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

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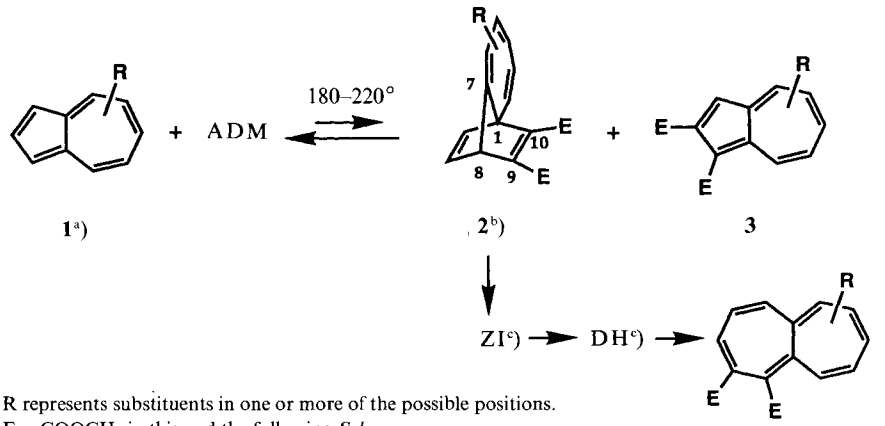
It is shown that azulenes react with dimethyl acetylenedicarboxylate (ADM) in solvents such as toluene, dioxan, or MeCN in the presence of 2 mol-% $[RuH_2(PPh_3)_4]$ already at temperatures as low as 100° and lead to the formation of the corresponding heptalene-1,2-dicarboxylates in excellent yields (*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 $[RuH_2(PPh_3)_4]$ 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[a]) 2[b]) 3 4

[a]) R represents substituents in one or more of the possible positions.
[b]) E = $COOCH_3$ in this and the following *Schemes*.
[c]) ZI = zwitterionic intermediate, DH = *Dewar* heptalene intermediate (*cf.* [4]).

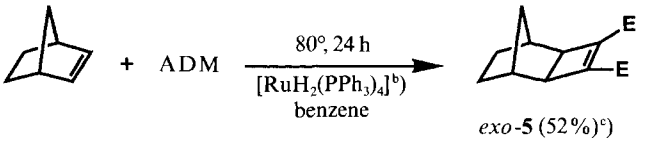
[1]) Part of the planned Ph.D. thesis of *A.J.R.*, University of Zurich.

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) (→**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 AMD in hexane at 30° under pressures of *ca.* 7 kbar [4] (*cf.* also [6]). At temperatures > 60° 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 ≤ 100° 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 $[RuH_2(PPh_3)_4]$ and comparable Ru complexes, to yield [2 + 2] adducts of type **5** (*Scheme 2*).

Scheme 2[a])



exo-**5** (52%)[c])

[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*)[2])[3]). The Ru-catalyzed addition reaction could also be performed in dry dioxan.

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[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.

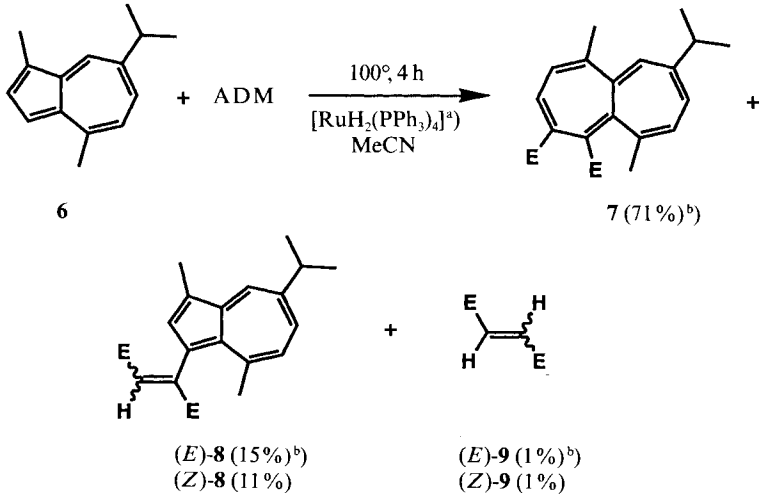
Table 1. *Thermal Reaction of Guaiazulene* (**6**) *with ADM in the Presence of 2 mol-% of* $[RuH_2(PPh_3)_4]$ [a])

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



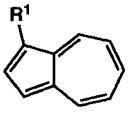
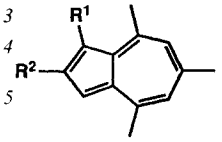
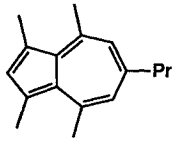
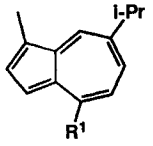
6 **7** (71%)[b])

(*E*)-**8** (15%)[b])
(*Z*)-**8** (11%)

(*E*)-**9** (1%)[b])
(*Z*)-**9** (1%)

[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-dicarboxy-lates[b])		Azulene-1,2-dicarb-oxylate[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.

