarbonylation of **2a** with *Wilkinson*'s catalyst in toluene at 110° (*cf.* [6])) in

$CH_2Cl_2$ (23 ml) at 0°. After stirring for 1 h at r.t., an additional small amount of *N,N,N′,N′*-tetramethylmethanediamine (0.05 ml, 0.37 mmol) was added, and stirring was continued for 0.5 h until no starting azulene was recognizable by TLC. Usual workup gave, after bulb-to-bulb distillation under high vacuum, pure product (1.27 g, 99%). Violet crystals. M.p. 71–72°.

3.1.1.2. *Ammonium Iodide Formation*. The ethanone from *Exper. 3.1.1.1* (1.27 g) was dissolved in EtOH (35 ml), and MeI (1.20 ml, 12.80 mmol) was added. The soln. was stirred for 2 h at r.t. EtOH was distilled off and the residue dried *in vacuo*: corresponding ammonium iodide (1.90 g). Violet crystals. M.p. >80° (dec.).

3.1.1.3. *Reduction of the Ammonium Iodide*. The ammonium iodide from *Exper. 3.1.1.2* (0.070 g, 0.16 mmol) was dissolved in DMF (10 ml), and Zn dust (0.354 g, 5.35 mmol; *Fluka*, purum) was added[14]). The mixture was heated under stirring during 2 h at 80°. After cooling, $CH_2Cl_2$ (50 ml) was added, and the soln. was filtered and then washed three times with $H_2O$ (150 ml). After drying and evaporation, the residue (0.082 g, green-blue oil) was separated by prep. TLC ($SiO_2$): pure **15a** (0.018 g, 46%). Blue crystals. M.p. 226–228° (acetone). $R_f$ (*Alox*, hexane/AcOEt 2:1) 0.46. IR ($CHCl_3$): 2965*w*, 1644*s*, 1578*w*, 1521*m*, 1491*w*, 1407*s*, 1373*m*, 932*w*, 861*w*, 804*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 8.15 (*d*, $^4J(4,6) = 2.1$, H–C(4)); 7.89 (*s*, H–C(2)); 7.51 (*dd*, $^3J(6,7) = 11.0$, $^4J(4,6) = 2.0$, H–C(6)); 7.30 (*d*, $^3J(6,7) = 11.0$, H–C(7)); 3.43 (*s*, $CH_2CH_2$); 2.94 (*sept.*, $J = 6.9$, $Me_2CH$–C(5)); 2.87 (*s*, Me–C(8)); 2.66 (*s*, MeCO–C(1)); 1.25 (*d*, $J = 6.9$, $Me_2CH$–C(5)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 196.48 (Me*C*O–C(1)); 149.00–127.51 (20 azulene C); 37.92 ($Me_2CH$–C(5)); 30.42 (*Me*CO–C(1)); 29.14 ($CH_2CH_2$); 28.62 (*Me*–C(8)); 24.39 ($Me_2CH$–C(5)). CI-MS ($NH_3$): 479 (100, $[M+H]^+$), 239 (8). Anal. calc. for $C_{34}H_{38}O_2$ (478.67): C 85.31, H 8.00; found: C 85.03, H 7.78.

*Oxidation of* **15a** (*cf. Scheme 8*). Products **16a** and **4a**. *1,2-Bis(3-acetyl-7-isopropyl-4-methylazulen-1-yl)ethane-1,2-dione* (**16a**): Red crystals. M.p. 193–195° (MeOH). $R_f$ (*Alox*, hexane/AcOEt 2:1) 0.36. IR (KBr): 2962*m*, 2929*w*, 2870*w*, 1666*s*, 1613*s*, 1505*s*, 1441*s*, 1408*s*, 1393*s*, 1369*s*, 1305*w*, 1207*m*, 1181*s*, 1146*w*, 1061*w*, 1029*w*, 960*m*, 879*m*, 826*w*, 727*s*, 697*m*, 660*w*, 608*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 10.30 (*d*, $^4J(6,8) = 2.1$, H–C(8)); 8.45 (*s*, H–C(2)); 7.91 (*dd*, $^3J(5,6) = 10.9$, $^4J(6,8) = 2.1$, H–C(6)); 7.77 (*d*, $^3J(5,6) = 10.9$, H–C(5)); 3.34 (*sept.*, $J = 6.9$, $Me_2CH$–C(7)); 2.91 (*s*, Me–C(4)); 2.66 (*s*, MeCO–C(3)); 1.47 (*d*, $J = 6.9$, $Me_2CH$–C(7)). $^{13}$C-NMR (150 MHz, $CDCl_3$): 197.04 (Me*C*O–C(3)); 191.04 (C(1,2)=O); 153.85–118.71 (20 azulene C); 38.55 ($Me_2CH$–C(7)); 30.29 (*Me*CO–C(3)); 29.16 (*Me*–C(4)); 24.51 ($Me_2CH$–C(7)). ESI-MS (NaI): 529 (100, $[M+Na]^+$). Anal. calc. for $C_{34}H_{34}O_4$ (506.64): C 80.60, H 6.76; found: C 80.40, H 6.80.

