146. Formation and Thermal Rearrangement of Dimethyl Tricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylates

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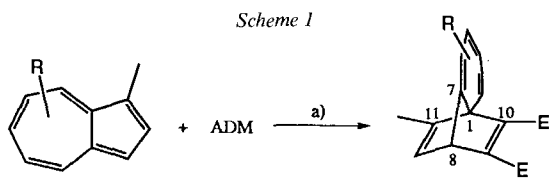
The high-pressure reaction of 1-methylazulenes **1** with excess of dimethyl acetylenedicarboxylate (ADM) in hexane at 30° and at pressures up to 7 kbar affords the tricyclic compounds **2** in reasonable-to-good yields (*cf. Table 1*). The crystalline compounds **2** decompose on melting into the starting materials and undergo rearrangement to the corresponding heptalene-1,2-dicarboxylates **6**. The X-ray crystal-structure analyses of **2f** and **2g** (*cf. Fig. 1*) reveal the presence of a perfectly planar seven-membered ring and comparably long C(1)–C(10) as well as C(1)–C(11) bonds (*cf. Tables 2* and *3*). The thermolysis of **2g** in different solvents leads in aprotic media to the formation of the starting azulene **1g** and, depending upon the polarity of the solvents, to varying amounts of the corresponding heptalene-1,2-dicarboxylate **6f** (*cf. Table 11*). The formed amounts of **1g** depends linearly on the E_T values of the solvents (*cf. Fig. 4*). The same is valid for the thermolysis of **2g** in protic media (*cf. Table 10* and *Fig. 3*). However, in these cases instead of the heptalene-1,2-dicarboxylate **6g**, the corresponding (*E*)- and (*Z*)-isomers of the 1-(azulen-1-yl)ethene-1,2-dicarboxylates **7g** are formed. The other tricyclic compounds **2** exhibit the same behavior on thermolysis in MeCN and BuOH (*cf. Tables 8* and *9*, resp.). The results show that the tricyclic compounds **2** undergo at temperatures up to 110° two competing reactions, namely heterolysis of the C(1)–C(10) bond, leading to the formation of heptalenes **6** in polar aprotic media, and the (*E*)- and (*Z*)-ethene-1,2-dicarboxylates **7** in polar protic media, and concerted homolysis of the C(1)–C(10) and C(8)–C(9) bonds in the sense of a *retro-Diels-Alder* reaction in apolar media, yielding the starting azulenes and ADM, the amount of which decrease with increasing polarity of the solvent. The kinetic and activation parameters measured for **2g** and the other tricyclic compounds **2** are collected in *Tables 12–15*. The tricyclic compounds **2a** and **2b** show in polar aprotic media (MeCN) a different behavior in that they form, instead of heptalenes, the corresponding 3,4-dihydrocyclopent[*cd*]azulene-1,2-dicarboxylates **16a** and **16b**, respectively (*Scheme 4*). Experiments with [8-^{2}H]-**2a** showed that these compounds are not formed *via* intramolecular H-shifts (*cf. Schemes 8* and *9*).

1. Introduction. – Three years ago, we reported on the high-pressure synthesis of dimethyl 11-methyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylates of type **2** by a *Diels-Alder*-type reaction of the azulenes **1** with dimethyl acetylenedicarboxylate (ADM; see *Scheme 1*) [1] (*cf.* [2]). These tricyclic compounds turned out to be the

Scheme 1

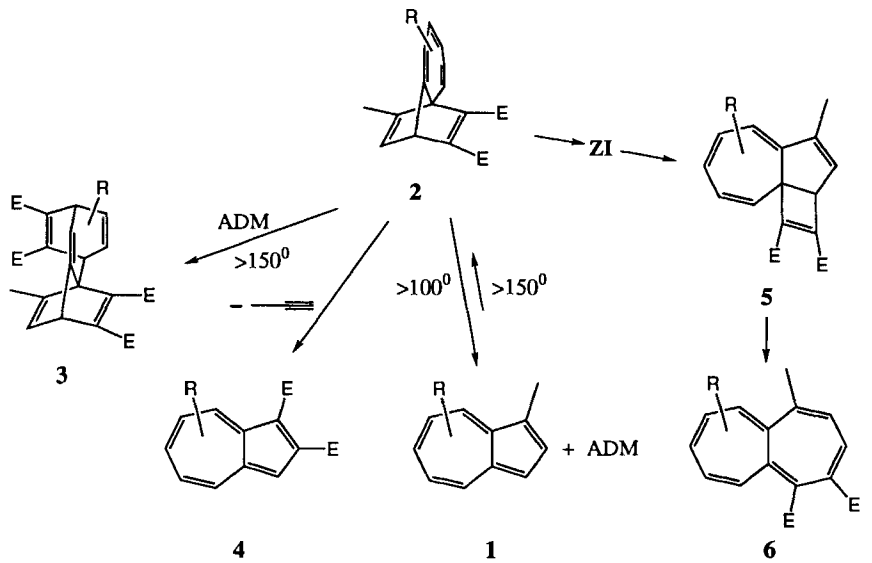


1 **2**

a) 6–7 kbar, 30°, hexane; 20–40%.

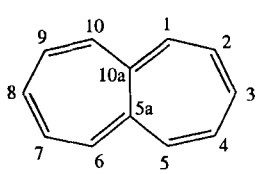
[1]) Part of the Ph. D. thesis of *R.-A.F.*, University of Zurich, 1994; new address: Institut für Anorganische Chemie der Universität, Spitalstrasse 51, CH–4056 Basel.

Scheme 2

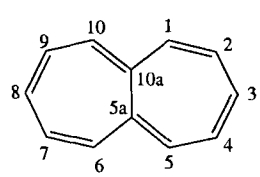


decisive primary intermediates in the formation of heptalene-1,2-dicarboxylates **6**[2]) from **1** and ADM in polar media such as tetralin or decalin [5] or supercritical CO_2 [6]. At temperatures > 150°, they may be trapped by excess ADM in a further *Diels-Alder* reaction resulting in the formation of tetracyclic compounds of type **3** (*Scheme 2*). On the other hand, already at temperatures ≥ 100°, the tricyclic compounds of type **2** are reverted to the starting azulenes **1** and ADM [1] [2], and it is the reversibility of the reaction of **1** with ADM at temperatures > 150° and normal pressure that makes the

[2]) From the very first edition of Sections A and B (Butterworths Scientific Publications, London, 1958) of the IUPAC 'Nomenclature of Organic Chemistry' up to 1979 edition of Sections A–F, and H [3], the numbering of the heptalene skeleton was as shown (*cf.* entry (5) in the accompanying list to *Rule A-21.1* [3]) which we strictly applied in all our preceding publications on heptalene chemistry. With the advent of the 1993 recommendations [4] of the 'IUPAC Nomenclature of Organic Compounds', the numbering had been changed as shown (see *Rule R-2.4.1.3.3* [4]). It reflects now indeed a better consistency with the numbering of other 'alenes' consisting of fused monocyclic rings such as pentalene. However, a change from the old to the new numbering of the heptalene skeleton corresponds to a reversible chemical process which may be induced thermally or photochemically, namely a double-bond shift (DBS process), *e.g.* a heptalene-1,2-dicarboxylate will be transformed into the corresponding heptalene-4,5-dicarboxylate (old numbering), or a heptalene-4,5-dicarboxylate will be changed into a heptalene-1,2-dicarboxylate (new numbering). To avoid any confusion and to preserve consistency with our earlier publications, we apply in this work the old numbering for heptalenes [3].



