

164. Ru-Catalyzed Heptalene Formation from Azulenes and Dimethyl Acetylenedicarboxylate

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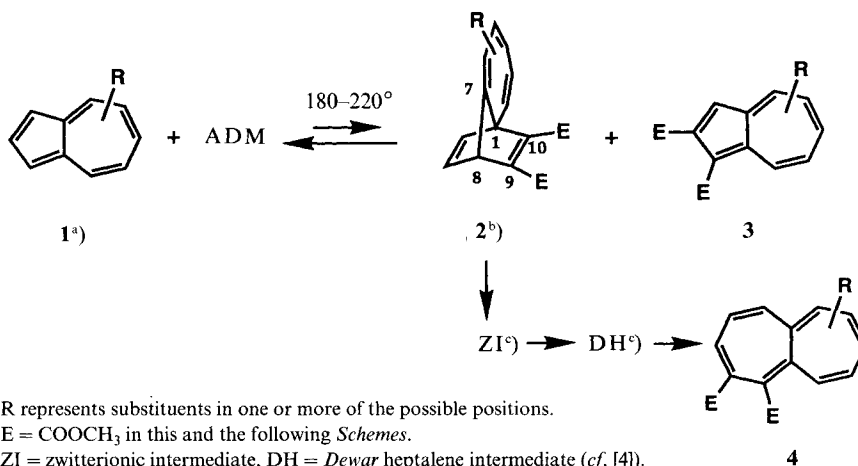
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It is shown that azulenes react with dimethyl acetylenedicarboxylate (ADM) in solvents such as toluene, dioxan, or MeCN in the presence of 2 mol-% $[\text{RuH}_2(\text{PPh}_3)_4]$ already at temperatures as low as 100° and lead to the formation of the corresponding heptalene-1,2-dicarboxylates in excellent yields (*Tables 1* and *2*). The Ru-catalyzed reaction of ADM with 1-(*tert*-butyl)-4,6,8-trimethylazulene (**31**) takes place even at room temperature, yielding the primary tricyclic addition product **32** and its thermal *retro-Diels-Alder* product dimethyl 4,6,8-trimethylazulene-1,2-dicarboxylate (**21**; *Scheme 4*). At 100° in MeCN, **32** yields 90% of **21** and only 10% of the corresponding heptalene. These observations demonstrate that $[\text{RuH}_2(\text{PPh}_3)_4]$ catalyzes the first step of the thermal formation of heptalenes from azulenes and ADM which occurs in apolar solvents such as tetralin or decalin at temperatures > 180° (*cf. Scheme 1*).

Introduction. – The most convenient synthesis of heptalene-1,2-dicarboxylates **4** is represented by the thermal reaction of azulenes **1** with dimethyl acetylenedicarboxylate (ADM) in apolar solvents such as tetralin or decalin (*Scheme 1*) [1–3]. Recently, we have shown that the tricyclic compounds **2**, which are reversibly formed in a concerted *Diels-Alder*-type reaction, showing only little or no polarity in the transition state, are the

Scheme 1

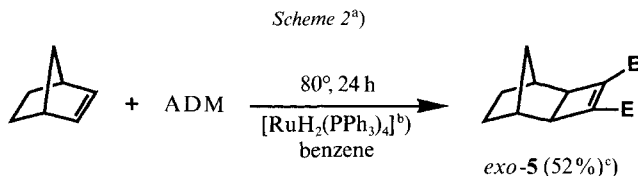


¹⁾ Part of the planned Ph.D. thesis of A.J.R., University of Zurich.

crucial primary intermediates in heptalene formation [4]. Important for the heptalene formation from **2** is the heterolysis of their C(1)–C(10) bond yielding a zwitterion **ZI** with the positive charge stabilized in a tropylium-like structure and the negative charge in a ketene-enolate-like structure. Bond formation between C(7) and C(10) ($\rightarrow$ **DH**) followed by an orbital-symmetry-allowed opening of the original C(7)–C(8) bond will then lead to the heptalene-1,2-dicarboxylates **4** (*cf.* [5] for thermal ring opening of *Dewar* heptalenes). Intermediates of type **2** can be obtained by the reaction of azulenes with ADM in hexane at 30° under pressures of *ca.* 7 kbar [4] (*cf.* also [6]). At temperatures $> 60^\circ$ and in apolar solvents, intermediates **2** decompose mainly to the starting materials, whereas in polar solvents, depending on the polarity of the solvent, the heptalenes **4** are formed in competition to the starting materials (*e.g.* in MeCN up to 70% of the heptalenes are formed at 110° [4]).