3.2. *Oxidation of* **1a** *in the Presence of 3-Acetyl-7-isopropyl-4-methylazulene-1-carboxylic Acid* (**17a**). 3.2.1. *Synthesis of* **17a**. To a soln. of carboxaldehyde **2a** (0.177 g, 0.70 mmol) in acetone/$H_2O$ 9:1 (13.5 ml) were added $Na_2CO_3$ (0.264 g, 2.49 mmol) and then gradually $KMnO_4$ (0.283 g, 1.79 mmol). The mixture was stirred for 1 h at r.t. The suspension was then treated with 10% aq. ascorbic acid. $H_2O$ and acetone were distilled off. The residue was distributed between *t*-BuOMe (40 ml) and $H_2O$ (40 ml), and ascorbic acid was added until two cleanly separated phases were formed. The aq. phase was two additional times washed with *t*-BuOMe (20 ml each). The combined org. layers were washed with $H_2O$ (5 × 30 ml) and then dried ($Na_2CO_3$). The residue of the *t*-BuOMe soln. was purified by CC ($SiO_2$ (30 g), toluene/EtOH 10:1): **17a** (0.143 g, 76%)[15]). Red-violet crystals. M.p. 184–189° (pentane-2,4-dione). $R_f$ (hexane/*t*-BuOMe 1:1) 0.16. IR ($CHCl_3$): 3528*w*, 2967*m*, 2933*m*, 2873*w*, 2728*w*, 2587*w*, 1652*vs*, 1528*w*, 1509*s*, 1456*s*, 1425*m*, 1409*s*, 1370*s*, 1254*w*, 1184*m*, 1143*w*, 1087*w*, 1071*w*, 1047*w*, 1015*w*, 966*w*, 953*w*, 911*w*, 900*w*, 871*w*, 827*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 12.0 (very br. *s*, OH); 9.95 (*d*, $^4J(6,8) = 2.0$, H–C(8)); 8.76 (*s*, H–C(2)); 7.81 (*dd*, $^3J(5,6) = 10.9$, $^4J(6,8) = 2.0$, H–C(6)); 7.65 (*d*, $^3J(5,6) = 10.9$, H–C(5)); 3.27 (*sept.*, $J = 6.9$, $Me_2CH$–C(7)); 2.93 (*s*, Me–C(4)); 2.78 (*s*, MeCO–C(3)); 1.43 (*d*, $J = 6.9$, $Me_2CH$–C(7)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 196.98 (Me*C*O–C(3)); 170.46 (COOH); 151.58–113.40 (10 azulene C); 38.48 ($Me_2CH$–C(7)); 30.18 (*Me*CO–C(3)); 29.16 (*Me*–C(4)); 24.48 ($Me_2CH$–C(7)).

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[14]) The yield of **15a** dropped to 5% when the reduction of the iodide was performed with activated Zn dust (pre-treated by washing with dil. HCl soln).

[15]) We applied the described procedure to the oxidation of a number of further azulene-1-carboxaldehydes to the corresponding 1-carboxylic acids (*cf. Table 6*). The presence of $Na_2CO_3$ is essential for the realization of acceptable yields of the acids.

