A New Method for the Synthesis of Nonsymmetrically Substituted Bis(azulen-1-yl) Ketones

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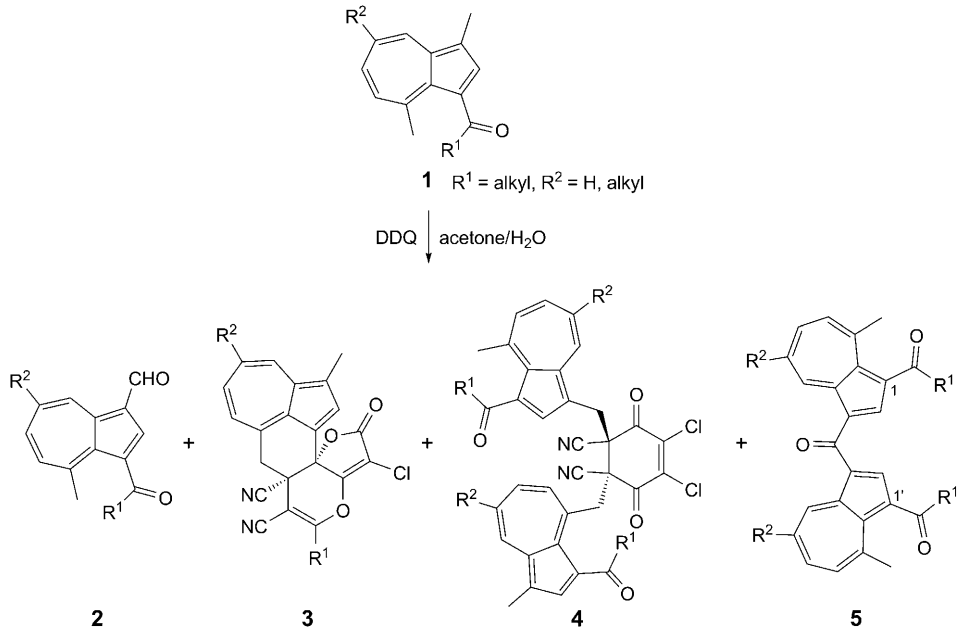
The 1-(3-methylazulen-1-yl)alkan-1-ones, when oxidized with excess 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (=4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile; DDQ) in aqueous acetone in the presence of 1-(3-demethylazulen-1-yl)alkan-1-ones, form the corresponding unsymmetrically substituted bis(3-acylazulen-1-yl)methanones in good to excellent yields (*Schemes 4*, *5*, *7*, and *10*). Intermediates are the corresponding disubstituted methane derivatives, which are formed by radical and radical-cation recombination (*Scheme 6*). The 1-(3-methylazulen-1-yl)alkan-1-ones can as well be coupled oxidatively with azulene itself, benz[*a*]azulene, or 1,3-dimethoxybenzene (*Schemes 9–11*).

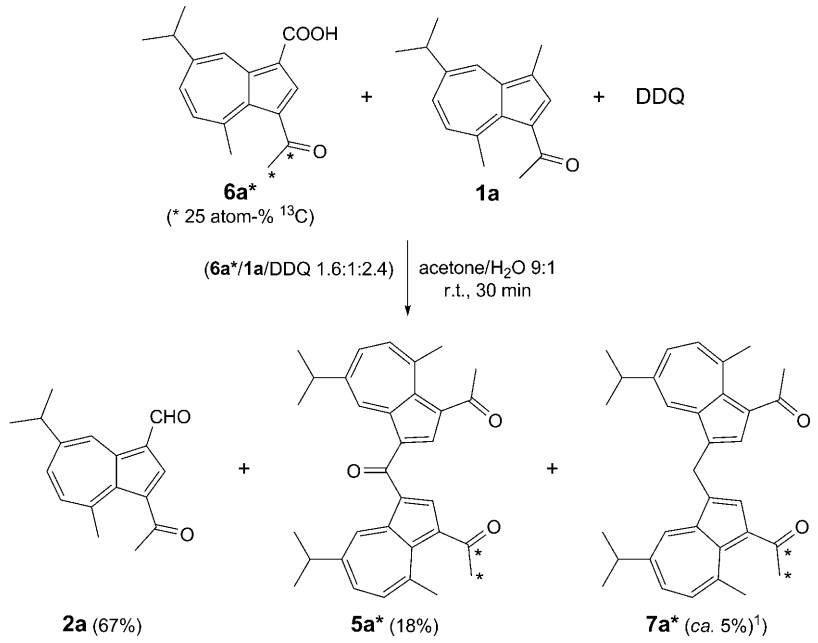
Introduction. – In the preceding communication, we reported on the oxidation of 1-(3,8-dimethylazulen-1-yl)alkan-1-ones **1** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (=4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile; DDQ) in aqueous acetone [1]. Beside the azulene-1-carboxaldehydes **2**, the expected products [2], we isolated in small amounts the pentacyclic compounds **3** and their precursors **4** and, in addition, the symmetrically substituted 1,1′-[(carbonylbis(8-methylazulene-3,1-diyl)]-bis[alkan-1-ones] (=bis(3-acyl-4-methylazulen-1-yl)methanones) **5** (*Scheme 1*). The observation that the formation of the latter compounds seemed to be dependent on the appearance of the corresponding carboxylic acids of **2** in the reaction as well as the possibility to base on this finding a general procedure for the synthesis of nonsymmetrically substituted bis(azulen-1-yl)methanones motivated us to study the mechanism of the formation of compounds of type **5** in more detail. We report in the following on these studies.

Synthesis of Nonsymmetrically Substituted Bis(azulen-1-yl)methanones. – The oxidation of **1a** (R^1 = Me, R^2 = i-Pr; *Scheme 1*) in the presence of the corresponding azulene-1-carboxylic acid **6a** with DDQ in aqueous acetone gave the triketone **5a** in a yield of 26%, accompanied by 6% of its methane precursor **7a** [1] (see *Scheme 2* for the corresponding labeled compounds). The combined yields of **5a** and **7a** of less than 50% gave, therefore, no unequivocal information on the involvement of acid **6a** in their formation. So we repeated the experiment with the ^{13}C-labeled acid **6a*** and isolated indeed the ^{13}C-labeled triketone **5a*** with almost half the percentage of label in the Ac groups on grounds of symmetry (*Scheme 2*). This experiment demonstrated that corresponding azulene-1-carboxylic acids are indeed precursors of the triketones, so

Scheme 1



Scheme 2

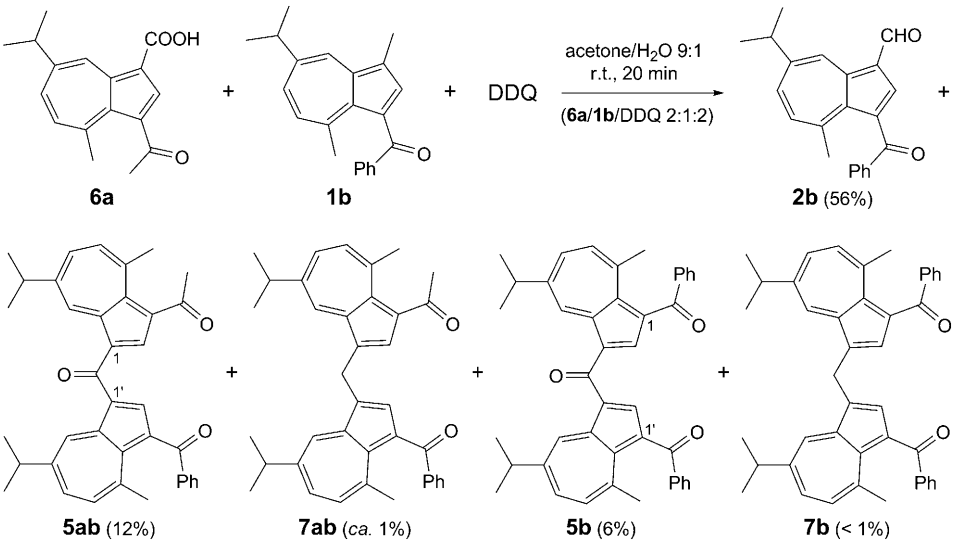


1) Proof of presence by TLC, but not isolated.

that on this way, the synthesis of methanones with two different azulenyl residues is possible.

However, a cross-experiment of oxidation with DDQ, acid **6a**, and the (azulen-1-yl)phenylmethanone **1b** failed more or less since the nonsymmetrically substituted methanone **5ab** was isolated in a yield of only 12%, accompanied by *ca.* 1% of its methane precursor **7ab** (*Scheme 3*). Main product was the azulene-1-carboxaldehyde **2b**, and also the symmetrically substituted triketone **5b** was found in 6% yield.

Scheme 3



These results were not very encouraging, so we argued that the intermediate azulene-1-carboxylic acids react too sluggishly with the 1-acylazulenyl-3-methyl[2]) cations, and they may decarboxylate to the corresponding (azulen-1-yl)alkan-1-ones before further reactions take place. Therefore, we treated 1-(5-isopropyl-3,8-dimethylazulen-1-yl)ethanone (= 3-acetylguaiazulene; **1a**) with its 3-demethyl compound **1c** in the presence of DDQ in aqueous acetone. The result was amazing since the symmetrically substituted methanone **5a** was now the main product (*Scheme 4*) and the oxidized azulene-1-carboxaldehyde **2a** was only present in trace amount. The yield of methanone **5a** could be increased to 80% by doubling the molar amount of DDQ. Similar results were obtained on DDQ oxidation of **1b** in the presence of twice the molar amount of its 3-demethyl derivative **1d** (*Scheme 4*). In this case, the symmetric methanone **5b** was obtained in a reasonable yield of 64%, beside small amounts of azulene-1-carboxaldehyde **2b**.