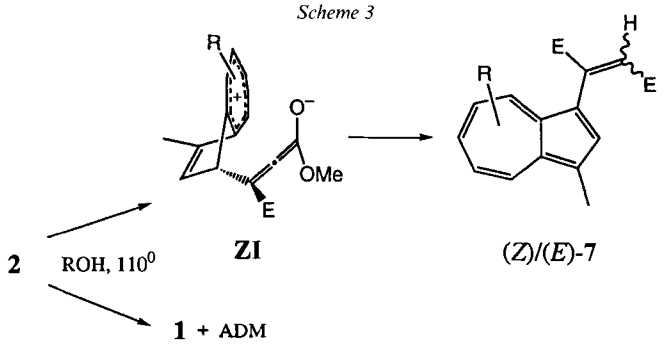
IUPAC Numbering of heptalene up to the 1979 edition [3]



IUPAC Numbering of heptalene according to the 1993 recommendations [4]

formation of **3** possible [5]. At these temperatures, the tricyclic compounds of type **2** may also undergo a *retro-Diels-Alder* type reaction affording azulene-1,2-dicarboxylates **4**. This reaction dominates in cases where the azulenes **1** carry at C(1), instead of the Me group, sterically demanding substituents such as a *t*-Bu group [7] [8] or conjugative substituents such as styryl groups [9]. The formation of the heptalene-1,2-dicarboxylates **6** takes its course *via* ring opening of the tricyclic intermediates of type **5**[3]) which, in turn, are formed by rearrangement of **2** *via* heterolytic cleavage of their C(1)–C(10) bond at temperatures > 150° in apolar media (*cf.* [12]). The thermal formation of **6** from **1** and ADM in apolar media moves thus on a narrow reaction ridge and, therefore, it is not astonishing that **6** are mostly produced in moderate yields and are accompanied by by-products such as **3** and **4** (*cf.* [15] [13])[4]). In our preliminary communication [1], we showed that the tricyclic compounds of type **2** undergo rearrangement in polar aprotic solvents such as MeCN, DMF, or DMSO already at 110° to yield mainly **6** in competition to the starting azulenes **1** and ADM. The latter compounds are formed by the *retro-Diels-Alder*-type reaction with a transition state of only little polarity. That zwitterions **ZI** are, indeed, formed as concrete intermediates could be demonstrated by their interception in polar protic media such as EtOH or formamide (*Scheme 3*). In these cases, (azulen-1-yl)-substituted maleates and fumarates, (*Z*)- and (*E*)-**7**, are formed in competition to the starting materials.

Scheme 3



In the meantime, we found that the formation of the tricyclic compounds **2** from azulenes **1** and ADM can be catalyzed by transition-metal complexes such as $[RuH_2(PPh_3)_4]$ [7] [16], $[RhH(PPh_3)_4]$, or $[Rh^I(azulene)(cod)]^+BF_4^-$ (cod = (*Z*,*Z*)-cycloocta-1,5-diene) [8] [17] as well as $[Pd^{II}Cl_2(cod)]$ [7b] and at temperatures as low as 25°. In MeCN as solvent,

[3]) Recently, we succeeded in the isolation, and structural and chemical characterization of a *Dewar*-heptalene derivative of type **5** from the reaction mixture of the Rh^I-catalyzed reaction of 5,9-diphenylbenz[*a*]azulene and ADM in MeCN [10]. The total synthesis of isomeric *Dewar* heptalenes, namely tricyclo[5.5.0.$0^{2,5}$]dodeca-3,6,8,10,12-pentaene derivatives, and their thermal ring opening in toluene at 110° heptalenes have already been reported (*cf.* [11] and lit. cit. there).

[4]) The picture of the reaction becomes still more complicated, when we take into account that the reversible HOMO(azulene)-controlled reaction of **1** with ADM, which has so far been considered, has to compete with an irreversible SHOMO(azulene)-controlled reaction resulting in the thermal addition of ADM to the seven-membered ring of the azulenes [5] [14]. Alkyl substituents at C(1) and C(3) of the azulenes (*cf.* [14b]) as well as π-acceptor substituents (*cf.* [15]) may completely suppress the heptalene formation or the addition of ADM at the five-membered ring of the azulenes, respectively, in favor of the addition at the seven-membered ring.

mostly excellent yields of the heptalene-1,2-dicarboxylates are attained at temperatures > 80°.

In the following, we describe additional experiments in relation to the high-pressure synthesis of **2**, their full structural characterization, and their thermal behavior in apolar and polar aprotic as well as protic media.

2. Dimethyl Tricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylates 2. – 2.1. *High-Pressure Synthesis from 1-Methylazulenes* **1** *and ADM.* The synthesis was performed according to a procedure applied by *Klärner et al.* [2] to the reaction of azulene itself with ADM in toluene at 50° and a pressure of 7 kbar [2][5]). We found that 1-Me-substituted azulenes **1** underwent the reaction with ADM at pressures of 5.5–7 kbar in hexane much easier. The reaction temperature could be lowered to 30° under these conditions at the expense of a prolongation of the reaction time. However, higher temperatures and shorter reaction times did not increase the yields of **2** (see *Table 1*), but

Table 1. *High-Pressure Synthesis of Dimethyl 11-Methyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylates* **2** *from 1-Methylazulenes* **1** *and ADM in Hexane at 30°*

Azulenes **1**		ADM[a]) [mol-equiv.]	Pressure[b]) [kbar]	Reaction time [h]	Turnover[c]) of **1** [%]	Tricycles **2**		By-products[e])	
No.	R					No.	Yield [%][d])	No.	Yield [%]
1a[f])	H	4.8	7.0	68	90	**2a**	24	–	
[3-^{2}H]-**1a**	[3-^{2}H]	4.6	7.0–6.2	67	88	[8-^{2}H]-**2a**	29	–	
1b	6-Me	3.9	7.0–6.9	48	43	**2b**	25	–	
1c	4,6-Me_2	4.3	7.0	48	84	**2c**	6.5	–	
1d	5,7-Me_2	2.8	6.9–6.8	61	60	**2d**	22	–	
1e	4,6,8-Me_3	2.3	7.0–6.3	69	> 98	**2e**	41	(*Z*)-**7e**	3.2[g])
								(*E*)-**7e**	5.3
1f	2,4,6,8-Me_4	34	7.0–6.9	42	> 98	**2f**	38	–[h])	
1g	4-Me, 7-(i-Pr)	4.0	5.5	95	83	**2g**	62	(*Z*)-**7g**	5.8[i])
								(*E*)-**7g**	9.1
1h	2,4,8-Me_3, 6-(*t*-Bu)	4.0	7.0–6.6	66	> 98	**2h**	40	–	

[a]) With respect to the amount of **1**. All reactions were performed in 12 ml of hexane with 0.1–3 mmol of **1**. See *Exper. Part* for the description of the used autoclave (*cf.* [1]).