The disadvantage of heptalene formation at high temperatures in tetralin or decalin is given by the fact that the intermediates of type **2** can undergo a sometimes very efficient, irreversible second *retro-Diels-Alder* reaction to yield the corresponding azulene-1,2-dicarboxylates **3** at the expense of heptalene formation (*cf.* [1–3]). Therefore, it would be of interest to find conditions under which ADM adds to azulenes already at temperatures $\leq 100^\circ$ to yield intermediates of type **2** or those such as **DH** which lie on the reaction path between **2** and **4** and may represent formal [2 + 2] cycloadducts of ADM and azulenes.

Result and Discussion. – It is known that transition metals catalyze formal [2 + 2] cycloadditions of olefins, especially of those with strained double bonds (*cf.* [7] and literature cited therein). In the last years, several examples of transition-metal-catalyzed [2 + 2] cross-cycloadditions [8] [9] as well as homo-*Diels-Alder* reactions [10] with ADM and other alkynes have been reported. For example, *Mitsudo et al.* [8] described the [2 + 2] cross-cycloaddition of ADM with norbornene and related bicyclic olefins in benzene at 80°, catalyzed by $[\text{RuH}_2(\text{PPh}_3)_4]$ and comparable Ru complexes, to yield [2 + 2] adducts of type **5** (*Scheme 2*).



^{a)} *Cf.* [8]. ^{b)} 2 mol-% of the catalyst in the presence of equimolar amounts of the reactants in 1M solution of benzene. ^{c)} Yield of distilled material.

We applied these conditions to the reaction of guaiazulene (**6**) as model compound and ADM in toluene and observed the formation of the corresponding dimethyl 7-isopropyl-5,10-dimethylheptalene-1,2-dicarboxylate (**7**) [2] within 24 h already at 110–125° in up to 90% yield (*cf. Table 1*)³⁾. The Ru-catalyzed addition reaction could also be performed in dry dioxan.

²⁾ The reaction conditions for this and the following described reactions have not been optimized systematically.

³⁾ The thermal reaction of **6** and ADM in tetralin at 207° yields 63.5% of **7** besides 5.7% of dimethyl 7-isopropyl-4-methylazulene-1,2-dicarboxylate (*cf.* **3** in *Scheme 1*) [2a]. The latter compound was not detected in the Ru-catalyzed reaction.

Table 1. Thermal Reaction of Guaiazulene (**6**) with ADM in the Presence of 2 mol-% of $[RuH_2(PPh_3)_4]^a)$

Entry	Molar ratio ADM/ 6	Solvent	Reaction temp. [°]	Reaction time [h]	Recovered 6 [%] ^{b)}	Heptalene-1,2-dicarboxylate 7 [%] ^{b)}
1	1	toluene	110	24	50	32 (64)
2	1	toluene	125	24	35	45 (69)
3	2	toluene	125	24	25	50 (66)
4	3	toluene	125	24	5	90 (95)
5	3	MeCN	100	8	0	78 ^{c)}
6	3	MeCN	100	24	0	80 ^{d)}
7	3	dioxan	120	24	13	85 (98)

a) The reactions were performed with 1 mmol of **6** in 10 ml of the solvent in a 25-ml *Schlenk* reaction vessel.

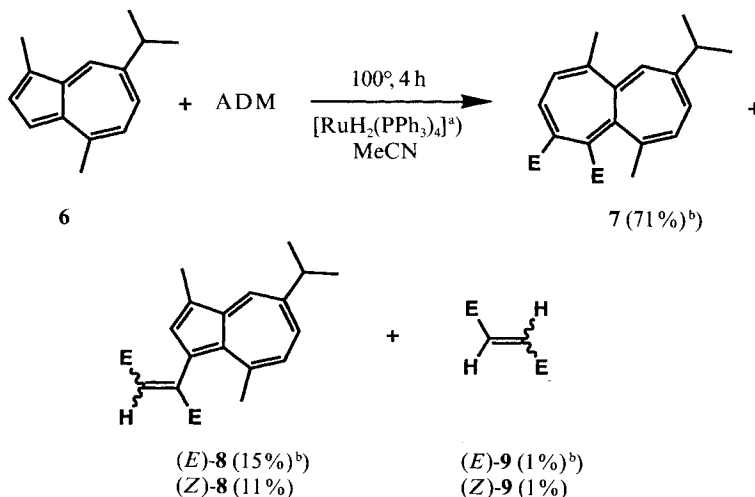
b) Yields of isolated and purified material. In brackets, yields with respect to reacted **6**.

c) 14% of (*E*)- and 8% of (*Z*)-**8** is also formed.

d) 8% of (*E*)- and 8% of (*Z*)-**8** is also formed.