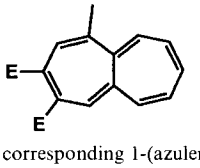
[c]) Yields of isolated and purified material.

[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 ^{1}H-NMR signals (300 MHz, $CDCl_3$) 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 ^3J(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]).



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[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]) R^1 = (*E*)-*p*-MeO–C_6H_4CH=CH.

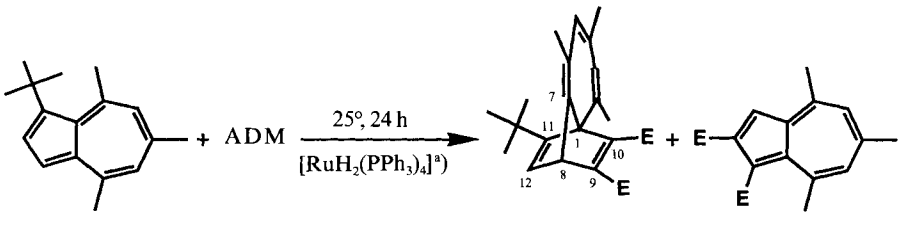
[m]) R^1 = (*E*)-2-(7-isopropyl-1-methylazulen-4-yl)ethenyl.

[n]) Tetramethyl (*E*)-7,7′-diisopropyl-5,5′-dimethyl-10,10′-ethenylenediheptalene-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 conditions[2]). 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 $[RuH_2(PPh_3)_4]$ 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

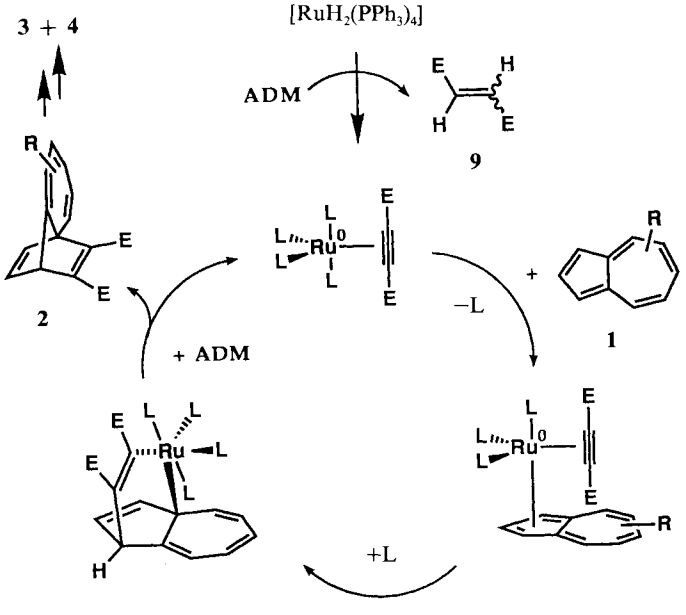
Scheme 4



31 **32** (23%) **23** (71%)

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}H-NMR spectrum (C_6D_6) that shows H–C(8) as a *d* at 4.48 ppm with ^3J(H–C(8),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 ($\log \varepsilon$). IR spectra on a *Perkin-Elmer* FT-IR spectrophotometer (model *FT-IR 1600*); band positions are given in cm^{-1}. ^{1}H-NMR spectra at 300 MHz on a *Bruker* instrument (model *AC300*). ^{13}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**, *Lancester*) 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 $[RuH_2(PPh_3)_4]$ 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 $[RuH_2(PPh_3)_4]$ 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 0.24[4]); 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.