Table 6. *Formation of Azulene-1-carboxylic Acids* **17** *by Oxidation of the Corresponding Azulene-1-carbaldehydes* **2**[a])

| | Molar ratios | | | Reaction conditions | | | | | Physical data | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Reactant | $Na_2CO_3$ | $KMnO_4$ | Solvent [*v*/*v*] | Conc. [solv./react.][b]) | Time [h] | Temp. [°] | Yield [%] | M.p. [°] | $\delta$(C=O) [ppm][c]) |
| **17a** | 1 | 3.6 | 2.6 | acetone/$H_2O$ 9 : 1 | 75 : 1 | 1 | r.t. | 76 | 184–189[d]) | 196.98 |
| **17a** | 1 | – | 4.3 | acetone/$H_2O$ 9 : 1 | 63 : 1 | 2 | r.t. | 59 | – | – |
| **17e** | 1 | 3.1 | 4.2 | acetone/$H_2O$ 9 : 1 | 64 : 1 | 3 | 0 | 85 | 202–204[e]) | 194.28 |
| **17e** | 1 | – | 4.2 | acetone/$H_2O$ 9 : 1 | 54 : 1 | 4.5 | 0 | 57 | – | – |
| **17d** | 1 | 3.2 | 4.1 | acetone/$H_2O$ 9 : 1 | 57 : 1 | 2.5 | 0 | 95 | 226–227[f]) | 212.23 |
| **17l**[g]) | 1 | 2.8 | 4.5 | acetone/$H_2O$ 9 : 1 | 75 : 1 | 3.5 | 0 | 71 | 173–174[f]) | – |
| **17g** | 1 | 3.2 | 5.0 | acetone/$H_2O$ 9 : 1 | 79 : 1 | 3.3 | 0 | 73 | 212–214 | 197.88[h]) |

[a]) With the exception of **17l**, the structures of the products **17a**, **17e**, **17d**, and **17g** correspondent to those of the starting material **2a**, **2e**, **2d**, and **2g**, *i.e.*, 3-acetyl-7-isopropyl-4-methylazulene-1-carboxylic acid (**17a**), 3-benzoyl-7-isopropyl-4-methylazulene-1-carboxylic acid (**17e**), 3-(2,2-dimethyl-1-oxopropyl)-7-isopropyl-4-methylazulene-1-carboxylic acid (**17d**), and 3-acetyl-4-methylazulene-1-carboxylic acid (**17g**), resp. [b]) Solvent [ml], reactant [g]. [c]) $CDCl_3$. [d]) From pentane-2,4-dione. [e]) From MeOH. [f]) From toluene. [g]) 7-Isopropyl-4-methylazulene-1-carboxylic acid (**17l**). [h]) ($D_6$)DMSO.

CI-MS ($NH_3$): 271 (100, $[M+H]^+$). Anal. calc. for $C_{17}H_{18}O_3$ (270.33): C 75.53, H 6.71; found: C 75.52, H 6.72.

3.2.2. *Oxidation of* **1a** *in the Presence of* **17a** (*cf. Scheme 9*). Products **2a**, **4a**, and **18a**. *1,1-[Methylenebis(5-isopropyl-8-methylazulene-3,1-diyl)]bis[ethanone]* (**18a**): Red crystals. $R_f$ (hexane/AcOEt 3:1) 0.13. IR ($CHCl_3$): 2965*m*, 2931*w*, 2871*w*, 1643*s*, 1521*m*, 1464*w*, 1408*s*, 1373*m*, 1303*w*, 959*w*, 918*w*, 867*w*, 819*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 8.42 (*d*, $^4J$(4,6) = 2.1, H–C(4)); 7.83 (*s*, H–C(2)); 7.57 (*dd*, $^3J$(6,7) = 11.0, $^4J$ (4,6) = 2.1, H–C(6)); 7.35 (*d*, $^3J$ (6,7) = 11.0, H–C(7)); 4.73 (*s*, $CH_2$); 3.05 (*sept.*, *J* = 6.9, $Me_2CH$–C(5)); 2.89, (*s*, Me–C(8)); 2.62 (*s*, MeCO–C(1)); 1.27 (*d*, *J* = 6.9, $Me_2$CH–C(5)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 196.63 (Me*C*O–C(1)); 149.28 – 126.86 (20 azulene C); 38.01 ($Me_2$*C*H–C(5)); 30.40 (*Me*CO–C(1)); 28.64 (*Me*–C(8)); 26.14 ($CH_2$); 24.47 ($Me_2$CH–C(5)). EI-MS: 464 (99, $M^{+\cdot}$), 449 (39, $[M-Me]^+$), 421 (100, $[M-MeCO]^+$), 372 (39), 325 (21), 217 (15). Anal. calc. for $C_{33}H_{36}O_2$ (464.65): C 85.30, H 7.81; found: C 85.21, H 7.80.

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