[b]) The range of the initial pressure and the pressure at the end of the reaction time is given.

[c]) With respect to recovered **1**; > 98% means that traces of **1** were still recognizable in chromatographic fractions of the reaction mixture.

[d]) With respect to the turnover. Only the reaction of guaiazulene (**1g**) was optimized with respect to the reaction conditions and the workup procedure. In our first experiments [1], we obtained **2g** in a yield of only 24%. All other pressure reactions are not optimized, *i.e.*, the yields correspond to a single experiment.

[e]) Compounds (*Z*)- and (*E*)-**7** accompanied all experiments. However, only in the two indicated cases they were isolated. In all other runs, only small amounts of (*Z*)- and (*E*)-**7** were detected by TLC analysis.

[f]) *Dogan* [18] reacted **1a** with ADM in toluene at 50° and 7 kbar and obtained **2a** in 50% yield with respect to 70% turnover of **1a**.

[g]) *Cf.* [1]. The heptalene-dicarboxylate **6e** was not observed.

[h]) *Cf.* [1].

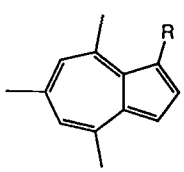
[i]) *Cf.* [1] and *Footnote d.* The heptalene-dicarboxylate **6g** was also isolated in a yield of 7.5%.

[5]) *Klärner et al.* [2] described also the reaction of azulene with methyl propiolate under these conditions. However, the expected tricyclic compound, methyl tricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9-carboxylate, was obtained only in a yield of 1% (11% with respect to the turnover).

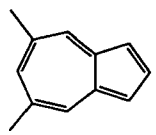
favored the formation of follow-up products. In some cases, the formation of larger amounts of (*Z*)- and (*E*)-**7** as by-products was observed. The yields, given in *Table 1*, represent in such cases, where **2** were isolated as oils, the lower limit, since the tricycles **2** are not very stable in solution or as oils. Purification had to be performed by rapid chromatography on silica gel, pretreated with Et_3N, and/or by HPLC.

In such cases, where the tricyclic compounds **2** crystallized well and could, therefore, be purified by crystallization, the yields of **2** were always much better. However, the turnover of **1** and ADM was also much better in these cases, since **2** crystallized out of the reaction mixture already in the course of the pressure reaction. The crystallized tricyclic compounds, *i.e.*, **2e–h**, were stable in the crystalline state and could be stored in the refrigerator without decomposition over longer periods. However, their melt turned blue at once, since they decomposed into the starting azulenes **1** and ADM and rearranged to the heptalene-dicarboxylates **6**.

Our high-pressure synthesis of tricyclic compounds of type **2** was not applicable to the azulenes **8–13**. All azulenes were recovered after exposure to 7 kbar in the presence of 4 mol-equiv. of ADM in hexane at 30°. It is astonishing that the azulenes **8–10** showed no reactivity, since *Klärner et al.* found, as already mentioned, that azulene itself reacts with ADM in toluene at 50° and 7 kbar [2]. The corresponding tricycle was isolated in a yield of 39% with respect to reacted azulene. Beyond that, azulene **8** (*cf.* [13] [19]), and especially **10** (*cf.* [14b] [20]), react easily with ADM in tetralin or decalin at temperatures of 207° and 120°, respectively. Of special interest is the 1-(*t*-Bu)-substituted azulene **9**, because this azulene forms with ADM the corresponding tricyclic compound in yields of up to 70% already at 25° and atmospheric pressure in the presence of 2 mol-% of $[RuH_2(PPh_3)_4]$ as catalyst [7].



R = H: **8**
R = *t*-Bu: **9**



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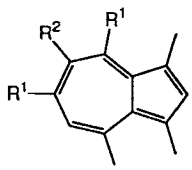
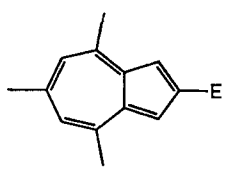


R^1 = Me, R^2 = H: **11**
R^1 = H, R^2 = i-Pr: **12**



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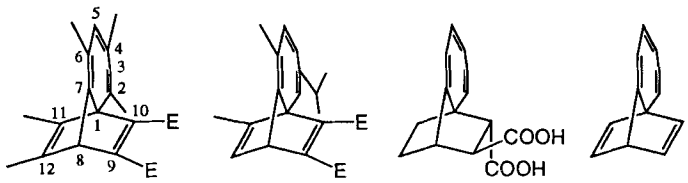
The fact that all 1-methylazulenes **1** give only the tricyclic compounds **2** with the Me group of the five-membered ring at C(11) and not the isomeric tricycles with the Me group at the bridgehead atom C(8) is in accordance with the results of the thermal reactions of these azulenes at atmospheric pressure. The structure of almost all products (*cf. Scheme 2*) are derived from tricyclic intermediates of type **2** (*cf.* [5] [7] [13] [14a]), *i.e.*, the isomeric structures of **2** (Me group at C(8)) seem to play no important rôle in the thermal equilibrium **1** + ADM⇌**2**. These facts reveal that azulenes **11** and **12** do not form their primary *Diels-Alder* adducts in the pressure reaction – at least not at a pressure of 7 kbar. On the other hand, this type of azulenes react with ADM at 200° in decalin or at 100° in MeCN in the $[RuH_2(PPh_3)_4]$-catalyzed variant at atmospheric pressure (*cf.* [5] [7] [13] [14a]).



2f **2g** **14** **15**

The thermal reaction of the azulene-2-carboxylate **13** takes place only sluggishly with ADM at 200° in decalin due to the π- and σ-acceptor substituent C(2) [5]. Therefore, it is comprehensible that the pressure reaction with ADM does not take place at 7 kbar.