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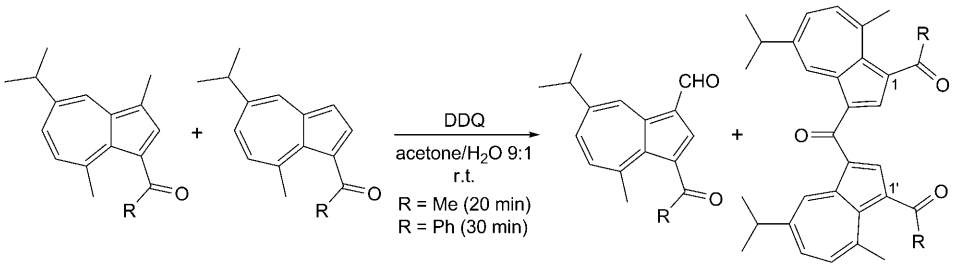
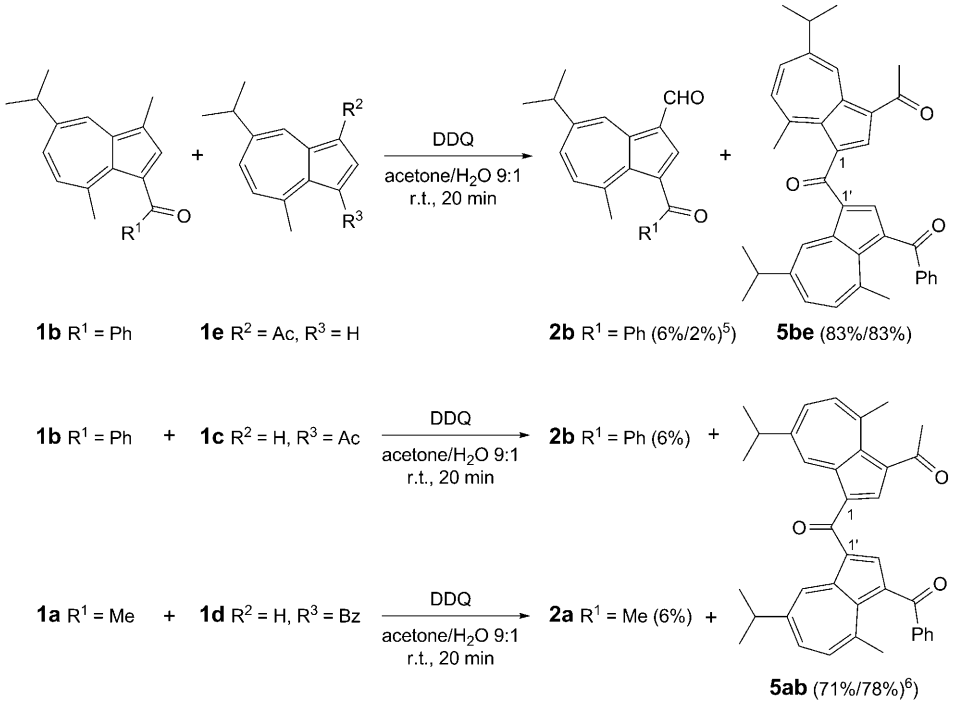
[2]) For convenience, the locant in the names of the type 1-acylazulen-3-methyl refers to the positions of the acyl and Me groups in the starting azulene derivative.

Scheme 4



Scheme 5



These experimental results gave an excellent basis for the aimed synthesis of nonsymmetrical bis(azulen-1-yl) ketones as displayed in *Scheme 5*. The observation that the formation of the azulene-1-carboxaldehydes **2** is strongly reduced in the

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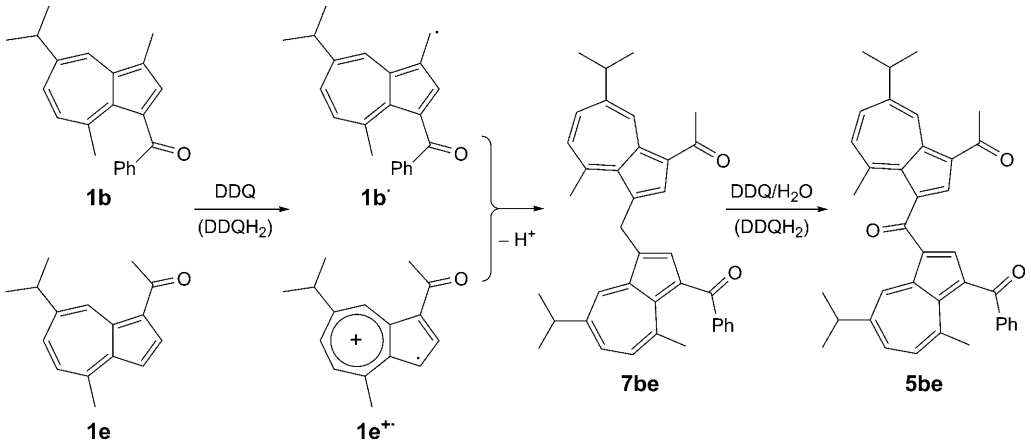
3) First/second number, molar ratio of reactants 1:2:4/1:2:8.
4) Molar ratio of reactants 1:2:8.
5) First number, molar ratio of reactants 1:2:4; second number 1:4:4.
6) First yield for **1b** + **1c**; second yield for **1a** + **1d**; molar ratio of reactants in both cases 1:2:8.

presence of the 3-demethylazulenes **1c**–**1e** in aqueous acetone speaks for the fact that the generation of (3-acylazulen-1-yl)methyl cations are not involved in the formation of the bis(azulen-1-yl) ketones as we have postulated in the preceding report [1].

We assume, therefore, that the ketone formation is based on the recombination of azulene radical cations and azulen-1-ylmethyl radicals as depicted in *Scheme 6* for the oxidative coupling of **1b** with **1e**. Crucial intermediates are the corresponding bis(azulenyl)methanes **7**, which are then oxidized by DDQ to the bis(azulen-1-yl)methanones **5**[7]). The global reaction ending with the formation of **5** needs, therefore, at minimum two moles of DDQ.

Scheme 6



In view of further evidence for the proposed coupling mechanism, we treated 1-(azulen-1-yl)ethanone (**1g**) under our standard conditions with 1-(5-isopropyl-3,8-dimethylazulen-1-yl)ethanone (**1a**). In this case, we obtained an almost 1:1 mixture of **2a** and the expected triketone **5ag** (*Scheme 7*). The 1-(4,6,8-trimethylazulen-1-yl)ethanone (**1h**) as well as the methyl 4,6,8-trimethylazulene-1-carboxylate (**1i**), on

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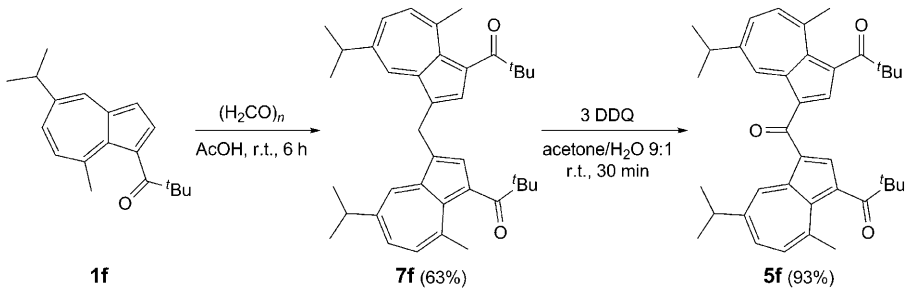
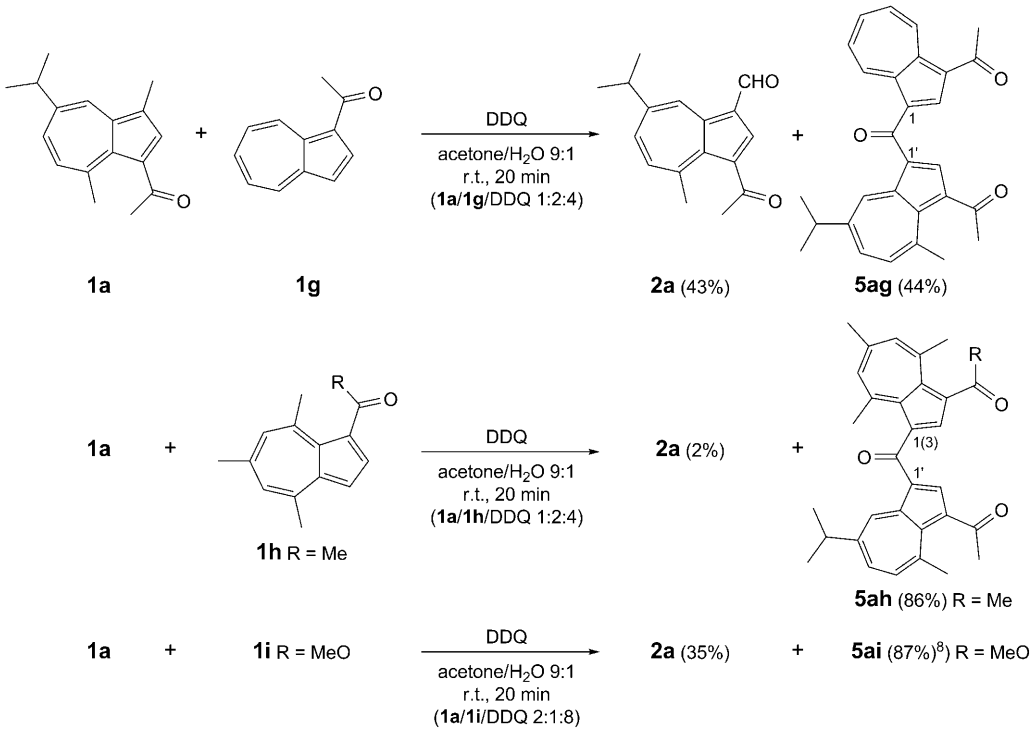
[7]) We checked the general ease of this DDQ oxidation in acetone/H_2O 9:1 only in the case of **7f**, which was separately prepared as shown below:



Scheme 7



the other hand, turned out to be excellent partners for the oxidative coupling with **1a** under the standard conditions (*Scheme 7*).

These results are in agreement with the assumption that the formation of azulene radical cations of type **1e**$^{+\cdot}$ by reaction with DDQ (*Scheme 6*) is easier for **1h** and **1i** than for **1g** due to the Me groups at the seven-membered ring of **1h** and **1i**[9]). The oxidative coupling of **1a** and **1i** was optimized with respect to a maximum yield of **5ai**, which was attained with a 2 : 1 : 8 molar ratio of the reactants. It was also of interest that we could isolate in this case the normal oxidation product **2a** of **1a** in a yield of 35% with respect to the 100% surplus of **1a** in view of the coupling process.

It has already been found by *Okajima* and *Kurokawa* [2] that 2,2,2-trifluoro-1-(5-isopropyl-3,8-dimethylazulen-1-yl)ethanone (= 3-(trifluoroacetyl)guaiazulene; **1j**) undergoes the oxidation with DDQ only very sluggishly, so that they obtained the azulenecarboxaldehyde **2j** solely in a yield of 29%. Therefore, it was of interest for us to look how **1j** would behave in the presence of the effective coupling partner **1h**. The results of this test reaction under our standard condition (reactant ratio 1 : 2 : 4, 20 min, r.t., acetone/H_2O 9 : 1) are displayed in *Scheme 8*.

The specific behavior of **1j** is understandable. The strong electron-acceptor substituent at C(1) makes the first one-electron oxidation by DDQ more difficult, which also should be true for the second one after proton loss of the formed radical

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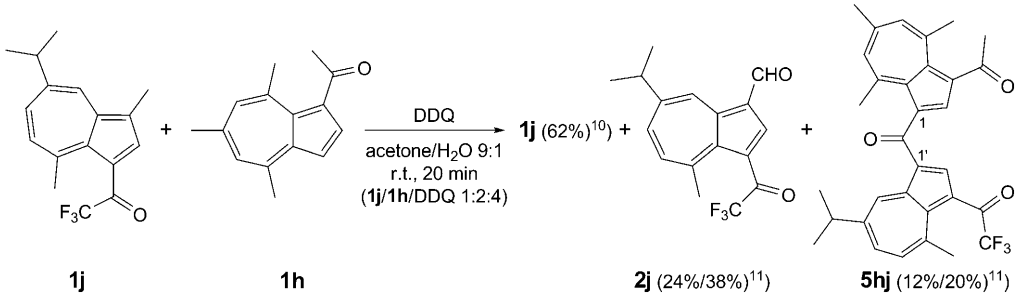
[8]) Trace amounts of the symmetric triketone **5a** were also found.

[9]) See [3] for EPR and ENDOR measurements of radical cations of alkylazulenes.

Scheme 8



1j **1h** **2j** (24%/38%)[11]) **5hj** (12%/20%)[11])

cation. It seems that there is no good matching of the production rate of the azulen-1-ylmethyl radicals of **1j** and that of the radical cation of **1h**. The yield of the coupling product **5hj** is thus low in comparison with the 86% of **5ah** of the oxidative coupling of **1a** with **1h** under the same conditions (*cf. Scheme 7*). Nevertheless, the sum of the absolute yields of **2j** and **5hj**, which reflects the formation of azulen-1-ylmethyl radicals from **1j**, is slightly higher than the yield reported for the formation of **2j** [2].

To establish that the oxidative coupling reaction of 1-(3-methylazulen-1-yl)alkan-1-ones and 1-(azulen-1-yl)alkan-1-ones is not bound to the presence of an acyl group at the latter, we oxidized **1a** with a large molar excess of DDQ in the presence of azulene (**8**) itself and with a longer exposure time to DDQ. Indeed, we isolated, beside **2a**, triketone **5a**, as products of **1a**, small amounts of the expected diketone **9** and, to our surprise, slightly larger amounts of the symmetric tetraketone **10**, built of **8** as central unit and two units of **1a** in 1,3-position of **8** (*Scheme 9*). To suppress the dominant formation of **2a**, a second 30 min run was performed in the presence of a fivefold molar amount of **8** with respect to **1a** under otherwise the usual reaction conditions. This time, we found only **9**, but again in small yield. The observation that we found in the first run roughly twice as much tetraketone **10** as diketone **9** could mean that indeed the first alkylation step **8** → methane intermediate, followed by DDQ oxidation to **9** (*cf. Scheme 6*), is more reluctant than the second alkylation step **9** → methane intermediate, followed by DDQ oxidation to **10**. In other words, an acyl group at C(1) of an azulene favors the oxidative coupling reaction with DDQ in aqueous acetone. Therefore, we oxidized **1a** in the presence of a fivefold molar amount of **8** and with a high excess of DDQ (*Scheme 9*). In this case, we found only **9** in isolable amounts, but again in low yield. These results together with those of the oxidation of **1a** in the presence of 1-(azulen-1-yl)ethanone (**1g**; see *Scheme 7*) clearly demonstrated that an acyl group at C(1) of an azulene favors its oxidative coupling with a 1-(3-methylazulen-1-yl)alkan-1-one by DDQ. As consequence of this finding, we treated finally **1a** and diketone **9** with a large excess of DDQ. The outcome of this oxidation is displayed in *Scheme 10*. Now, beside larger amounts of **2a**, the tetraketone **10** was the main product, which was obtained in pure state in a yield of 54%.

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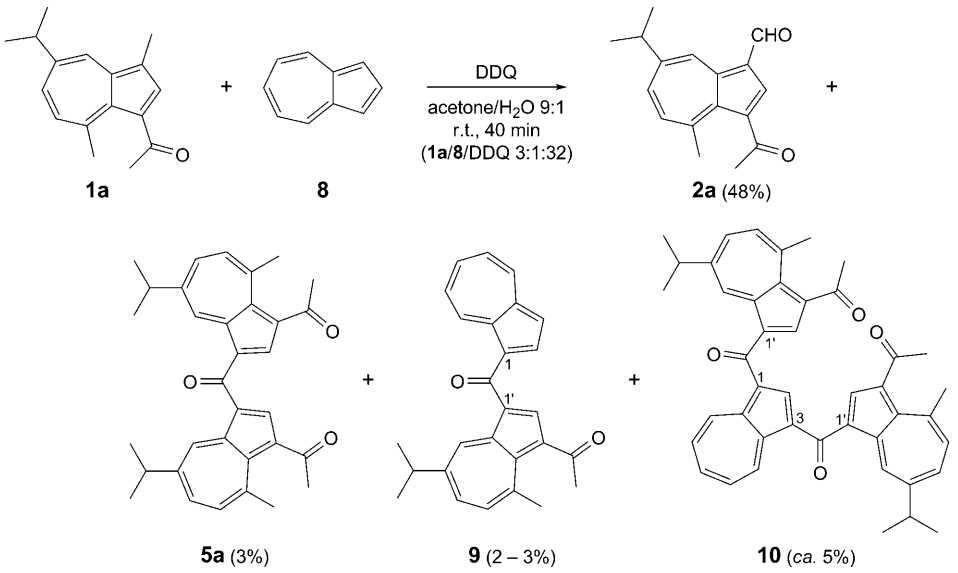
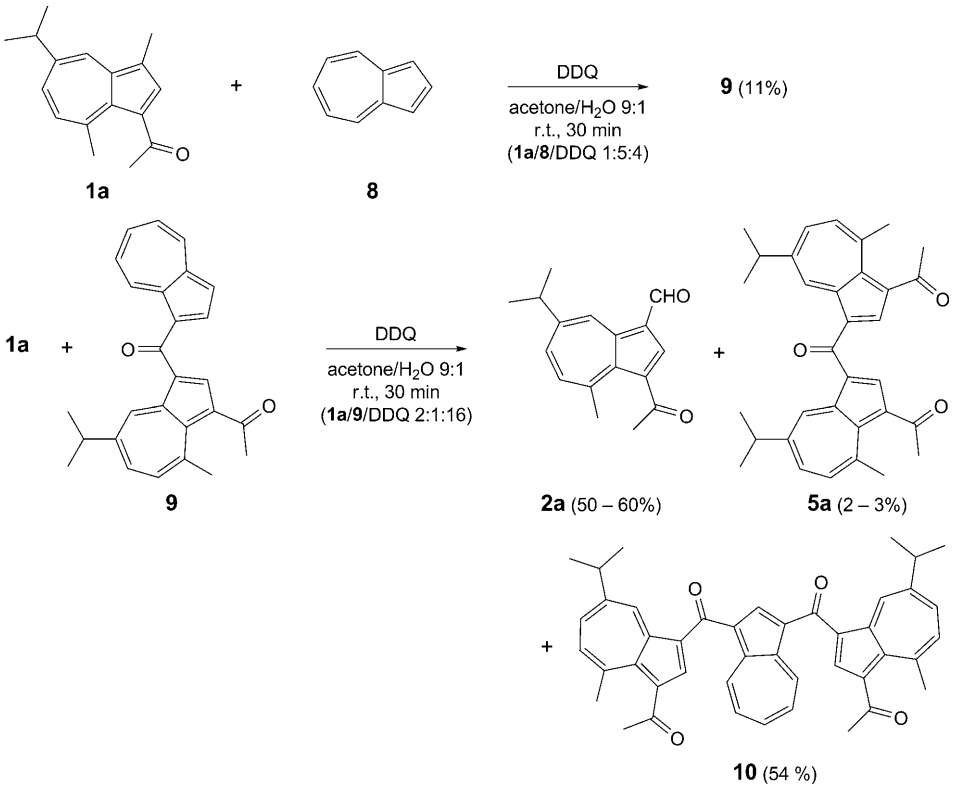
10) Recovered **1j** after reaction.