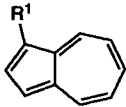
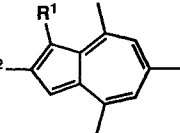
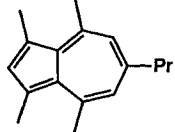
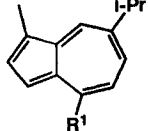
The Ru-catalyzed reaction was much faster in MeCN and took place already at 100°. However, under these conditions the formation of (*E*)- and (*Z*)-**8** as by-products was also observed. The results of a preparative run on a 2-g scale of **6** in 0.5M solution in MeCN in the presence of a three-fold molar excess of ADM are shown in *Scheme 3*. (*E*)- and (*Z*)-**8** are typical products of the protonation of the zwitterionic intermediates formed by heterolysis of the C(1)–C(10) bond in the primary tricyclic adducts of type **2** (*Scheme 1*; cf. [4]). Dimethyl fumarate and dimethyl maleate ((*E*)- and (*Z*)-**9**, respectively) are the hydrogenation products of ADM which indicate that the hydrido catalyst interacts with ADM in the catalytic cycle (cf. *Scheme 5* as well as [8]).

Scheme 3



a) 2 mol-% of the catalyst in 0.5M solution of **6** in MeCN in the presence of 3 mol-equiv. of ADM. b) Yield of crystallized material.

Table 2. Thermal Reaction of Various Azulenes with ADM in the Presence of 2 mol-% of $[RuH_2(PPh_3)_4]$ in MeCN at 100°^{a)}

Entry	Starting azulene	R ¹	R ²	No.	Heptalene-dicarboxylates ^{b)}		Azulene-1,2-dicarboxylate ^{c)}		Recovered starting azulene	Reported yields of the thermal reaction ^{d)}	
					[%]	No.	[%]	No.		[%]	Ref.
1		H	—	10	31 (40)	18	8	19	22 ^{e)}	25/2	[1b]
2		Me	—	11	20 (27) ^{f)}	20	6	19	28	40 ^{g)} /3	[1b]
3		H	H	12	75 (78) ^{h)}	22a/b	8	23	4	56/8	[1b]
4		Me	H	13	90 ⁱ⁾	24a	—	—	—	40/39	[2b] [1b]
5		H	Me	14	100 ^{j)}	25a/b	—	—	—	84/10	[3] [1b]
6		—	—	15	42 (60) ^{k)}	26a/b	10	27	30	19.5/40	[3]
7		l)	—	16	30 (50)	28a	—	—	40	10/—	[11]
8		m)	—	17	30	29a ⁿ⁾	—	—	—	—	—

^{a)} 0.5 mmols of the azulenes were reacted with 1.5 mmol of ADM in 5 ml of MeCN over 24 h.

^{b)} Yields of isolated and purified material. In brackets, yields with respect to the amount of reacted azulenes.

^{c)} Yields of isolated and purified material.

^{d)} Yields of heptalenedicarboxylates/azulene-1,2-dicarboxylate.

^{e)} Besides 6% of the corresponding dimethyl 1-(azulen-1-yl)fumarate and maleate and 5% of dimethyl 3,4-dihydrocyclopent[*c,d*]azulene-1,2-dicarboxylate (**33**; *cf.* [1a]).

^{f)} Only the 1,2-dicarboxylate **20** was detected and isolated. In addition, in fractions containing **19** the ¹H-NMR signals (300 MHz, CDCl₃) of dimethyl 11-methyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate (in total 10%; H—C(8) as *d* at 4.19 ppm with ³*J*(H—C(8), H—C(12)) = 3.4 Hz; *cf.* Scheme 4) could be identified. As further products, dimethyl 4-methyl-3,4-dihydrocyclopent[*c,d*]azulene-1,2-dicarboxylate (in total 5%; *cf.* **28** in Footnote *e*) and presumably methyl bis(3-methylazulen-1-yl)acetate (in total 9%) were isolated.

^{g)} 1.35:1 mixture of **20** and the corresponding heptalene-2,3-dicarboxylates **21** (*cf.* [1b]).

^{h)} Thermal equilibrium mixture of 79% of the 1,2-dicarboxylate **22a** and 21% of the 4,5-dicarboxylate **22b** (*cf.* [1b]).

ⁱ⁾ The 1,2-dicarboxylate **24a** was isolated (*cf.* [2c]) and, in addition, 6% of the corresponding 1-(azulen-1-yl)fumarate and maleate (*cf.* [4]).

^{j)} Thermal equilibrium mixture of 73% of the 1,2-dicarboxylate **25a** and 27% of the 4,5-dicarboxylate **25b** (*cf.* [3]).

^{k)} Thermal equilibrium 1:1 mixture of 1,2- (**26a**) and 4,5-dicarboxylate **26b** (*cf.* [3]).