2.2. *Structural and Spectroscopic Characterization of the Tricyclic Compounds.* The structure of the well crystallized tricyclic compounds **2g** and **2f** was determined by an

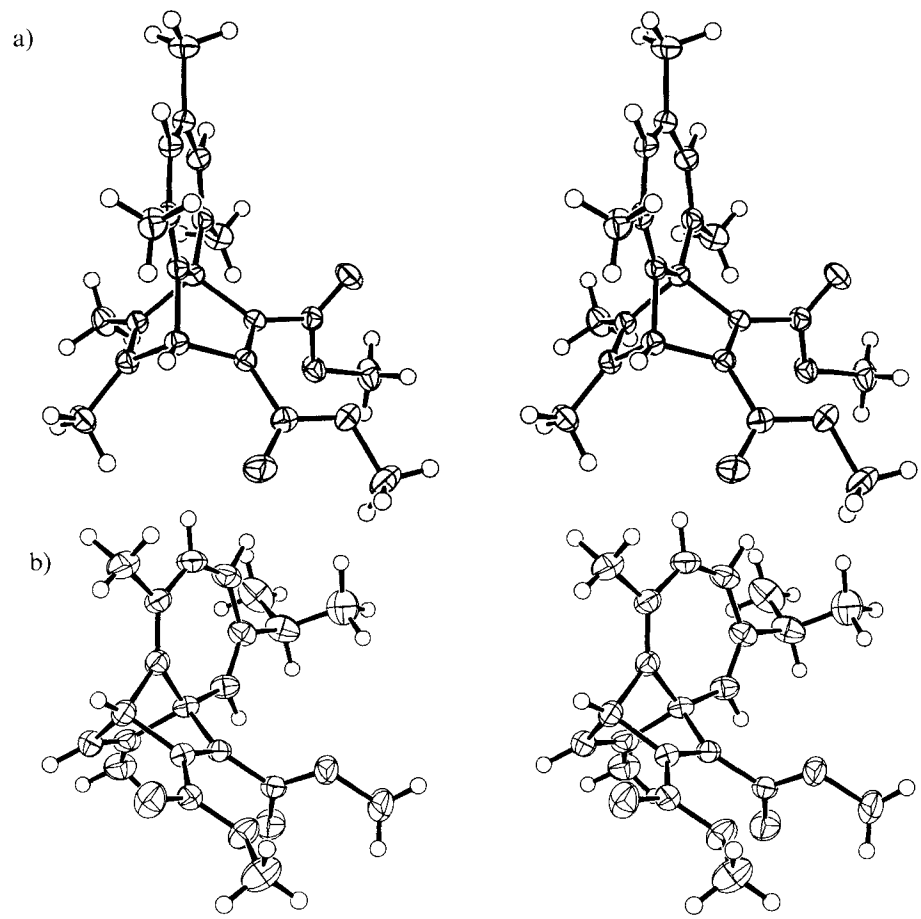


Fig. 1. *Stereoscopic views of the X-ray crystal structure of* a) *dimethyl 2,4,6,11,12-pentamethyl- and* b) *dimethyl 3-isopropyl-6,11-dimethyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**2f** and **2g**, resp.)

X-ray crystal-structure analysis. The stereoscopic view of the two structures are shown in *Fig. 1*. Characteristic bond lengths, bond angles, and torsion angles are collected in *Table 2*. A comparable structure, namely that of the dicarboxylic acid **14**, which had been obtained from the corresponding tricyclic compound of azulene and ADM by hydrogenation [2] and saponification, had already been determined by an X-ray crystal-structure analysis by *Ermer at al.* [21]. The X-ray data of **14** and the MM3-calculation data of the parent hydrocarbon **15** (*cf.* [5]) have also been included for comparison purposes in *Table 2*. It is obvious that the seven-membered ring of all three compounds – as for the calculated structure – is perfectly planar as can be seen by comparison of the sum of the bond angles of the seven-membered ring which should amount to 900° in the case of

Table 2. *Characteristic X-Ray Crystal-Structure Data of the Tricyclic Compounds* **2f**, **2g**, *and* **14a**[a]) *as well as Calculated Data of* **15**[b])

Structure Parameter[c])	**2f**[d])	**2g**[e])	**14**[f])	**15**[g])	Structure Parameter[c])	**2f**[d])	**2g**[e])	**14**[f])	**15**
Bond lengths *d* [pm]					C(5)–C(6)–C(7)	125.5	123.8	127.9	125.9
C(1)–C(2)	150.5	149.4	149.2	149.2	C(7)–C(1)–C(10)	96.6	96.8	99.5	97.0
C(1)–C(7)	154.4	153.5	151.5	151.2	C(7)–C(1)–C(11)	97.1	97.9	100.0	97.0
C(1)–C(10)	157.5	156.0	158.4	153.8	C(7)–C(8)–C(9)	98.5	97.8	101.7	96.8
C(1)–C(11)	157.8	156.4	154.5	153.8	C(7)–C(8)–C(12)	99.0	97.6	101.4	96.8
C(2)–C(3)	134.1	133.7	134.0	134.5	C(8)–C(9)–C(10)	107.6	107.4	103.1	107.3
C(3)–C(4)	146.5	146.1	142.5	146.0	C(8)–C(12)–C(11)	107.4	108.7	103.1	107.3
C(4)–C(5)	134.4	134.5	132.3	135.4	C(9)–C(8)–C(12)	106.1	105.9		106.5
C(5)–C(6)	146.9	146.6	143.5	145.5	C(10)–C(1)–C(11)	104.5	104.0		104.4
C(6)–C(7)	133.2	133.3	132.3	133.6					
C(7)–C(8)	152.5	152.4	150.2	151.2	Torsion angles Θ [°]				
C(8)–C(9)	153.1	153.7	155.5	153.3	C(1)–C(2)–C(3)–C(4)	–0.5	–1.8	–0.4	0.0
C(8)–C(12)	153.9	153.6	152.9	153.3	C(2)–C(3)–C(4)–C(5)	0.7	1.3	1.7	0.0
C(9)–C(10)	133.8	133.2		134.8	C(3)–C(4)–C(5)–C(6)	1.2	1.4	–1.7	0.0
C(11)–C(12)	133.7	132.4		134.8	C(4)–C(5)–C(6)–C(7)	–2.3	–1.5	–0.2	0.0
					C(5)–C(6)–C(7)–C(1)	0.9	–1.4	1.0	0.0
Bond angles δ [°]					C(6)–C(7)–C(1)–C(2)	1.1	2.9	–0.6	0.0
C(1)–C(2)–C(3)	126.3	130.1	129.6	129.3	C(6)–C(7)–C(1)–C(10)	126.3	128.3	124.3	127.2
C(1)–C(7)–C(6)	134.0	132.9	134.0	133.9	C(6)–C(7)–C(1)–C(11)	–127.7	–126.5	–125.6	–127.2
C(1)–C(7)–C(8)	95.2	95.5	97.1	97.2	C(7)–C(1)–C(2)–C(3)	–1.1	–0.7	–0.2	0.0
C(1)–C(10)–C(9)	107.2	107.6	104.2	107.8	C(8)–C(7)–C(1)–C(2)	–178.7	–178.4	179.1	180.0
C(1)–C(11)–C(12)	107.3	106.6	103.2	107.8	C(8)–C(7)–C(6)–C(5)	–179.4	–179.5	–178.6	180.0
C(2)–C(1)–C(7)	122.4	123.5	119.4	122.2	C(8)–C(7)–C(6)–CH_3	0.5	1.7	–	–
C(2)–C(1)–C(10)	115.2	114.4	114.3	116.3	C(9)–C(10)–C=O	109.4	104.7	–	–
C(2)–C(1)–C(11)	117.3	116.6	113.9	116.3	C(9)–C(10)–C–O	–71.4	–78.5	–	–
C(2)–C(3)–C(4)	133.5	126.7	130.8	129.1	C(10)–C(9)–C=O	–150.5	–177.5	–	–
C(3)–C(4)–C(5)	127.8	131.6	130.2	130.5	C(10)–C(9)–C–O	27.5	2.3	–	–
C(4)–C(5)–C(6)	130.5	131.3	128.0	129.1					

[a]) Data of **14** taken from [21].