11) First number absolute yield, second number yield with respect to recovered **1j**.

Scheme 9



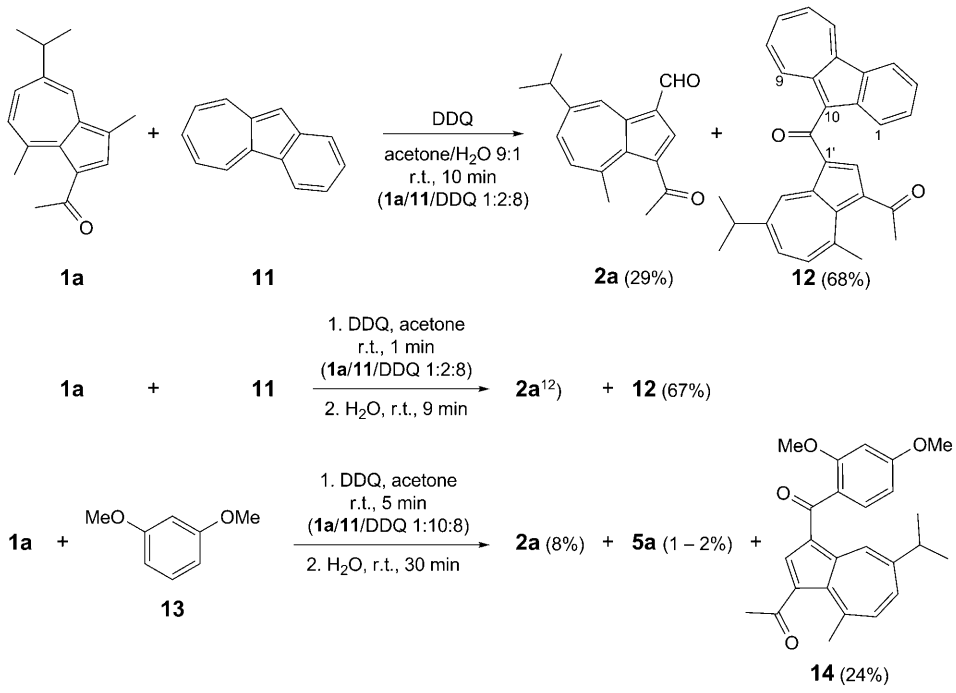
Scheme 10



The résumé of the oxidative coupling reactions of the azulenes, so far investigated, is that alkyl substituents at the seven-membered ring and acyl or alkoxycarbonyl groups at C(1) of the five-membered ring favor the coupling reaction, whereby the Me group at C(3) becomes the later central C=O group in the coupling products. Both azulene reactants should have similarly high-lying HMO, so that their SET reaction with DDQ produces the corresponding radical cations with almost the same rate to get high yields of coupling products. The presence of H_2O in the solvent mixture is obligatory for the oxidative formation of the central C=O group. Moreover, H_2O is also an indicator for the appearance of azulen-1-ylmethyl cations, which are trapped by H_2O and then further oxidized by DDQ to azulene-1-carboxaldehydes. This will happen always in cases where the production rate of azulene radical cations of the reaction partner is too low, so that the azulen-1-ylmethyl radical can couple only to a small extent with radical cations leading after proton loss to the intermediate bis(azulen-1-yl)methanes. In a more general perspective, one would, therefore, expect that 1-(3-methylazulen-1-yl)alkan-1-ones can be coupled with any substrate provided that its HMO are energetically close to those of the azulene.

We tested this idea by reacting our reference azulene **1a** with benz[*a*]azulene (**11**) [4] under the usual conditions for an oxidative coupling reaction driven by DDQ (*Scheme 11*). Indeed, we found, beside **2a** (29%), the new diketone **12** in a good yield. More interesting was the fact that the repetition of this oxidative coupling, however,

Scheme 11



12) At best trace amounts.

with the difference that we ran the reaction during the first minute in pure acetone and added then H_2O to get the 9:1 solvent mixture, led to almost pure **12**, accompanied at best by traces of **2a**. These results mean that in the present case, the reactants have been oxidatively consumed within the very first minute after mixing. The disubstituted methane intermediate is then further oxidized to **12** after addition of H_2O. That the radical-cation formation from **11** and radical production from **1a** is in this case not fully balanced, demonstrates the experiment in aqueous acetone, where also the azulene-1-carboxaldehyde **2a** is formed without touching the yield of **12**.

Finally, we chose 1,3-dimethoxybenzene (**13**) as partner for the DDQ-mediated oxidative coupling with **1a**. The first experiment under the usual conditions and with a molar ratio 1:2:8 of the reactants was disappointing since no coupling products at all were formed. However, when we proceeded as in the case of **1a** and **11**, *i.e.*, reaction first in pure acetone, followed by later addition of H_2O, and with **13** in a tenfold molar amount with respect to **1a**, we found 24% of the desired coupling product **14**, accompanied by small amounts of **2a** and **5a** (*Scheme 11*).

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Experimental Part

General. See [1]. TLC: Silica gel (SiO_2) coated aluminium sheets, if not otherwise stated. General procedure: see *2.4*.

1. *DDQ Oxidation of 1-(3-Methylazulen-1-yl)alkan-1-ones in the Presence of Azulene-1-carboxylic Acid* **6a**. The reactions were performed as described in [1]. 1.1. *1-(5-Isopropyl-3,8-dimethylazulen-1-yl)ethanone* (**1a**) *in the Presence of* **6a***[13] (*cf. Scheme 2*). Products **2a**, **5a***, and **7a***. *(3-[$^{13}C_2$]Acetyl-5-isopropyl-8-methylazulen-1-yl)(3-acetyl-5-isopropyl-8-methylazulen-1-yl)methanone* (*=1-{3-[(3-Acetyl-7-isopropyl-4-methylazulen-1-yl)carbonyl]-5-isopropyl-8-methylazulen-1-yl}[1,2-$^{13}C_2$]ethanone*; **5a***): See compound 4a in [1]. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.91 and 2.89, 2.48 and 2.46 (*dd*, $^1J(H,^{13}C) = 127.3$, $^2J(H,^{13}C) = 5.7$, $^{13}CH_3-^{13}C=O$); 2.69 (*s*, Me−C=O). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.11 and 196.54 (*d*, $^1J(O=^{13}C-^{13}CH_3) = 42.6$, $^{13}CH_3-^{13}C=O$); 196.83 (*s*, Me−*C*=O); 30.49 and 29.93 (*d*, $^1J(O=^{13}C-^{13}CH_3) = 42.6$, $^{13}CH_3-^{13}C=O$); 30.22 (*Me*−C=O). CI-MS ($C_{33}H_{34}O_3$ (478.63)): 481.2 (53, $[M+3]^+$), 479.2 (100, $[M+1]^+$).