^{l)} R¹ = (*E*)-*p*-MeO—C₆H₄CH=CH.

^{m)} R¹ = (*E*)-2-(7-isopropyl-1-methylazulen-4-yl)ethenyl.

ⁿ⁾ Tetramethyl (*E*)-7,7'-diisopropyl-5,5'-dimethyl-10,10'-ethylenediheptalene-1,1',2,2'-tetracarboxylate (**29a**). The compound was not resolved on a CHIRACEL OD HPLC column, *i.e.* it should have *meso*-configuration. As a by-product, dimethyl 7-isopropyl-1-methylacenaphthylene-3,4-dicarboxylate (**30**) was isolated in 2% yield.

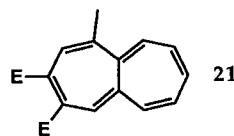
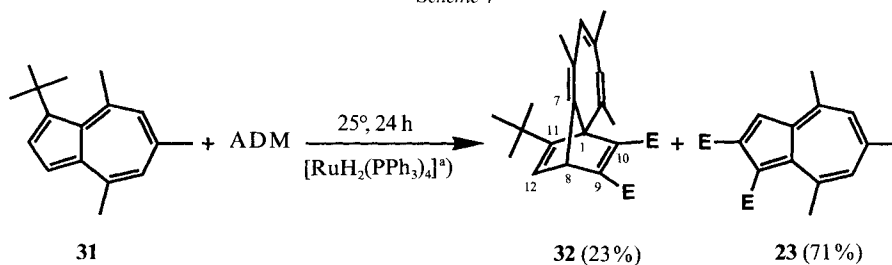


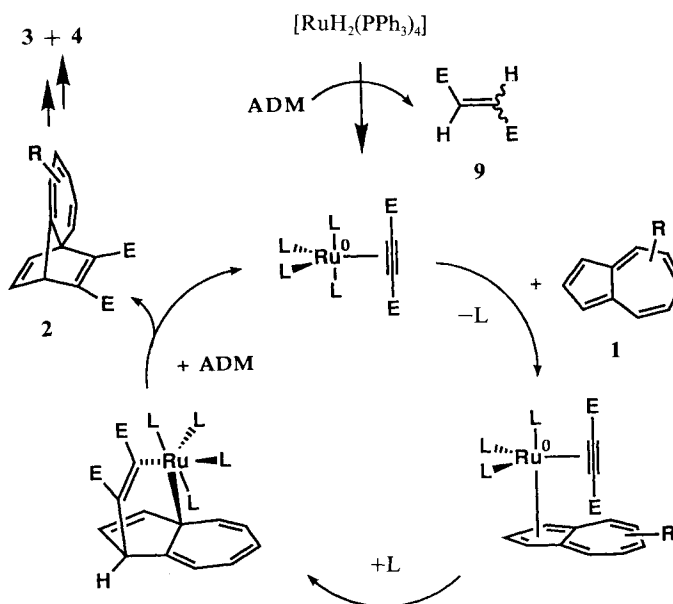
Table 2 shows the results of a number of Ru-catalyzed addition experiments of ADM with other azulenes under standardized conditions²⁾. In all cases, the catalyzed reactions gave higher yields than their purely thermal variants at 180–220°. The addition reactions with the azulenes **16** and **17** [11] demonstrate that azulenes with unsaturation in the side chain undergo also heptalene formation. In the case of azulene **17**, both azulenyl moieties are transformed into the corresponding heptalenyl structures of **29a**.

The reaction of 1-(*tert*-butyl)-4,6,8-trimethylazulene (**31**) with ADM in the presence of $[\text{RuH}_2(\text{PPh}_3)_4]$ took place already at 25° (Scheme 4). The main product was the azulene-1,2-dicarboxylate **23** which is the sole product in the purely thermal reaction of **31** with ADM at 100° in tetralin [12]. The second product, isolated in 23% yield, was the tricyclic compound **32**. Compounds of this type have so far been obtained from azulenes

Scheme 4



^{a)} The reaction was performed under the described conditions in a 2.5:1 mixture of MeCN and toluene.

Scheme 5^{a)}

^{a)} Cf. also Scheme 1; L = PPh_3 .

and ADM only under pressures of *ca.* 7 kbar [4] [6]. Characteristic for **32** is its $^1\text{H-NMR}$ spectrum (C_6D_6) that shows $\text{H-C}(8)$ as a *d* at 4.48 ppm with $^3J(\text{H-C}(8), \text{H-C}(12)) = 4.1$ Hz which is quite typical for this structural type (*cf.* [4] [13] as well as *Footnote f* in *Table 2*). The other chemical shifts of **32** are in perfect agreement with those of other tricyclic structures with Me groups at C(2), C(4), and C(6) (*cf.* [4]). When **32** was heated at 100° in MeCN, it decomposed to **23** (90%) and formed a second product (10%) which represented, according to its UV spectrum, presumably the corresponding dimethyl 5-(*tert*-butyl)-6,8,10-trimethylheptalene-1,2-dicarboxylate.