[b]) Data of **15** calculated with the MM3 program [22] (*cf.* [5]).

[c]) Numbering of C-atoms as given for **2g**.

[d]) Average estimated standard deviations of *d*, δ, and Θ are 0.2 pm, 0.2°, and 0.3°, respectively (see also *Exper. Part*).

[e]) Average estimated standard deviations of *d*, δ, and Θ are 0.2 pm, 0.2°, and 0.2°, respectively (see also *Exper. Part*).

[f]) Average estimated standard deviations of *d*, δ, and Θ are 0.3 pm, 0.2°, and 0.4°, respectively (according to [21]).

Table 3. *Comparison of X-Ray Data of the Tricyclic Compounds* **2f**, **2g**, *and* **14**, *and the Calculated Structure of* **15**[a])

Quality		**2f**	**2g**	**14**	**15**
$\Sigma\,\delta$ (7-ring) [°][b])		900.0	899.9	900.0	900.0
$\Sigma\,\Theta$ (7-ring) [°]		0.0	0.2	0.0	0.0
Deviation [%] of *d*					
(C(1)–C(10))	*A*[c])	+2.9	+1.5	+1.9	+0.5
	B[d])	+2.4	+1.4	–	–
	C[e])	+2.1	+1.6	+2.0	+0.9
Deviation [%] of *d*					
(C(1)–C(11))	*A*[f])	+2.5	+1.8	+1.0	+0.5
	B[d])	+2.6	+1.7	–	–
	C[e])	+2.3	+1.9	−0.5	+0.9

[a]) *Cf. Table 2* and *Scheme 5*.
[b]) Calculated for an *n*-membered polygon: $180° \cdot (n-2)$; *i.e.*, 900° for a planar seven-membered ring.
[c]) With respect to *d* of the opposite C(8)–C(9) bond.
[d]) With respect to the calculated value of *d* (C(1)–C(10)) in **15**.
[e]) With respect to the average values of *d* for all $C(sp^2)$–$C(sp^3)$ and $C(sp^3)$–$C(sp^3)$ bonds, respectively, in the considered tricycle.
[f]) With respect to *d* of the opposite C(8)–C(12) bond.

planarity (*cf. Table 3*). Similarly, all individual torsion angles of the seven-membered ring deviate only slightly and mostly close to the estimated standard deviations from 0°, and their sum is indeed 0° (*cf. Table 3*). Consequently, there are only very small variations within the discussed values of all three compounds submitted to X-ray analysis, and of the calculated basis structure **15**. Noteworthy is the fact that the C(1)–C(10) bond represents in all three compounds by far the longest $C(sp^2)$–$C(sp^3)$ bond (**2f**, **2g**) and $C(sp^3)$–$C(sp^3)$ bond (**14**), followed by the C(1)–C(11) bond (*cf. Table 3*). Such a bond-elongation effect is not or only faintly recognizable within the precision of the calculation for the computed structure **15**. Since δ(C(2)–C(1)–C(7)) and δ(C(10)–C(1)–C(11)) are almost the same for **2f**, **2g**, and the computed structure **15**, the elongation of the C(1)–C(10) and the C(1)–C(11) bond cannot be due to the rehybridization of C(1) induced by strain. Strain effects should be reflected in the computed length of the C(1)–C(10) and C(1)–C(11) bond, respectively. Therefore, we have to assume that the bond elongation of the C(1)–C(10) and C(1)–C(11) bond in **2f** and **2g** as well as in **14** is due to hyperconjugation of these two C–C bonds with the adjacent planar π system of the cycloheptatriene substructure. Indeed, δ(C(7)–C(1)–C(10)) and δ(C(7)–C(1)–C(11)) amount to (97.1 ± 0.4°) for **2f**, **2g**, and **15**, and are only slightly different for **14** (100°) according to the altered hybridization at C(10) and C(11). The two other bond angles of interest, namely δ(C(2)–C(1)–C(10)) and δ(C(2)–C(1)–C(11)), possess values of (116.0 ± 1.0°) for **2f**, **2g**, and **15**, and 114° for the slightly different structure **14**, *i.e.*, the angles of the planar π system, and C(10) and C(11) amount to 105–107° for all four structures and should result in a strong hyperconjugative effect of both C-atoms[6]).

[6]) *Laube* [23], who determined the X-ray crystal structure of the rigid 3,5,7-trimethyladamant-1-yl cation, found, for the hyperconjugative stabilization of the only slightly pyramidalized cationic center (deviation of C(1) from the plane, defined by C(2), C(8), and C(9), amounts to 2.1 pm), an elongation of the β-C–C bonds

The hyperconjugative weakening of the C(1)–C(10) and C(1)–C(11) bonds in the tricyclic compounds **2** is responsible for the ease of their homolytic or heterolytic cleavage resulting in the formation of the discussed products (see *Chapt. 1*). That the *retro-Diels-Alder* reactions of **2** with transition states of only little polarity are indeed also determined by the weakened C(1)–C(11) bond is clearly recognizable by comparison of the thermal behavior of 1- and 2-substituted styryl- or phenylazulenes in the presence of ADM (*cf.* [9] [25]). Whereas the first type of azulenes yields exclusively the azulene-1,2-dicarboxylates **4** from the intermediate tricyclic compounds of type **2** (*cf. Scheme 2*), the second type of azulenes leads *via* **2** (R = *p*-RC_6H_4CH=CH or *p*-RC_6H_4 at C(12) in *Scheme 2*) mainly to the corresponding 4-substituted heptalene-1,2-dicarboxylates of type **6**, and the azulene-1,2-dicarboxylates **4** represent only minor products.