1.2. *1-(5-Isopropyl-3,8-dimethylazulen-1-yl)phenylmethanone* (**1b**) *in the Presence of* **6a** (*cf. Scheme 3*). Products **2b**, **5ab**, **7ab**, **5b**, and **7b**. *(3-Acetyl-7-isopropyl-4-methylazulen-1-yl)(3-benzoyl-7-isopropyl-4-methylazulen-1-yl)methanone* (*=1-{3-[(3-Benzoyl-7-isopropyl-4-methylazulen-1-yl)carbonyl]-5-isopropyl-8-methylazulen-1-yl}ethanone*; **5ab**). Red glassy powder. M.p. 109–113°. R_f (toluene/*t*-BuOMe 6:1) 0.40. IR ($CHCl_3$): 3059v*w*, 2966*w*, 2931*w*, 2871*w*, 1651*m*, 1598*w*, 1580*w*, 1505*m*, 1443*m*, 1408*s*, 1386*w*, 1371*w*, 1303*w*, 1164*w*, 994*w*, 960*w*, 947*w*, 900*w*, 876*w*, 851*w*, 828*w*, 817*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.84, 9.80 (2*d*, $^4J(6,8) = J(6',8') = 2.1$, H−C(8,8′)); 8.32 (*s*, H−C(2)); 8.06 (*s*, H−C(2′)); 7.98 (*dd* with f.s., $J_o \approx 8.2$, $J_m \approx 1.5$, H_o of Ph); 7.86, 7.78 (2*dd*, $^3J(5,6) = J(5',6') = 10.9$, $^4J(6,8) = J(6',8') = 2.1$, H−C(6,6′)); 7.63, 7.62 (2*d*, $^3J(5,6) = J(5',6') = 10.9$, H−C(5,5′)); 7.55 (*tt*, $J_o \approx 7.4$, $J_m \approx 1.3$, H_p of Ph); 7.44 (*t* with f.s., $J_o \approx 7.5$, H_m of Ph); 3.28 (*sept.*, $J = 6.9$, $Me_2CH-C(7')$); 3.23 (*sept.*, $J = 6.9$, $Me_2CH-C(7)$); 2.91 (*s*, Me−C(4)); 2.88 (*s*, Me−C(4′)); 2.66 (*s*, MeCO−C(3)); 1.43 (*d*, $J = 6.9$, $Me_2CH-C(7')$); 1.39 (*d*,

[13]) The acid **6a*** with a [$^{13}C_2$]Ac group (25 atom-% ^{13}C) was obtained by oxidation of the correspondingly labeled azulene-1-carboxaldehyde **2a*** with $KMnO_4$ in the presence of Na_2CO_3 in acetone/water 9:1 (*cf.* [1]).

$J = 6.9$, $Me_2CH-C(7)$). ^{13}C-NMR (75 MHz, $CDCl_3$): 196.62 (Me*C*O–C(3)); 194.38 (Ph*C*O–C(3′)); 189.11 (C=O); 151.45–126.30 (20 azulene C)[14]); 38.48 $Me_2CH-C(7')$); 38.36 ($Me_2CH-C(7)$); 30.21 (*Me*CO–C(3)); 29.07 (*Me*–C(4)); 28.77 (*Me*–C(4′)); 24.45 ($Me_2CH-C(7')$); 24.37 ($Me_2CH-C(7)$). CI-MS (NH_3): 541 (100, $[M+H]^+$). Anal. calc. for $C_{38}H_{36}O_3$ (540.70): C 84.41, H 6.71; found: C 84.25, H 6.80.

Bis(3-benzoyl-7-isopropyl-4-methylazulen-1-yl)methanone (**5b**): See compound 4e in [1].

2. *DDQ Oxidation of 1-(3-Methylazulen-1-yl)alkan-1-ones in the Presence of 1-(3-demethylazulen-1-yl)alkan-1-ones or Methyl 3-Demethylazulene-1-carboxylate.* 2.1. *1-(5-Isopropyl-3,8-dimethylazulen-1-yl)ethanone* (**1a**) *and 1-(5-Isopropyl-8-methylazulen-1-yl)ethanone* (**1c**) (*cf. Scheme 4*). Products **2a** and **5a**. Data of **5a**: See **4a** in [1].

2.2. *1-(5-Isopropyl-3,8-dimethylazulen-1-yl)ethanone* (**1a**) *and 1-(5-Isopropyl-8-methylazulen-1-yl)phenylmethanone* (**1d**) (*cf. Scheme 5*). Products **2a** and **5ab**. Data of **5ab**: See *1.2*.

2.3. *1-(5-Isopropyl-3,8-dimethylazulen-1-yl)ethanone* (**1a**) *and 1-Azulen-1-yl)ethanone* (**1g**) (*cf. Scheme 7*). Products **2a** and **5ag**. *(3-Acetylazulen-1-yl)(3-acetyl-7-isopropyl-4-methylazulen-1-yl)methanone* (=*1-{3-[(3-Acetylazulen-1-yl)carbonyl]-5-isopropyl-8-methylazulen-1-yl}ethanone*; **5ag**). Dark red crystals. M.p. 211–213° (EtOH). R_f (hexane/AcOEt 1:1) 0.27. IR (KBr): 1651*m*, 1640*m*, 1585*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.10 (*dd*, $^3J(4,5) = 9.9$, $^4J(4,6) = 0.8$, H–C(4)); 9.85 (*d*, $^4J(6',8') = 2.1$, H–C(8′)); 9.72 (*dd*, $^3J(7,8) = 9.9$, $^4J(6,8) = 0.8$, H–C(8)); 8.55 (*s*, H–C(2)); 8.35 (*s*, H–C(2′)); 8.04 (*t*-like, $^3J(5,6) \approx {}^3J(6,7) = 9.7$, H–C(6)); 7.88–7.77 (superimp. signals of H–(5), H–C(6′), H–C(7)); 7.69 (*d*, $^3J(5',6') = 10.9$, H–C(5′)); 3.23 (*sept.*, $J = 6.9$, $Me_2CH-C(7')$); 2.97 (*s*, Me–C(4′)); 2.70 (*s*, MeCO–C(3)); 2.68 (*s*, MeCO–C(3′)); 1.41 (*d*, $J = 6.9$, $Me_2CH-C(7')$). ^{13}C-NMR (75 MHz, $CDCl_3$): 196.95 (Me*C*O–C(3′)); 195.57 (Me*C*O–C(3)); 188.94 (C=O); 151.65–123.66 (20 azulene C); 38.37 ($Me_2CH-C(7')$); 30.37 (*Me*CO–C(3)); 29.10 (*M*eCO–C(3′)); 24.35 ($Me_2CH-C(7')$). CI-MS (NH_3): 423 (100, $[M+1]^+$), 310 (6), 309 (24), 290 (30), 200 (16). Anal. calc. for $C_{29}H_{26}O_3$ (422.52): C 82.44, H 6.20; found: C 82.30, H 6.25.

2.4. *1-(5-Isopropyl-3,8-dimethylazulen-1-yl)ethanone* (**1a**) *and 1-(4,6,8-Trimethylazulen-1-yl)ethanone* (**1h**) (*cf. Scheme 7*). The reactants **1a** (0.048 g, 0.20 mmol) [1] and **1h** (0.085 g, 0.40 mmol) [5] were dissolved in acetone (9 ml), followed by gradual addition of H_2O (1 ml), and then DDQ (0.181 g, 0.80 mmol) was added. The mixture was stirred during 20 min at r.t., and just thereafter subjected to a first purification (method *A* [1], dioxane). The product separation was realized with method *B* (hexane/AcOEt) [1]. The first fraction contained **1h** (0.015 g, 35% of the excess). The second one delivered a small amount of carboxaldehyde **2a** (0.001 g, 2%) [1]. The third, red fraction gave the coupling product *(3-acetyl-7-isopropyl-4-methylazulen-1-yl)(3-acetyl-4,6,8-trimethylazulen-1-yl)methanone* (=*1-{3-[(3-acetyl-7-isopropyl-4-methylazulen-1-yl)carbonyl]-4,6,8-trimethylazulen-1-yl}ethanone*; **5ah**; 0.080 g, 86%). Red crystals. M.p. 196–197° (EtOH). R_f (hexane/AcOEt 3:1) 0.06. IR (KBr): 3096v*w*, 2962*w*, 2927*w*, 2867*w*, 1661*s*, 1606*m*, 1584*m*, 1548*w*, 1505*m*, 1436*s*, 1401*s*, 1368*s*, 1310*w*, 1221*w*, 1190*s*, 1159*w*, 1103*w*, 1028*w*, 955*w*, 915*w*, 881*m*, 853*w*, 795*w*, 731*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.06 (*d*, $^4J(6',8') = 2.1$, H–C(8′)); 8.22 (*s*, H–C(2′)); 8.01 (*s*, H–C(2)); 7.83 (*dd*, $^3J(5',6') = 10.9$, $^4J(6',8') = 2.1$, H–C(6′)); 7.69 (*d*, $^3J(5',6') = 10.9$, H–C(5′)); 7.43, 7.36 (2*s*, H–C(5), H–C(7)); 3.23 (*sept.*, $J = 6.9$, $Me_2CH-C(7')$); 2.93 (*s*, Me–C(4′)); 2.91, 2.83, 2.69 (3*s*, Me–C(4), Me–C(6), Me–C(8)); 2.66 (*s*, *Me*CO–C(3′)); 2.61 (*s*, *Me*CO–C(3)); 1.38 (*d*, $J = 6.9$, $Me_2CH-C(7')$). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.51 (Me*C*O–C(3)); 197.27 (Me*C*O–C(3′)); 191.72 (C=O); 152.24–125.27 (20 azulene C); 38.37 ($Me_2CH-C(7')$); 30.31 (Me–C(4′)); 29.92 (*Me*–C(4), Me–C(8)); 29.22 (*Me*CO–C(3)); 29.06 (*Me*CO–C(3′)); 28.14 (*Me*–C(6)); 24.34 ($Me_2CH-C(7')$). CI-MS (NH_3): 465 (100, $[M+H]^+$), 451 (12), 423 (8). Anal. calc. for $C_{32}H_{32}O_3$ (464.60): C 82.73, H 6.94; found: C 82.54, H 6.89.