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[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}H-NMR ($CDCl_3$): 8.85 (*d*, $^3J(7,8) = 10.0$, H–C(8)); 7.61 (*t*, $^3J(8,7) \approx {}^3J(6,7) = 10.0$, H–C(7)); 7.25 (*t*, $^3J(7,6) \approx {}^3J(5,6) = 9.8$, H–C(6)); 7.20 (*d*, $^3J(6,5) = 10.1$, H–C(5)); 3.98, 3.96 (2*s*, 2 MeOCO); 3.76, 3.42 (*AA'BB'* system, CH_2–C(4), CH_2–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): 2950*m*, 1731*s*, 1709*s*, 1645*w*, 1604*m*, 1560*m*, 1510*s*, 1434*m*, 1395*w*, 1269*s*, 1253*s*, 1223*m*, 1173*m*, 1158*m*, 1108*m*, 1051*m*, 1033*m*. ^{1}H-NMR ($CDCl_3$): 7.58 (*d*, $^3J(4,3) = 6.4$, H–C(3)); 7.28, 6.82 (*AA'BB'* system, $J_{ortho} = 8.8$, 4 arom. H); 6.74 (*d*, $^3J(1,2) = 16.0$, *p*-MeO–C_6H_4CH=CH); 6.50 (*d*, $^3J(2,1) = 16.0$, *p*-MeO–C_6H_4CH=C*H*); 6.42 (*d*, f.s., $^3J(9,8) = 6.9$, H–C(8)); 6.36 (*d*, $^3J(8,9) = 6.9$, H–C(9)); 6.32 (*dq*, $^3J(3,4) = 6.4$, $^4J(CH_3$–C(5),4) = 1.6, H–C(4)); 5.92 (*s*, H–C(6)); 3.79, 3.72 (2*s*, 2 MeOCO); 3.49 (*s*, CH_3O–C_6H_4); 2.53 (*sept.*, $J = 6.8$, Me_2CH–C(7)); 2.07 (*s*, f.s., CH_3–C(5)); 1.08, 1.05 (2*d*, $J = 6.9, 6.7$, $(CH_3)_2$CH–C(7)). CI-MS: 459 (100, $[M + 1]^+$), 458 (1). Anal. calc. for $C_{29}H_{30}O_5$ (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): 2952*m*, 1731*s*, 1717*s*, 1438*m*, 1363*m*, 1268*m*, 1225*m*, 1197*m*, 1161*m*. ^{1}H-NMR ($CDCl_3$): 7.95 (*s*, H–C(6)); 7.55 (*s*, H–C(8)); 7.29 (*s*, H–C(5)); 7.00 (*q*-like, $^4J(H,CH_3$–C(1)) = 1.67, H–C(2)); 3.99 (*s*, MeOCO–C(3)); 3.88 (*s*, MeOCO–C(4)); 3.22 (*sept.*, $J = 6.9$, $(CH_3)_2CH$–C(7)); 2.43 (*d*, $^4J(CH_3$, H–C(2)) = 1.54, CH_3–C(1)); 1.38 (*d*, $J = 6.9$, $(CH_3)_2$CH–C(7)). ^{1}H-NOE (400 MHz, $CDCl_3$): 7.95 (H–C(6)) → 7.29 (*s*, H–C(5)), 3.88 (*m*, MeOCO–C(4)), 3.22 (*s*, $(CH_3)_2CH$–C(7)), and 1.38 (*m*, $(CH_3)_2$CH–C(7)); 7.29 (H–C(5)) → 7.95 (*s*, H–C(6)), 3.88 (*m*, MeOCO–C(4)); 3.22 (($(CH_3)_2CH$–C(7)) → 7.95 (*s*, H–C(6)), 7.55 (*s*, H–C(8)), 1.38 (*s*, $(CH_3)_2$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): 2957*m*, 1725*s*, 1434*m*, 1269*s*, 1195*m*, 1159*m*. ^{1}H-NMR ($CDCl_3$): 7.54 (*d*, f.s., $^3J(H,$H–C(4)) = 6.46, H–C(3,3')); 6.32 (*d*, $^3J(H,$H–C(9)) = 6.70, H–C(8,8')); *ca.* 6.30 (*dq*-like, mainly covered, H–C(4,4')) (in C_6D_6 at 6.00 as *dq*-like); 6.29 (*s*, H–C(1,2)); 6.18 (*d*, $^3J(H,$H–C(8)) = 6.78, H–C(9,9')); 5.86 (*s*, H–C(6,6')); 3.69 (*s*, MeOCO–C(2,2')); 3.43 (*s*, MeOCO–C(1,1')); 2.48 (*sept.*, $J = 6.85$, $(CH_3)_2CH$–C(7,7')); 2.07 (br. *s*, CH_3–C(5,5')); 1.08, 1.05 (2*d*, $J = 6.94, 6.77$, $(CH_3)_2$CH–C(7,7')). EI-MS: 676 (100, M^+), 644 (11), 617 (18), 585 (16), 553 (35), 277 (36). Anal. calc. for $C_{42}H_{44}O_8$ (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*-configurated.