Fig. 2 shows the UV spectrum of dimethyl 2,4,6,11-tetramethyltricyclo[6.2.2.$0^{1,7}$]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate (**2e**). In the long-wavelength part, it resembles very much the UV spectrum of **14** in 95% EtOH that had been measured and depicted by *Ermer et al.* [21]. The position of the four vibrational bands of **2e**, which are

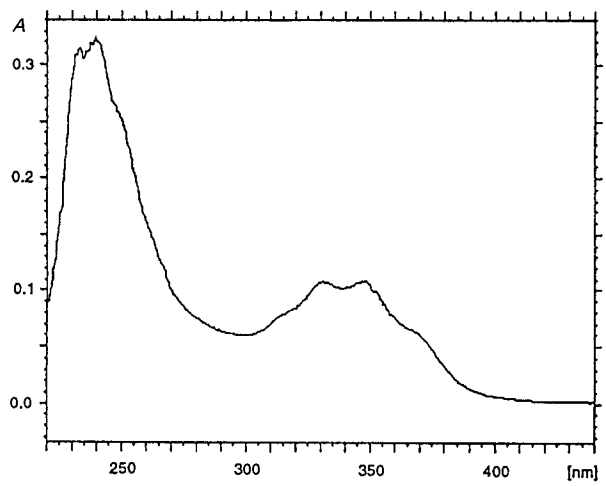


Fig. 2. *UV Spectrum* (hexane) *of dimethyl 2,4,6,11-tetramethyltricyclo[6.2.2.*$0^{1,7}$*]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**2e**) *with the vibrationally structured maxima at 365 (sh), 347, 331, and 318 (sh) [nm]*

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[6]) (cont.)
of +6% as compared to the other C–C bonds in the cation. The discussed hyperconjugative elongation effects for **2f**, **2g**, and **14** (*cf. Table 3*) are as expected well below of this value. *Arnett* and *Molter* investigated the reversible heterolysis of 1,2,3-trimethylcyclopropenyl-substituted 3- and 4-X-phenylmalononitriles in MeCN (*cf.* also *Chapt. 4*) and determined in this context the X-ray crystal structure of the corresponding 4-NO_2 and 4-MeO derivatives (X=NO_2, MeO; *cf.* [24] and lit. cit. there). The central C(sp^3)–C(sp^3) σ bonds showed bond lengths of 158.8 (4) (X=NO_2) and 158.1 (3) pm (X=MeO). As compared to the average bond length of the Me–C(sp^3) σ bond at the cyclopropene ring (150.5 (5) pm; both compounds possess different conformations around the central C(sp^3)–C(sp^3) σ bond in the crystal structure, which results in Me–C(sp^3) bond lengths of 148.5 (5) and 152.4 (4) pm, respectively), this corresponds to a bond elongation effect of 5.5 to 5.0% due to hyperconjugation. It should be noted that the comparable C(1)–C(10) bond length of the tricyclic compound **14** falls with 158.4 pm (*cf. Table 2*) well within the range of the length of the central σ bond of the cyclopropenyl compounds.

an expression of the rigidity of the planar cycloheptatriene substructure, are shifted by (10 ± 1) nm to longer wavelengths as compared with those of **14**. This wavelength shift can be attributed to the hyperconjugative effect of the three Me groups at C(2), C(4), and C(6) of **2g**[7]). Therefore, we can exclude a through-space interaction of the π systems of the planar cycloheptatriene and the norbornadiene substructure in the tricycles of type **2**. That the planarization of the cycloheptatriene ring system induces an appreciable long-wavelength shift of the π,π^* absorption as compared to cycloheptatriene structures in the boat conformation (*e.g.* λ_{max} 258 nm for cycloheptatriene and 278 nm for 1,7,7-trimethylcycloheptatriene; both in 95% EtOH) has already been discussed by *Ermer et al.* [21]. If we consider the hyperconjugative effect of the C(1)–C(10) and C(1)–C(11) bond in **2e** as well as in **14** (*vide supra*), a wavelength shift of +55 nm seems to be realistic for the planarization of the cycloheptatriene structure.

The conformation of the MeOCO groups at C(9) and C(10) with respect to the C(9)=C(10) bond is also noteworthy. Whereas the C=O group at C(9) occupies more or less an s-*trans*-conformation (Θ(C(10)=C(9)–C=O) = −150.5° and −177.5°, resp.), *i.e.*, it shows conjugation with the C(9)=C(10) bond, the orientation of the C=O group at C(10) is almost perpendicular to the C(9)=C(10) bond (Θ(C(9)=C(10)–C=O) = 109.4° and 104.7°, resp.). If the latter orientation represents an energy minimum also in solution, the C=O group at C(10) would be in an optimal position for the conjugative stabilization of the developing negative charge at C(10) in the course of the heterolysis of the C(1)–C(10) bond (see also *Chapt. 3*).

Characteristic for the tricyclic compounds **2a–h** are their ^{1}H-NMR spectra in C_6D_6[8]). Typical shift ranges for H-atoms and Me substituents at the tricyclic skeleton of **2a–h** are given in *Table 4*. All compounds possess a Me group at C(11), whose signal appears as a *d* at (1.81 ± 0.03) ppm with ^4J(H–C(12),Me–C(11)) = 1.7–1.8 Hz. The corresponding signal of H–C(12) is found in these cases at (6.04 ± 0.07) ppm as a *sext.*-like *multiplet*, since ^3J(H–C(8),H–C(12)) = 3.4–3.7 Hz is just twice as large as ^4J(Me–C(11),H–C(12)) and well in the range of ^3J of other norbornadiene derivatives (*cf.* [5] [14] [27] [28]). Quite characteristic for the tricyclic compounds is the signal of the bridgehead H-atom at C(8) which shows the already mentioned ^3J coupling with H–C(12). On the other hand, in none of the three compounds, which carry an H-atom at C(6) (*e.g.* **2a**, **2b**, and **2d**), we observed a ^4J coupling between H–C(8) and H–C(6) against the expectation, based on the torsion angle between H–C(8) and the C(6)=C(7) bond (*cf.* [29]). However, the calculated bond angle δ(H–C(8)–C(7)) of **15** deviates with 116° substantially from a tetrahedral bond angle. The chemical shift of H–C(8) is markedly dependent on the substitution pattern at C(6) and C(12) (*cf. Table 4*). According to the strained bond angle δ(C(1)–C(7)–C(8)), which amounts only to 95° in **2f** and **2g** (*cf. Table 2*), electron density is shifted from C(7) to C(6) in the tricyclic compounds. As a consequence, the signals for H–C(6) and Me–C(6) appear at the highest field as compared to the signals of the other H-atoms and Me groups at the seven-membered ring (*cf. Table 4*).

Of special interest are the vicinal H,H-coupling constants of the planar seven-membered ring. They amount to 11.8–12.6 Hz across C=C bonds and to 7.3–7.8 Hz across

[7]) According to the *Woodward-Fieser* rules (*cf. e.g.* [26]) for the UV absorption spectra of dienes and related unsaturated hydrocarbons, no solvent corrections are necessary, and the wavelength increment for an alkyl group amounts to +5 nm.