2.5. *1-(5-Isopropyl-3,8-dimethylazulen-1-yl)ethanone* (**1a**) *and Methyl 4,6,8-Trimethylazulene-1-carboxylate* (**1i**) (*cf. Scheme 7*). Products **2a** and **5ai**. *Methyl 3-[(3-Acetyl-7-isopropyl-4-methylazulen-1-yl)carbonyl]-4,6,8-trimethylazulene-1-carboxlate* (**5ai**). Red crystals. M.p. 206–208° (EtOH). R_f (hexane/AcOEt 2:1) 0.16. IR (KBr): 3091v*w*, 2958*w*, 2930*w*, 2868*w*, 1704*m* (COOMe), 1662*m* (MeCO), 1606*m* (C=O), 1582*m*, 1549*w*, 1506*m*, 1439*s*, 1402*s*, 1369*s*, 1313*w*, 1214*m*, 1193*s*, 1159*m*, 1106*w*, 1053*w*,

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

1026*w*, 994*w*, 956*w*, 881*m*, 854*w*, 782*w*, 772*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.02 (*d*, $^4J(6',8')=2.1$, H–C(8′)); 8.25 (*s*, H–C(2′)); 8.02 (*s*, H–C(2)); 7.81 (*dd*, $^3J(5',6')=10.9$, $^4J(6',8')=2.1$, H–C(6′)); 7.67 (*d*, $^3J(5',6')=10.9$, H–C(5′)); 7.40, 7.34 (2*s*, H–C(5), H–C(7)); 3.88 (*s*, MeOCO–C(1)); 3.22 (*sept.*, $J=6.9$, Me_2CH–C(7′)); 3.00, 2.92, 2.85, 2.68 (4*s*, Me–C(4), Me–C(6), Me–C(8), Me–C(4′)); 2.62 (*s*, MeCO–C(3′)); 1.38 (*d*, $J=6.9$, Me_2CH–C(7′)). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.36 (Me*C*O–C(3′)); 191.55 (C=O); 167.78 (MeO*C*O–C(1)); 152.09–118.79 (20 azulene C); 51.93 (*Me*OCO–C(1)); 38.37 (Me_2CH–C(7′)); 30.44 (*Me*–C(4′)); 29.06 (*Me*CO–C(3′)); 29.31, 28.85, 28.20 (*Me*–C(4), *Me*–C(6), *Me*–C(8)); 24.36 (Me_2CH–C(7′)). EI-MS: 480 (38, $M^{+\bullet}$), 465 (98), 437 (100). Anal. calc. for $C_{32}H_{32}O_4$ (480.60): C 79.97, H 6.71; found: C 80.01, H 6.73.

2.6. *5-Isopropyl-3,8-dimethylazulen-1-yl)phenylmethanone* (**1b**) *and 1-(5-Isopropyl-8-methylazulen-1-yl)ethanone* (**1c**) (*cf. Scheme 5*). Products **2b** and **5ab**. Data of **5ab**: See *1.2*.

2.7. *(5-Isopropyl-3,8-dimethylazulen-1-yl)phenylmethanone* (**1b**) *and (5-Isopropyl-8-methylazulen-1-yl)phenylmethanone* (**1d**) (*cf. Scheme 4*). Products **2b** and **5b**. Data of **5b**: See compound 4e in [1].

2.8. *(5-Isopropyl-3,8-dimethylazulen-1-yl)phenylmethanone* (**1b**) *and 1-(7-Isopropyl-4-methylazulen-1-yl)ethanone* (**1e**) (cf. *Scheme 5*). Products **2b** and **5be**. *(3-Acetyl-5-isopropyl-8-methylazulen-1-yl)(3-benzoyl-7-isopropyl-4-methylazulen-1-yl)methanone* (=*1-{3-[(3-Benzoyl-7-isopropyl-4-methylazulen-1-yl)carbonyl]-7-isopropyl-4-methylazulen-1-yl}ethanone*; **5be**). Dark red crystals. M.p. 210–212° (octane). R_f (hexane/AcOEt 1:1) 0.39. IR (KBr): 2962*m*, 1639*s*, 1615*m*, 1598*m*. ^{1}H-NMR (300 MHz, C_6D_6): 10.76 (*d*, $^4J(4,6)=2.1$, H–C(4)); 10.58 (*d*, $^4J(6',8')=2.1$, H–C(8′)); 8.23 (*s*, H–C(2)); 8.18 (*s*, H–C(2′)); 8.02 (*d* with f.s., $J_o=8$, H_o of Ph); 7.23 (*dd*, $^3J(5',6')=10.8$, $^4J(6',8')=2.1$, H–C(6′)); 7.16–6.99 (overlapping signals of H_p, H_m, H–C(6), H–C(7)); 6.93 (*d*, $^3J(5',6')=10.8$, H–C(5′)); 2.92 (*sept.*, $J=6.9$, Me_2CH–C(7′)); 2.88 (*s*, Me–C(8)); 2.84 (*sept.*, $J=6.9$, Me_2CH–C(5)); 2.79 (*s*, Me–C(4′)); 2.35 (*s*, MeCO–C(3)); 1.23 (*d*, $J=6.9$, Me_2CH–C(7′)); 1.18 (*d*, $J=6.9$, Me_2CH–C(5)). ^{13}C-NMR (75 MHz, $CDCl_3$): 195.18 (Me*C*O–C(3)); 194.29 (Ph*C*O–C(3′)); 191.33 (C=O); 151.80–122.23 (20 azulene C); 38.40, 38.36 (Me_2CH–C(5), Me_2CH–C(7′)); 29.04 (*Me*CO–C(3)); 28.65 (*Me*–C(4′)); 28.31 (*Me*–C(8)); 24.41, 24.38 (Me_2CH–C(5), Me_2CH–C(7′)). CI-MS: 541 (100, $[M+1]^+$). Anal. calc. for $C_{38}H_{36}O_3$ (540.70): C 84.41, H 6.71; found: C 84.25, H 6.65.

2.9. *2,2,2-Trifluoro-1-(5-isopropyl-3,8-dimethylazulen-1-yl)ethanone* (**1j**) *and 1-(4,6,8-Trimethylazulen-1-yl)ethanone* (**1h**) (*cf. Scheme 8*). Products **2j** and **5hj**. *(3-Acetyl-4,6,8-trimethylazulen-1-yl)[7-isopropyl-4-methyl-3-(trifluoroacetyl)azulen-1-yl]methanone* (=*1-{3-[(3-Acetyl-4,6,8-trimethylazulen-1-yl)carbonyl]-5-isopropyl-8-methylazulen-1-yl}-2,2,2-trifluoroethanone*; **5hj**). Red crystals. M.p. 175–177° (EtOH). R_f (hexane/AcOEt 2:1) 0.29. IR (KBr): 2966*w*, 2931*w*, 2873*w*, 1666*s*, 1610*m*, 1583*m*, 1547*w*, 1511*s*, 1434*m*, 1410*s*, 1365*s*, 1311*w*, 1280*m*, 1200*m*, 1168*s*, 1133*s*, 1107*w*, 1078*m*, 1031*w*, 950*m*, 923*w*, 844*s*, 795*w*, 733*w*, 716*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.16 (*d*, $^4J(6',8')=2.1$, H–C(8′)); 8.50 (*q*, $^5J(F,2')=2.1$, H–C(2′)); 8.06 (*s*, H–C(2)); 7.97 (*dd*, $^3J(5',6')=10.9$, $^4J(6',8')=2.1$, H–C(6′)); 7.86 (*d*, $^3J(5',6')=10.9$, H–C(5′)); 7.48, 7.42 (2*s*, H–C(5), H–C(7)); 3.29 (*sept.*, $J=6.9$, Me_2CH–C(7′)); 2.97 (*s*, Me–C(4′)); 2.92, 2.85, 2.69 (3*s*, Me–C(4), Me–C(6), Me–C(8)); 2.65 (*s*, MeCO–C(3)); 1.42 (*d*, $J=6.9$, Me_2CH–C(7′)). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.06 (Me*C*O–C(3)); 190.71 (C=O); 176.55 (*q*, $^2J(^{13}C,F)=33.9$, CF_3CO–C(3′)); 154.99–118.69 (20 azulene C); 117.33 (*q*, $^1J(^{13}C,F)=292.3$, CF_3CO–C(3′)); 38.59 (Me_2CH–C(7′)); 30.14 (*Me*–C(4′)); 29.98, 29.55, 29.23 (3*s*, *Me*–C(4), *Me*–C(6), *Me*–C(8)); 28.12 (*Me*CO–C(3)); 24.34 (Me_2CH–C(7′)); EI-MS: 518 (46, $M^{+\bullet}$), 503 (100, $[M-Me]^+$), 475 (19, $[M-CO]^{+\bullet}$), 421 (40, $[M-CF_3CO]^+$), 307 (17), 281 (30), 197 (61). Anal. calc. for $C_{32}H_{29}F_3O_3$ (518.58): C 74.12, H 5.64; found: C 73.69, H 5.45.