The observation that the azulene **31** and ADM are transformed by Ru-catalysis into **32** demonstrates convincingly that the primary adducts of the thermal reaction (*cf.* *Scheme 1*) are also the crucial intermediates in the catalyzed process which yield, in the established uncatalyzed thermal reactions [4], the corresponding heptalenes. Therefore, we propose the catalytic cycle shown in *Scheme 5* to explain the reaction of azulenes with ADM in the presence of Ru catalysts.

We thank Prof. M. Hesse and his coworkers for mass spectra, Prof. W. von Philipsborn and his coworkers for NMR support, and our microanalytical laboratory under the direction of H. Frohofer for elemental analysis. The financial support of this work by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung is gratefully acknowledged.

Experimental Part

General. See [2–4]. HPLC on a Hewlett-Packard instrument (model 1040A) with a Milton-Roy pump (model CM 4000) on a Spherisorb (ODS, 5 μm) column (length 250, diameter 4.5 mm). Column chromatography (CC) on silica gel (230–400 mesh, ASTM). UV spectra on an Otsuka spectrophotometer (model MCPD 1100). Maxima and minima (λ_{max} and λ_{min}) are given in nm ($\log \epsilon$). IR spectra on a Perkin-Elmer FT-IR spectrophotometer (model FT-IR 1600); band positions are given in cm^{-1} . $^1\text{H-NMR}$ spectra at 300 MHz on a Bruker instrument (model AC 300). $^{13}\text{C-NMR}$ spectra at 50 MHz on a Varian instrument (model XL200). Chemical shifts with respect to TMS (= 0) as internal standard; f.s. fine structure. Coupling constants *J* in Hz. MS on a Finnigan instrument (model MAT SSQ 700); EI at 70 eV; ions in *m/z* (rel. %).

Ru-Catalyzed Addition of Dimethyl Acetylenedicarboxylate (ADM) to Azulenes. All reactions were performed under Ar in Schlenk reaction vessels. Toluene (*purum*, Merck) was applied without further purification. Acetonitrile (MeCN; *puriss.*, Fluka) was stored over molecular sieves (4 Å). Dioxan (*puriss.*, Fluka) was distilled over Na and under Ar before use. ADM (*purum*, Fluka), hexane, and Et_2O were distilled before use. Azulene (**10**, Lancaster) and guaiazulene (**6**, *puriss.*, Fluka) were applied without further purification. 1-Methyl- (**11**) [14], 4,6,8-trimethyl- (**12**) [15], 1,4,6,8- (**13**) [2b], and 2,4,6,8-tetramethylazulene (**14**) [3] as well as 6-propyl-1,3,4,8-tetramethyl- (**15**) [3] and 1-(*tert*-butyl)-4,6,8-trimethylazulene (**31**) [16] were synthesized according to literature procedures. 7-Isopropyl-4-[(*E*)-2-(4-methoxyphenyl)ethen-1-yl]-1-methylazulene (**16**) and (*E*)-1,2-bis(7-isopropyl-1-methylazulen-4-yl)ethene (**17**) were supplied by A. Briquet [11]. The catalyst $[\text{RuH}_2(\text{PPh}_3)_4]$ was prepared according to [17].

All addition reactions were performed in the same way: 0.5 mmol of the azulene (1.0 mmol in the case of **6**), 1.5 (3.0) mmol of ADM, and 0.01 (0.02) mmol of $[\text{RuH}_2(\text{PPh}_3)_4]$ were placed, together with 5 ml (10 ml) of the solvent, in a 25-ml Schlenk reaction vessel. The vessel was stoppered and heated at the given temp. and time in an oil bath. The reaction mixture was diluted with Et_2O and washed with H_2O (3×30 ml each). After drying (MgSO_4), the solvent was distilled off in a rotatory evaporator and subjected to CC with hexane/ Et_2O 3:2. The results are collected in *Tables 1* and *2*.

Azulene (10) and ADM. After a forerun of unreacted **10** (22%), fractions of pure dimethyl heptalene-1,2-dicarboxylate (**18**; R_f 0.24⁴); 31%) [1], dimethyl azulene-1,2-dicarboxylate (**19**; R_f 0.20; 8%) [1], dimethyl (*E*)- and (*Z*)-1-(azulen-1'-yl)ethene-1,2-dicarboxylate (R_f 0.36; 6%), and dimethyl 3,4-ethanoazulene-1,2-dicarboxylate (**28**; R_f 0.17; 5%) [1] were obtained.