[8]) The tricycles **2** are much less stable in $CDCl_3$ solution due to the presence of traces of DCl in this solvent.

Table 4. *Typical ^1H Chemical-Shift Ranges* [ppm] *of the Tricyclic Compounds* **2a**–**2h** *in* C_6D_6[a])

H–C(2)	Me–C(2)	H–C(3)	Me–C(3)	H–C(4)
5.94 ± 0.06(5) (5.78; **2d**)	1.98 ± 0.06(3)	5.79 ± 0.04(6) (6.23; **2h**)	1.54(1)[b])	5.44 ± 0.06(4)
Me–C(4)	**H–C(5)**	**Me–C(5)**	**H–C(6)**	**Me–C(6)**
1.64 ± 0.04(4)[c])	5.43 ± 0.03(4)[d]) 5.24 ± 0.04(4)[e])	1.75(1)	4.61 ± 0.04(4)	1.44 ± 0.02(4) (1.27; **2h**)
H–C(8)	**Me–C(11)**	**H–C(12)**	**Me–C(12)**	
4.17 ± 0.03(3)[f]) 4.28 ± 0.01(2)[g]) 4.50 ± 0.04(3)[h])	1.81 ± 0.03(7) 1.68(2)[i])	6.04 ± 0.07(7)	1.65(2)	

[a]) In parentheses the number of examples or the chemical shifts of indicated tricyclic compounds (see also [1] for the spectra of **2e**–**g**).
[b]) i-Pr–C(3): 2.21 (*sept.*, Me_2CH), and 1.06, 1.04 (*2d*, Me_2CH) in **2g** [1].
[c]) *t*-Bu–C(4): 1.07 in **2h**.
[d]) For tricycles **2** with H–C(4) or *t*-Bu–C(4).
[e]) For tricycles **2** with Me–C(4).
[f]) For tricycles **2** with H–C(6,12).
[g]) For tricycles **2** with Me–C(6,12), *i.e.*, **2f** and **2h**.
[h]) For tricycles **2** with Me–C(6) and H–C(12).
[i]) For **2f** and **2h** with Me–C(12).

C–C bonds[9]). They are definitely larger than those in comparable non-planar heptalene derivatives which show ^3J(H–C=C–H) $\leqslant$ 11.8 Hz (*cf.* [30])[10]) and ^3J(H–C–C–H) < 6.5 Hz (*cf.* [14] [30–32]). The latter coupling constants are dependent on the corresponding torsion angle which is in the range of 15–35° in heptalenes. ^4J(H–C(n), Me–C(n + 1)) amounts to $\leqslant$ 1.5 Hz in the seven-membered ring. Therefore, in some cases, the signals of the Me groups appear only as broad *s*. The signals of the MeOCO groups at C(9) and C(10) appear well separated in the range of (3.46 ± 0.03) ppm and (3.31 ± 0.02) ppm. We assume that MeOCO–C(9), which is, according to the X-ray crystal structure of **2f** and **2g**, in conjugation with the C(9)=C(10) bond (*vide supra*) is responsible for the signal at lower field, and that MeOCO–C(10) absorbs at higher field, since it is mainly out of conjugation with the C(9)=C(10) bond. Beyond that, it may well be close to the shielding area of the planar cycloheptatriene ring.

In one case, namely **2g**, we determined the solvent shifts $\Delta\delta$ (δ($CDCl_3$) – δ(C_6D_6)) of the ^{1}H-NMR signals (*cf. Table 5*). They are negative for H–C(2) and H–C(8), *i.e.*, these

[9]) The vicinal coupling constants of the benzo derivative of **2a** (*i.e.*, benzo annelation at C(11)–C(12) instead of Me–C(11) lie well within these ranges [16]. The corresponding 2,6-diphenyl derivative exhibits ^3J(H–C=C–H) = 12.0 Hz and ^3J(H–C–C–H) = 8.7 Hz [16], *i.e.*, ^3J(H–C–C–H) may be still enlarged by substituent effects in the planar seven-membered ring of tricyclic compounds of type **2**.

[10]) For rigid, fully unsaturated tetracyclic structures, we found a perfect linear correlation (r = 0.9998) between the average skeletal C–C–C bonds angles (Θ_{av}), taken from X-ray crystal data, and the observed olefinic ^3J coupling constants, *i.e.*, $\Theta_{av} = 3.07 \cdot J$[Hz] + 92.3 [20] [31]. If we take Θ_{av} for the C(2)=C(3) and the C(4)=C(5) bonds from the X-ray crystal data of **2f** and **2g** (see *Table 2*), we find $^3J_{av}$(H–C=C–H) = (129.7–92.3)/3.07 = 12.2 Hz in perfect agreement with the observed range for ^3J(H–C=C–H) = 11.8–12.6 Hz. Indeed, $^3J_{av}$(H–C=C–H) for all measured values in **2a**–**c**, and **2g** is also 12.2 Hz.

Table 5. *Solvent Shifts in the ^{1}H-NMR Spectrum of Dimethyl 3-Isopropyl-6,11-dimethyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**2g**)

Solvent[a])	H–C(12)	H–C(2)	H–C(4)	H–C(5)	H–C(8)
$\delta(CDCl_3)$	6.28	5.57	5.53	5.46	4.38
$\delta(C_6D_6)$	6.07	5.87	5.46	5.37	4.50
$\Delta\delta$	0.21	−0.30	0.07	0.09	−0.12

Solvent[a])	MeOCO–C(10)	MeOCO–C(9)	Me–C(11)[b])	Me–C(6)
$\delta(CDCl_3)$	3.82	3.74	1.91	1.64
$\delta(C_6D_6)$	3.48	3.32	1.83	1.43
$\Delta\delta$	0.34	0.42	0.08	0.21

[a]) ^{1}H-NMR Spectra at 300 MHz; δ and $\Delta\delta$ in ppm. For the spectrum of **2g** in C_6D_6, see also [1].
[b]) i-Pr–C(3): 2.32 ($CDCl_3$) and 2.21 (C_6D_6) as well as 1.06/1.04 ($CDCl_3$ and C_6D_6).

H-atoms are more deshielded in C_6D_6 solution. Both H-atoms are close to the C=O groups of MeOCO–C(10) and MeOCO–C(9). Since one would expect negative solvent shifts for these H-atoms (*cf.* [33]), the observed negative $\Delta\delta$ values reconfirm the assignments of H–C(2) and H–C(8).

Table 6 contains the ^{13}C chemical shifts of **2g** in $CDCl_3$. Most obvious is the remarkable chemical-shift difference between the olefinic C(6) and C(7), again demonstrating the enormous bond-angle strain at C(7) and the shift of electron density from C(7) to C(6).