3. *DDQ Oxidation of 1-(5-Isopropyl-3,8-dimethylazulen-1-yl)ethanone* (**1a**) *in the Presence of Azulenes and 1,3-Dimethoxybenzene.* – 3.1. *With Azulene* (**8**) (*cf. Scheme 9*). Products **2a**, **5a**, **9**, and **10**. *(3-Acetyl-7-isopropyl-4-methylazulen-1-yl)(azulen-1-yl)methanone* (=*1-[3-(Azulen-1-ylcarbonyl)-5-isopropyl-8-methylazulen-1-yl]ethanone*; **9**). Red crystals. M.p. 152–154° (EtOH). R_f (toluene/*t*-BuOMe 6:1) 0.32. IR (KBr): 2962*w*, 2928*w*, 2872*w*, 1648*m*, 1586*m*, 1534*w*, 1506*m*, 1495*m*, 1456*m*, 1417*s*, 1407*s*, 1396*s*, 1370*m*, 1315*w*, 1285*w*, 1221*w*, 1202*m*, 1191*m*, 1143*w*, 1051*w*, 1020*w*, 954*w*, 890*w*, 788*m*, 777*m*, 751*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.80 (*d*, $^4J(6',8')=2.1$, H–C(8′)); 9.64 (*d*, $^3J(7,8)=9.7$, H–C(8)); 8.54 (*d*, $^3J(4,5)=9.2$, H–C(4)); 8.37 (*s*, H–C(2′)); 8.18 (*d*, $^3J(2,3)=4.1$, H–C(2)); 7.85 (*t*, $^3J(5,6)\approx{}^3J(6,7)=9.7$, H–C(6)); 7.80 (*dd*, $^3J(5',6')=10.9$, $^4J(6',8')=2.1$, H–C(6′)); 7.64 (*d*, $^3J(5',6')=11.1$, H–C(5′)); 7.58, 7.49 (2*t*, $^3J=9.9$, resp. 9.6, H–C(5), H–C(7)); 7.37 (*d*, $^3J(2,3)=4.1$, H–C(3)); 3.21 (*sept.*, $J=6.9$,

$Me_2CH-C(7')$); 2.95 (*s*, Me–C(4′)); 2.70 (*s*, MeCO–(3′)); 1.39 (*d*, $J = 6.9$, $Me_2CH-C(7')$). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.00 (Me*C*O–C(3′)); 189.15 (CO); 151.19–117.47 (20 azulene C); 38.33 ($Me_2CH-C(7')$); 30.35 (*Me*CO–C(3′)); 29.05 (*Me*–C(4′)); 24.34 ($Me_2CH-C(7')$). CI-MS (NH_3): 381 (100, $[M+H]^+$). Anal. calc. for $C_{27}H_{24}O_2$ (380.49): C 85.23, H 6.36; found: C 85.13, H 6.52.

1,3-Bis[(3-acetyl-7-isopropyl-4-methylazulen-1-yl)carbonyl]azulene (=*1,1′-{Azulene-1,3-diylbis[carbonyl(5-isopropyl-8-methylazulene-3,1-diyl)]}bis[ethanone]*; **10**). Red crystals. M.p. 264–265° (EtOH/AcOEt 3:1). R_f (hexane/AcOEt 1:1) 0.16. IR (KBr): 3053v*w*, 2962*m*, 2928*w*, 2869*w*, 1661*m*, 1618*m*, 1589*m*, 1505*s*, 1441*s*, 1418*s*, 1387*m*, 1370*m*, 1298*w*, 1218*m*, 1195*s*, 1164*m*, 960*w*, 938*w*, 899*w*, 889*w*, 870*w*, 783*m*, 769*w*, 756*w*, 608*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.89 (*d*, $^4J(6',8') = 2.1$, H–C(8′)); 9.74 (*d*, $^3J(4,5) = {}^3J(7,8) = 9.8$, H–C(4), H–C(8)); 8.34 (*s*, H–C(2)); 8.25 (*s*, H–C(2′)); 8.05 (*t*, $^3J(5,6) = {}^3J(6,7) = 9.7$, H–C(6)); 7.81 (*dd*, $^3J(5',6') = 10.9$, $^4J(6',8') = 2.1$, H–C(6′)); 7.80 (*t*, $^3J(4,5) = {}^3J(7,8) \approx 10.0$, H–C(5), H–C(7)); 7.63 (*d*, $^3J(5',6') = 10.9$, H–C(5′)); 3.24 (*sept.*, $^3J = 6.9$, $Me_2CH-C(7')$); 2.89 (*s*, Me–C(4′)); 2.57 (*s*, MeCO–C(3′)); 1.42 (*d*, $^3J = 6.9$, $Me_2CH-C(7')$). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.25 (Me*C*O–C(3′)); 189.44 (*C*O–C(1), *C*O–C(3)); 151.49–125.75 (30 azulene C; signal ratio 1:2); 38.44 ($Me_2CH-C(7')$); 30.50 (*Me*CO–C(3′)); 29.05 (2 *Me*–C(4′)); 24.40 ($Me_2CH-C(7')$). ESI-MS (NaI): 655 (100, $[M+Na]^+$). Anal. calc. for $C_{44}H_{40}O_4$ (632.80): C 83.52, H 6.37; found: C 83.57, H 6.39.

3.2. *With (3-Acetyl-7-isopropyl-4-methylazulen-1-yl)(azulen-1-yl)methanone* (**9**) (*cf. Scheme 10*). Products **2a**, **5a**, and **10**. Data of **10**: See *3.1*.

3.3. *With Benz[a]azulene* (**11**) (*cf. Scheme 11*). Products **2a** and **12**.

(3-Acetyl-7-isopropyl-4-methylazulen-1-yl)(benz[a]azulen-10-yl)methanone (=*1-[3-(Benz[a]azulen-10-ylcarbonyl)-5-isopropyl-8-methyl]ethanone*; **12**). Red crystals. M.p. 152–154° (amorphous). R_f (toluene/*t*-BuOMe 20:1) 0.23. IR (KBr): 3050*w*, 2962*w*, 2927*w*, 2868*w*, 1662*m*, 1601*m*, 1555*w*, 1518*m*, 1505*m*, 1478*m*, 1451*s*, 1411*s*, 1371*m*, 1312*w*, 1263*w*, 1248*w*, 1191*m*, 1160*w*, 1139*w*, 1078*w*, 957*w*, 927*w*, 876*w*, 788*w*, 760*w*, 731*w*, 690*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 9.93 (*d*, $^4J(6',8') = 2.1$, H–C(8′)); 8.71 (*dd*, $^3J(5,6) = 8.6$, $^4J(5,7) = 0.9$, H–C(5)); 8.66 (*d*, $^3J(8,9) = 11.1$, H–C(9)); 8.47 (*d*, $^3J(3,4) = 7.9$, H–C(4)); 8.25 (*s*, H–C(2′)); 7.84 (*d*, $^3J(1,2) = 8.0$, H–C(1)); 7.80 (*dd*, $^3J(5',6') = 11.0$, $^4J(6',8') = 2.1$, H–C(6′)); 7.66 (*d*, $^3J(5',6') = 11.0$, H–C(5′)); 7.60 (*ddd*, $^3J(1,2) = 8.0$, $^3J(2,3) = 7.0$, $^4J(2,4) = 1.0$, H–C(2)); 7.52 (*ddd*, $^3J(3,4) = 8.0$, $^3J(2,3) = 7.0$, $^4J(1,3) = 0.9$, H–C(3)); 7.49 (br. *ddt*, $^3J(6,7) = 10.9$, $^3J(7,8) = 8.6$, $^4J(5,7) \approx {}^4J(7,9) \approx 1.0$, H–C(7)); 7.38 (br. *dd*, $^3J(6,7) = 10.9$, $^3J(5,6) = 8.6$, H–C(6)); 7.14 (*ddd*, $^3J(8,9) = 11.1$, $^3J(7,8) = 8.6$, $^4J(6,8) = 0.7$, H–C(8)); 3.19 (*sept.*, $J = 6.9$, $Me_2CH-C(7')$); 2.95 (*s*, Me–C(4′)); 2.50 (*s*, MeCO–C(3′)); 1.35 (*d*, $J = 6.9$, $Me_2CH-C(7')$). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.10 (Me*C*O–C(3′)); 189.74 (*C*O–C(10)); 151.60–120.84 (20 azulene C, 4 benzo C); 38.33 ($Me_2CH-C(7')$); 30.25 (*Me*CO–C(3′)); 29.09 (*Me*–C(4′)); 24.26 ($Me_2CH-C(7')$). EI-MS: 430 (100, $M^{+\cdot}$), 415 (55, $[M-Me]^+$), 402 (37, $[M-CO]^{+\cdot}$), 387 (93, $[M-MeCO]^+$). Anal. calc. for $C_{31}H_{26}O_2$ (430.54): C 86.48, H 6.09; found: C 86.45, H 6.21.