⁴) All R_f values refer to TLC on silica gel (60-F-254 aluminium plates, Merck; thickness of the layer 0.2 mm) with hexane/ Et_2O 3:2 as moving phase if not otherwise stated.

Data of 33. Violet crystals. M.p. 138.2–138.6° ([1a]: 138–139°). $^1\text{H-NMR}$ (CDCl_3): 8.85 (d , $^3J(7,8) = 10.0$, $\text{H-C}(8)$); 7.61 (t , $^3J(8,7) \approx ^3J(6,7) = 10.0$, $\text{H-C}(7)$); 7.25 (t , $^3J(7,6) \approx ^3J(5,6) = 9.8$, $\text{H-C}(6)$); 7.20 (d , $^3J(6,5) = 10.1$, $\text{H-C}(5)$); 3.98, 3.96 (2s, 2 MeOCO); 3.76, 3.42 ($AA'BB'$ system, $\text{CH}_2\text{-C}(4)$, $\text{CH}_2\text{-C}(3)$).

7-Isopropyl-4-[(*E*)-2-(4-methoxyphenyl)ethenyl]-1-methylazulene (**16**) and ADM. After a forerun of **16** (40%) pure dimethyl 7-isopropyl-10-[(*E*)-2-(4-methoxyphenyl)ethenyl]-5-methylheptalene-1,2-dicarboxylate (**28a**; 30%) [11] was obtained.

Data of 28a. Slightly yellow crystals. M.p. 182–183° (hexane). R_f (hexane/ Et_2O 1:1) 0.24. UV (hexane): λ_{max} 351.2 (sh, 4.06), 312.0 (4.37), 257.4 (4.31), 243.8 (sh, 4.28), 211.0 (4.37); λ_{min} 279.6 (4.20), 228.2 (4.26), 206.8 (4.37). IR (KBr): 2950m, 1731s, 1709s, 1645w, 1604m, 1560m, 1510s, 1434m, 1395w, 1269s, 1253s, 1223m, 1173m, 1158m, 1108m, 1051m, 1033m. $^1\text{H-NMR}$ (CDCl_3): 7.58 (d , $^3J(4,3) = 6.4$, $\text{H-C}(3)$); 7.28, 6.82 ($AA'BB'$ system, $J_{\text{ortho}} = 8.8$, 4 arom. H); 6.74 (d , $^3J(1,2) = 16.0$, $p\text{-MeO-C}_6\text{H}_4\text{CH=CH}$); 6.50 (d , $^3J(2,1) = 16.0$, $p\text{-MeO-C}_6\text{H}_4\text{CH=CH}$); 6.42 (d , f.s., $^3J(9,8) = 6.9$, $\text{H-C}(8)$); 6.36 (d , $^3J(8,9) = 6.9$, $\text{H-C}(9)$); 6.32 (dq , $^3J(3,4) = 6.4$, $^4J(\text{CH}_3\text{-C}(5), 4) = 1.6$, $\text{H-C}(4)$); 5.92 (s, $\text{H-C}(6)$); 3.79, 3.72 (2s, 2 MeOCO); 3.49 (s, $\text{CH}_3\text{O-C}_6\text{H}_4$); 2.53 (sept., $J = 6.8$, $\text{Me}_2\text{CH-C}(7)$); 2.07 (s, f.s., $\text{CH}_3\text{-C}(5)$); 1.08, 1.05 (2d, $J = 6.9$, 6.7, $(\text{CH}_3)_2\text{CH-C}(7)$). CI-MS: 459 (100, $[M + 1]^+$), 458 (1). Anal. calc. for $\text{C}_{29}\text{H}_{30}\text{O}_5$ (458.56): C 75.96, H 6.59; found: C 76.03, H 6.68.

(*E*)-1,2-Bis(7-isopropyl-1-methylazulen-4-yl)ethene (**17**) and ADM. CC yielded in a first fraction dimethyl 7-isopropyl-1-methylacenaphthylene-3,4-dicarboxylate (**30**; 2%) followed by tetramethyl (*E*)-7,7'-diisopropyl-5,5'-dimethyl-10,10'-ethenylenediheptalene-1,1',2,2'-tetracarboxylate (**29a**; 30%). Both compounds were recrystallized from hexane/ Et_2O .