*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 $[RuH_2(PPh_3)_4]$ (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}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): 2961*m*, 1725*s*, 1714*s*, 1621*m*, 1432*m*, 1318*m*, 1249*s*, 1108*m*, 1028*m*. ^{1}H-NMR (C_6D_6)[5]: 6.35 (*d*, $^3J(12,8) = 4.06$, H–C(12)); 5.69 (*s*, H–C(5)); 5.25 (*s*, H–C(3)); 4.48 (*d*, $^3J(8,12) = 4.06$, H–C(8)); 3.54, 3.27 (2*s*, MeOCO–C(9,10)); 2.22 (*s*, CH_3–C(2)); 1.67 (*s*, CH_3–C(4)); 1.46 (*s*, CH_3–C(6)); 1.22 (*s*, $(CH_3)_3$C–C(11)). ^{13}C-NMR (C_6D_6): 166.1, 164.8, 164.2 (MeO*C*O–C(9,10) and C(7)); 159.7, 156.0 (C(9,10)); 143.6, 140.5 (C(11,12)); 134.1, 133.3, 131.2, 130.6 (C(2–5)); 100.6 (C(6)); 75.5 (C(1)); 57.2 (C(8)); 51.8, 51.3 (CH_3OCO–C(9,10)); 37.8 (($(CH_3)_3C$–C(12)); 29.8 (($CH_3)_3$C–C(12)); 27.2 (CH_3–CC(2)); 24.7 (CH_3–C(4)); 20.0 (CH_3–C(6)). EI-MS: 368

[5]) *Cf.* the ^{1}H- 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}H-NMR. In addition, (*Z*)-**9** showed b.p. of 101°/18 Torr and (*E*)-**9** melted at 103–104°.

REFERENCES

[1] a) K. Hafner, H. Diehl, H.U. Süss, *Angew. Chem.* **1976,** *88,* 121; *ibid. Int. Ed.* **1976,** *15,* 104; b) K. Hafner, G.L. Knaup, H.J. Lindner, *Bull. Chem. Soc. Jpn.* **1988,** *61,* 155, and lit. cit. therein.

[2] a) W. Bernhard, H.-R. Zumbrunnen, H.-J. Hansen, *Chimia* **1979,** *33,* 324; b) W. Bernhard, P. Brügger, J.J. Daly, P. Schönholzer, R.H. Weber, H.-J. Hansen, *Helv. Chim. Acta* **1985,** *68,* 415; c) W. Bernhard, P. Brügger, P. Schönholzer, R.H. Weber, H.-J. Hansen, *ibid.* **1985,** *68,* 429.

[3] Y. Chen, R.W. Kunz, P. Uebelhart, R.H. Weber, H.-J. Hansen, *Helv. Chim. Acta,* in press.

[4] R.A. Fallahpour, H.-J. Hansen, High Pressure Res., Special volume on 'High Pressure in Organic Synthesis', Ed. J. Jurczak, 1992, in press.

[5] a) Y. Sugihara, S. Wakabayashi, I. Murata, *J. Am. Chem. Soc.* **1983,** *105,* 6718; b) I. Murata, Y. Sugihara, T. Sugimura, S. Wakabayashi, *Tetrahedron* **1986,** *42,* 1745.

[6] F.K. Klärner, B. Dogan, W.R. Roth, K. Hafner, *Angew. Chem.* **1982,** *94,* 721; *ibid. Int. Ed.* **1982,** *21,* 708.

[7] a) P.N. Rylander, 'Organic Synthesis with Nobel Metal Catalysts', Academic Press, Inc., New York 1973, 181ff.; b) 'Transition Metal Organometallics in Organic Synthesis', Ed. H. Alper, Academic Press, Inc., New York, 1978, Vol. I, p. 57ff.; c) J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, 'Principles and Applications of Organotransition Metal Chemistry', University Science Books, Mill Valley, 1987, 816ff.

[8] T. Mitsudo, K. Kokuryo, T. Shinsugi, Y. Nakagawa, Y. Watanabe, Y. Takegami, *J. Org. Chem.* **1979,** *44,* 4494.

[9] T. Mitsudo, Y. Hori, Y. Watanabe, *J. Organomet. Chem.* **1987,** *334,* 157.

[10] I.-F. Duan, Ch.-H. Cheng, J.-S. Shaw, Sh.-S. Cheng, K.F. Lion, *J. Chem. Soc., Chem. Commun.* **1991,** 1347.

[11] A. Briquet, H.-J. Hansen, unpublished results.

[12] R.H. Weber, Ph.D. Thesis, University of Basel, 1988.

[13] F.K. Klärner, B. Dogan, W.R. Roth, K. Hafner, *Angew. Chem., Suppl.* **1982,** 1499.

[14] K. Hafner, C. Bernhard, *Liebigs Ann. Chem.* **1959,** *625,* 108.

[15] K. Hafner, H. Kaiser, *Org. Synth., Coll. Vol.* **1973,** *5,* 1088.

[16] M. Oki, N. Nakamura, *Bull. Chem. Soc. Jpn.* **1971,** *44,* 1880.

[17] J.J. Levison, S.D. Robinson, *J. Chem. Soc.,* A **1970,** 2947.

[18] P. Brügger, Ph.D. Thesis, No. 858, University of Fribourg, 1983.