3.4. *With 1,3-Dimethoxybenzene* (**13**) (*cf. Scheme 11*). Products **2a**, **5a**, and **14**. *(3-Acetyl-7-isopropyl-4-methylazulen-1-yl)(2,4-dimethoxyphenyl)methanone* (=*1-[3-(2,4-Dimethoxybenzoyl)-5-isopropyl-8-methylazulen-1-yl]ethanone*; **14**). Red crystals. M.p. 108–109° (EtOH). R_f (*t*-BuOMe/hexane 2:1) 0.26. IR (KBr): 3073v*w*, 2963*m*, 2869*w*, 2840*w*, 1655*s*, 1614*s*, 1579*m*, 1504*s*, 1445*s*, 1407*s*, 1371*m*, 1360*s*, 1308*m*, 1290*m*, 1265*s*, 1245*m*, 1209*s*, 1183*s*, 1159*s*, 1139*m*, 1100*w*, 1041*m*, 1029*m*, 984*w*, 962*m*, 925*m*, 905*w*, 888*m*, 828*m*, 793*m*, 616*m*, 608*w*, 573*w*. ^{1}H-NMR (300 MHz, C_6D_6): 10.58 (br. *s*, H–C(8)); 8.27 (*s*, H–C(2)); 7.60 (*d*, $^3J(5',6') = 8.4$, H–C(6′)); 7.20 (br. *d*, $^3J(5,6) = 10.9$, H–C(6)); 7.03 (br. *d*, $^3J(5,6) = 10.8$, H–C(5)); 6.46 (*d*, $^4J(3',5') = 2.2$, H–C(3′)); 6.39 (*dd*, $^3J(5',6') = 8.4$, $^4J(3',5') = 2.2$, H–C(5′)); 3.36 (*d*, $^4J(5,Me) = 1.1$, Me–C(4)); 3.17 (*s*, MeO–C(2′)); 2.82 (*sept.*, $^3J = 6.9$, Me_2CH); 2.82 (*s*, MeO–C(4′)); 2.30 (*s*, MeCO–C(3)); 1.16 (*d*, $^3J = 6.9$, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.06 (Me*C*O–C(3)); 191.53 (*C*O–C(1)); 162.57–99.03 (10 azulene C, 6 benzene C); 55.70 (*Me*O–C(2′)); 55.51 (*Me*O–C(4′)); 38.44 ($Me_2CH-C(7)$); 30.27 (*Me*CO–C(3)); 29.04 (*Me*–C(4)); 24.39 ($Me_2CH-C(7)$). EI-MS: 390 (88, $M^{+\cdot}$), 375 (100, $[M-Me]^+$), 373 (16), 347 (23, $[M-MeCO]^+$). Anal. calc. for $C_{25}H_{26}O_4$ (390.48): C 76.90, H 6.71; found: C 76.82, H 6.83.

4. *Syntheses.* 4.1. *1-(5-Isopropyl-8-methylazulen-1-yl)alkan-1-ones* **1** *by Decarbonylation of the Corresponding Carboxaldehydes* **2** (*cf.* [6]). 4.1.1. *1-(5-Isopropyl-8-methylazulen-1-yl)ethanone* (**1c**). To a soln. of carboxaldehyde **2a** (0.65 g, 2.56 mmol) in toluene (200 ml) was gradually added $[RhCl(Ph_3P)_3]$ (5.42 g, 5.86 mmol). After 20 h heating under reflux, the mixture was filtered through *Celite*. Toluene was

distilled off and the volume-reduced filtrate (20–30 ml) purified by method *B* (hexane/*t*-BuOMe 15:1) [1]. Bulb-to-bulb distillation (120–140°/7 · 10^{-5} mbar) gave pure **1c** (0.50 g, 86%). Black violet solid (*cf. Table*). M.p. 77–78°. R_f (hexane/AcOEt 3:1) 0.44. IR ($CHCl_3$): 2965*m*, 1645*s*, 1545*w*, 1523*m*, 1497*m*, 1463*m*, 1393*s*, 1372*s*, 1315*s*, 1178*w*, 1140*w*, 1062*w*, 1036*w*, 997*w*, 985*w*, 928*w*, 891*m*, 866*w*, 821*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.35 (*d*, ^4J(4,6) = 2.1, H–C(4)); 8,10 (*d*, ^3J(2,3) = 4.3, H–C(2)); 7.60 (*dd*, ^3J(6,7) = 11.0, ^4J(4,6) = 2.1, H–C(6)); 7.40 (*d*, ^3J(6,7) = 11.0, H–C(7)); 7.12 (*d*, ^3J(2,3) = 4.2, H–C(3)); 2.95 (*sept.*, *J* = 6.9, Me_2CH–C(5)); 2.92 (*s*, Me–C(8)); 2.74 (*s*, *Me*CO–C(1)); 1.36 (*d*, *J* = 6.9, Me_2CH–C(5)). ^{13}C-NMR (75 MHz, $CDCl_3$): 196.66 (Me*C*O–C(1)); 149.79–117.29 (10 azulene C); 37.75 (Me_2*C*H–C(5)); 30.39 (*Me*CO–C(1)); 28.60 (*Me*–C(8)); 24.35 (Me_2CH–C(5)). GC/MS: 226 (29, $M^{+\bullet}$), 211 (100, $[M - Me]^+$), 196 (9, $[M - 2\,Me]^+$), 183 (4), 167 (6), 165 (8), 152 (9). Anal. calc. for $C_{16}H_{18}O$ (226.32): C 84.91, H 8.02; found: C 84.90, H 8.07.

4.1.2. *(5-Isopropyl-8-methylazulen-1-yl)phenylmethanone* (**1d**). Carboxaldehyde **2b** was decarbonylated as described for **2a**. For main data, see *Table*.

4.1.3. *1-(5-Isopropyl-8-methylazulen-1-yl)-2,2-dimethylpropan-1-one* (**1f**). The corresponding carboxaldehyde (see compound 2d in [1]) was decarbonylated as described for **2a**. For main data, see *Table*.

4.2. *1,1′-[Methylenebis(5-isopropyl-8-methylazulene-3,1-diyl)]bis[2,2-dimethylpropan-1-one]* (**7f**)[7]). We applied the procedure of *Takekuma*, *Yamamoto*, and co-workers [7] (see also [8]). **7f**: Red crystals. M.p. 187–188° (EtOH). R_f (*Alox*, toluene/*t*-BuOMe 30:1) 0.34. IR (KBr): 3082v*w*, 2959*s*, 2929*s*, 2902*m*, 2868*m*, 1664*s*, 1637*s*, 1545*m*, 1521*m*, 1476*m*, 1459*s*, 1407*s*, 1363*s*, 1286*w*, 1250*w*, 1156*m*, 1119*w*, 1076*m*, 978*m*, 921*w*, 847*m*, 815*w*, 789*m*, 704*w*, 630*w*, 565*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.41 (*d*, ^4J (6,8) = 2.0, H–C(8)); 7.59 (*s*, H–C(2)); 7.49 (*dd*, ^3J (5,6) = 10.8, ^4J (6,8) = 2.0, H–C(6)); 7.16 (*d*, ^3J (5,6) = 10.9, H–C(5)); 4.79 (*s*, CH_2); 3.03 (*sept.*, *J* = 6.9, Me_2CH–C(7)); 2.67 (*s*, Me–C(4)); 1.29 (*s*, Me_3CCO–C(3)); 1.28 (*d*, *J* = 6.9, Me_2CH–C(7)). ^{13}C-NMR (75 MHz, $CDCl_3$): 212.59 (Me_3CCO–C(3)); 146.51–127.10 (20 azulene C); 45.03 (Me_3CCO–C(3)); 38.00 (Me_2*C*H–C(7)); 28.73 (Me_3CCO–C(7)); 28.11 (*Me*–C(4)); 26.02 (CH_2); 24.56 (Me_2CH–C(7)). EI-MS: 548 (12, $M^{+\bullet}$), 491 (100, $[M - Me_3C]^+$), 217 (24). Anal. calc. for $C_{39}H_{48}O_2$ (548.81): C 85.35, H 8.82; found: C 85.63, H 8.56.

Table. *1-(5-Isopropyl-8-methyl-azulen-1-yl)alkan-1-ones* **1** *by Decarbonylation of the Corresponding Carboxaldehydes* **2**

	Molar ratios		Reaction conditions				Purification[b])	Yield [%]	Physical data	
	reactant	[$RhCl(Ph_3P)_3$]	solvent	conc. [react./solv.][a])	time [h]	temp. [°]			M.p. [°]	δ(C=O) [ppm][c])
1c	1	2.3	toluene	1:300	20	reflux	CC(*A*)[d]), CC(*B*)[e]), dist.[f])	86	77–78	196.66
1d	1	2.6	toluene	1:120	20	reflux	CC(*B*)[g]), dist.[h])	84	78–80	194.27
1f	1	2.7	toluene	1:180	28	reflux	CC(*B*)[i]), CC(*B*)[e]), dist.[f])	92	56–57	212.39

[a]) Reactant ratio [g]/solvent [ml]. [b]) For *A* and *B*, see [1] (Exper. Part). [c]) In $CDCl_3$. [d]) Toluene (*cf.* [1]). [e]) Hexane/*t*-BuOMe 15:1 (*cf.* [1]). [f]) Bulb-to-bulb distillation at 120–140°/high vacuum. [g]) Hexane/AcOEt 50:1. [h]) Bulb-to-bulb distillation at 140–160°/high vacuum. [i]) CH_2Cl_2.

4.2.1. *DDQ Oxidation of* **7f** (see [7])). Product **5f**. *Bis(7-isopropyl-4-methyl-3-pivaloylazulen-1-yl)methanone* (*=1,1′-[Carbonylbis(5-isopropyl-8-methylazulene-3,1-diyl)]bis[2,2-dimethylpropan-1-one]*; **5f**): See compound 4d in [1].

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