Data of 30. Red-orange needles. M.p. 193–194°. R_f (hexane/ Et_2O 1:1) 0.28. UV (hexane): λ_{max} 357.0 (sh, 3.70), 342.0 (3.72), 252.7 (4.30), 241.8 (4.26); λ_{min} 311.7 (3.53), 245.1 (4.25). IR (KBr): 2952m, 1731s, 1717s, 1438m, 1363m, 1268m, 1225m, 1197m, 1161m. $^1\text{H-NMR}$ (CDCl_3): 7.95 (s, $\text{H-C}(6)$); 7.55 (s, $\text{H-C}(8)$); 7.29 (s, $\text{H-C}(5)$); 7.00 (q -like, $^4J(\text{H}, \text{CH}_3\text{-C}(1)) = 1.67$, $\text{H-C}(2)$); 3.99 (s, $\text{MeOCO-C}(3)$); 3.88 (s, $\text{MeOCO-C}(4)$); 3.22 (sept., $J = 6.9$, $(\text{CH}_3)_2\text{CH-C}(7)$); 2.43 (d , $^4J(\text{CH}_3, \text{H-C}(2)) = 1.54$, $\text{CH}_3\text{-C}(1)$); 1.38 (d , $J = 6.9$, $(\text{CH}_3)_2\text{CH-C}(7)$). $^1\text{H-NOE}$ (400 MHz, CDCl_3): 7.95 ($\text{H-C}(6)$) $\rightarrow$ 7.29 (s, $\text{H-C}(5)$), 3.88 (m, $\text{MeOCO-C}(4)$), 3.22 (s, $(\text{CH}_3)_2\text{CH-C}(7)$), and 1.38 (m, $(\text{CH}_3)_2\text{CH-C}(7)$); 7.29 ($\text{H-C}(5)$) $\rightarrow$ 7.95 (s, $\text{H-C}(6)$), 3.88 (m, $\text{MeOCO-C}(4)$); 3.22 ($(\text{CH}_3)_2\text{CH-C}(7)$) $\rightarrow$ 7.95 (s, $\text{H-C}(6)$), 7.55 (s, $\text{H-C}(8)$), 1.38 (s, $(\text{CH}_3)_2\text{CH-C}(7)$).

Data of 29a. Yellow-orange crystals. M.p. 109°. R_f (hexane/ Et_2O 1:1) 0.19. UV (hexane): λ_{max} 379.0 (3.88), 285.0 (sh, 4.25), 251.4 (4.46), 241.8 (4.46); λ_{min} 363.1 (3.86), 245.8 (4.43). IR (KBr): 2957m, 1725s, 1434m, 1269s, 1195m, 1159m. $^1\text{H-NMR}$ (CDCl_3): 7.54 (d , f.s., $^3J(\text{H}, \text{H-C}(4)) = 6.46$, $\text{H-C}(3,3')$); 6.32 (d , $^3J(\text{H}, \text{H-C}(9)) = 6.70$, $\text{H-C}(8,8')$); ca. 6.30 (dq -like, mainly covered, $\text{H-C}(4,4')$) (in C_6D_6 at 6.00 as dq -like); 6.29 (s, $\text{H-C}(1,2)$); 6.18 (d , $^3J(\text{H}, \text{H-C}(8)) = 6.78$, $\text{H-C}(9,9')$); 5.86 (s, $\text{H-C}(6,6')$); 3.69 (s, $\text{MeOCO-C}(2,2')$); 3.43 (s, $\text{MeOCO-C}(1,1')$); 2.48 (sept., $J = 6.85$, $(\text{CH}_3)_2\text{CH-C}(7,7')$); 2.07 (br. s, $\text{CH}_3\text{-C}(5,5')$); 1.08, 1.05 (2d, $J = 6.94$, 6.77, $(\text{CH}_3)_2\text{CH-C}(7,7')$). EI-MS: 676 (100, M^+), 644 (11), 617 (18), 585 (16), 553 (35), 277 (36). Anal. calc. for $\text{C}_{42}\text{H}_{44}\text{O}_8$ (676.81): C 74.53, H 6.55; found: C 74.66, H 6.46.

On a Chiracel OD HPLC column, which separates configurationally stable heptalene-1,2-dicarboxylates at r.t. into their antipodes, **29a** showed only a single peak; i.e. **29a** should be *meso*-configured.

1-(*tert*-Butyl)-4,6,8-trimethylazulene (**31**) and ADM. Azulene **31** (0.226 g, 1.00 mmol), ADM (0.36 ml, 3.00 mmol), and $[\text{RuH}_2(\text{PPh}_3)_4]$ (0.024 g, 0.02 mmol) were dissolved in a mixture of MeCN (5 ml) and toluene (2 ml) and stirred during 24 h at r.t. The solvent mixture was distilled off and the residue subjected to CC on silica gel (hexane/ Et_2O 1:1) which had been pretreated with 1% of Et_3N (cf. [4]). The first fraction contained pure dimethyl 4,6,8-trimethylazulene-1,2-dicarboxylate (**23**; 0.202 g; 71.0%) followed by fractions composed of pure dimethyl 11-(*tert*-butyl)-2,4,6-trimethyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate (**32**) which was recrystallized from hexane (0.085 g, 23.0%).

Data of 21. M.p. 140.2–140.8° ([2b]: 141–142°). R_f (hexane/ Et_2O 1:1) 0.40. $^1\text{H-NMR}$: identical with that reported in [2b].

Data of 32. Colorless fine needles. M.p. 96.1–97.1° (decomposition under blue coloring; formation of **23**). R_f (hexane/ Et_2O 1:1) 0.32. UV (hexane): λ_{max} 333.0 (3.47), 299.6 (sh, 3.60), 291.9 (3.75), 231.5 (4.06); λ_{min} 325.5 (3.45), 270.6 (3.75). IR (KBr): 2961m, 1725s, 1714s, 1621m, 1432m, 1318m, 1249s, 1108m, 1028m. $^1\text{H-NMR}$ (C_6D_6): 6.35 (d , $^3J(12,8) = 4.06$, $\text{H-C}(12)$); 5.69 (s, $\text{H-C}(5)$); 5.25 (s, $\text{H-C}(3)$); 4.48 (d , $^3J(8,12) = 4.06$, $\text{H-C}(8)$); 3.54, 3.27 (2s, $\text{MeOCO-C}(9,10)$); 2.22 (s, $\text{CH}_3\text{-C}(2)$); 1.67 (s, $\text{CH}_3\text{-C}(4)$); 1.46 (s, $\text{CH}_3\text{-C}(6)$); 1.22 (s, $(\text{CH}_3)_3\text{C-C}(11)$). $^{13}\text{C-NMR}$ (C_6D_6): 166.1, 164.8, 164.2 ($\text{MeOCO-C}(9,10)$ and $\text{C}(7)$); 159.7, 156.0 ($\text{C}(9,10)$); 143.6, 140.5 ($\text{C}(11,12)$); 134.1, 133.3, 131.2, 130.6 ($\text{C}(2\text{--}5)$); 100.6 ($\text{C}(6)$); 75.5 ($\text{C}(1)$); 57.2 ($\text{C}(8)$); 51.8, 51.3 ($\text{CH}_3\text{OCO-C}(9,10)$); 37.8 ($(\text{CH}_3)_3\text{C-C}(12)$); 29.8 ($(\text{CH}_3)_3\text{C-C}(12)$); 27.2 ($\text{CH}_3\text{-CC}(2)$); 24.7 ($\text{CH}_3\text{-C}(4)$); 20.0 ($\text{CH}_3\text{-C}(6)$). EI-MS: 368

⁵⁾ Cf. the ^1H - and ^{13}C -NMR spectra of analogous tricyclic compounds reported in [4].

(1, M^+), 353 (3), 309 (22), 286 (45), 255 (46), 254 (38), 224 (10), 223 (23), 197 (39), 196 (100). Anal. calc. for $C_{23}H_{28}O_4$ (368.48): C 74.97, H 7.66; found: C 74.88, H 7.63.

Control Experiment. A small amount of **32** (0.010 g) was dissolved in MeCN (5 ml) and heated at 100° during 1 h. HPLC revealed the presence of 90% of **23** and 10% of a compound the UV of which was similar to that of dimethyl 5,6,8,10-tetramethylheptalene-1,2-dicarboxylate (**24a**; cf. [2b]) and of other heptalene-1,2-dicarboxylates (cf. [3]).

Reaction of Guaiazulene (6) and ADM on a Larger Scale. Azulene **6** (1.98 g, 0.01 mmol), ADM (3.69 ml, 0.03 mol), and the catalyst (0.23 g, 0.2 mmol) were dissolved in MeCN (20 ml) and transferred into a 50-ml Schlenk reaction vessel. After 4 h at 100°, all **6** was consumed (TLC). CC under the usual conditions yielded in foreruns small amounts of dimethyl fumarate ((*E*)-**9**; 0.014 g; 1%) and maleate ((*Z*)-**9**; 0.014 g, 1%) and then pure dimethyl 7-isopropyl-5,10-dimethylheptalene-1,2-dicarboxylate (**7**; 2.42 g, 71.0% [2]), followed by (*Z*)- and (*E*)-1-(5-isopropyl-3,8-dimethylazulen-1-yl)ethene-1,2-dicarboxylate ((*Z*)- and (*E*)-**8**; 0.37 g (11.0%) and 0.58 g (15.0%), respectively) [4] [18].

(*Z*)- and (*E*)-**9** were identified by their $^1\text{H-NMR}$. In addition, (*Z*)-**9** showed b.p. of 101°/18 Torr and (*E*)-**9** melted at 103–104°.

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