Table 6. *^{13}C-NMR Data* ($CDCl_3$) *of Dimethyl 3-Isopropyl-6,11-dimethyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**2g**)[a])

C-atom	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
δ [ppm]	68.4[b])	116.4	145.0	125.9	132.2	103.6[c])	164.4

C-atom	C(8)	C(9)	C(10)	C(11)	C(12)	Me–C(6)
δ [ppm]	50.9[d])	163.3	162.0	140.9	127.5	18.9

C-atom	Me–C(11)	$(Me)_2CH$–C(3)	MeOCO–C(9)	MeOCO–C(10)
δ [ppm]	14.3	37.7; 22.4/22.3	166.2; 52.1	164.1; 52.0

[a]) ^{13}C-NMR Spectrum at 150 MHz [1]. Assignments *via* ^{1}H,^{13}C-correlation spectra. For the assignments of the quaternary C-atoms, see also [2] [27] [34].
[b]) 75.0 and 75.5 ppm for **2e** and **2f**, respectively, in C_6D_6 (*cf.* [1]).
[c]) 101.9 and 101.6 ppm for **2e** and **2f**, respectively, in C_6D_6 (*cf.* [1]).
[d]) 50.9 and 56.0 ppm for **2e** and **2f**, respectively, in C_6D_6(*cf.* [1]).

Similar chemical shifts of C(6) and C(7) are observed for the tricyclic compounds **2e** and **2f** in C_6D_6 (*cf. Table 6* and [1]). The chemical shifts for the bridgehead atoms C(1) and C(8) are in the expected range for norbornadiene structures (*cf.* [35]).

The mass spectra of the tricyclic compounds **2** were not studied systematically. However, according to the ease with which **2** undergo thermal *retro-Diels-Alder* reactions (*cf. Scheme 2*), one can expect these processes also to occur under mass-spectrometric conditions. *Table 7* shows the main ions in the EI-MS of **2e** and **2g**, and, for comparison,

Table 7. *Relative Intensities* [%] *of the Main Ions in the Mass Spectra of the Tricyclic Compounds* **2e**, **2f**, *and* **2g**

Tricycle	$M^{+\cdot}$	$[M - Me^{\cdot}]^+$	$[M - MeOH]^{+\cdot}$	$[M - Me{-}C{\equiv}C{-}R]^{+\cdot}$	$[M - (Me^{\cdot} + MeOH)]^+$	$[M - (Me{-}C{\equiv}CH + MeO^{\cdot})]^+$	$[M - ADM]^{+\cdot}$
2e	40	12	11	57 (R = H)	11	19	100
2g[a])	40	9	8	82 (R = H)	12	21	18
2f[b])	100	2	2	2 (R = Me)	n.o.[c])	n.o.	5

[a]) EI-MS at 70 eV; basis peak (100%): $[COOMe]^+$.

[b]) CI-MS (NH_3); the intensities of the corresponding $[M + 1]^+$ ions are given (*cf. Exper. Part*).

[c]) n.o. = not observed.

those of **2f** in the CI mode. Indeed, important fragment ions are found at *m/z* 286 for **2e** and at *m/z* 300 for **2g**, which correspond to the loss of propyne from the parent ion. Similarly, the fragment ions at *m/z* 184 and 198, respectively, indicate the loss of ADM[11]). Both fragmentation patterns are also observed in the case of the chemical ionization of **2f** (*cf. Table 7*). The other observed fragment ions are linked to the presence of two MeOCO substituents in the tricyclic compounds. Since the mass spectra of **2g** shows no ion at *m/z* 260, which would correspond to the loss of i-Pr–C≡CH, we can conclude that the ionized tricyclic compounds are not rearranged to the corresponding ionized heptalene-4,5-carboxylates. In such a case, we would expect the appearance of the said fragment ion, which is found in the mass spectrum of the corresponding heptalene-dicarboxylate (*cf.* [30b]).

2.3. *Thermal Behavior of the Tricyclic Compounds* **2**. The thermolyses were performed in *ca.* $3 \cdot 10^{-3}$ M solutions in sealed flasks at 110 ± 1° during 1 h. The tricyclic compounds reacted quantitatively under these conditions. Their solutions were directly subjected to HPLC analysis at a detection wavelength of 290 nm. The products, *i.e.*, the corresponding azulenes **1**, the heptalenedicarboxylates **6** as well as most of the 1-(azulen-1-yl)ethene-1,2-dicarboxylates, (*E*)- and (*Z*)-**7**, were available in pure form from earlier work (*cf.* [8] [14] [31] [37]). In some cases, the compounds were isolated from preparative runs and spectroscopically characterized (*cf. Exper. Part*). UV Spectra of all compounds were recorded in the course of the HPLC analyses. In this way, unknown (*E*)- and (*Z*)-pairs of **7** could easily be distinguished, since all (*Z*)-forms of the azulenes **7**, which carry no substituent at C(2) of the azulene ring, exhibit a characteristic broad absorption band at *ca.* 400 nm (*cf.* [37]). The HPLC analyses did not allow to distinguish the DBS isomers of the heptalenedicarboxylates **6** – also in those cases where the DBS process occurs at temperatures > 100°.

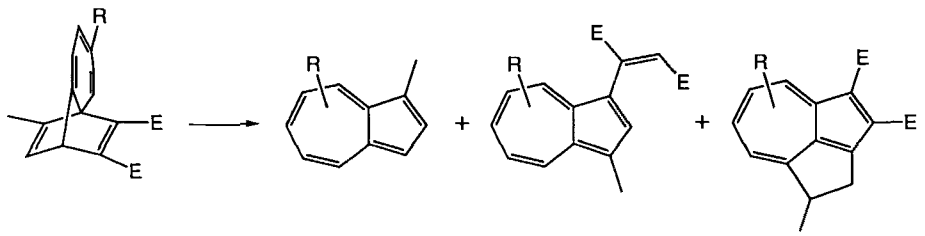
2.3.1. *Thermolysis of* **2** *in Polar Aprotic and Protic Solvents*. We chose MeCN (E_T = 46.0 kcal mol^{-1} [38]) as typical polar aprotic solvent and BuOH (E_T = 50.2 kcal mol^{-1} [38]) as characteristic polar protic solvent for a comparative thermolysis of all tricyclic compounds **2** (*cf. Table 1*). The study of the thermolysis of **2e**, derived from 1,4,6,8-tetramethylazulene (**1e**), and **2g**, derived from guaiazulene (**1g**), was extended to other solvents (*cf.* also [1]). Therefore, we established calibration curves for the products of these tricyclic compounds at a detection wavelength of 290 nm (*cf. Exper. Part*). Since all products of type **1**, **6**, and **7** showed in their family a similar absorption behavior at

[11]) Of course, the discussed fragmentions may also take place in a pure thermal reaction before ionization occurs (*cf. Scheme 2*). However, the other observed fragment ions document that indeed the tricyclic compounds had been ionized and not their thermal *retro-Diels-Alder* products.

290 nm, the calibration curves were also used for the analysis of the product mixtures of the other tricyclic compounds.

Of the eight tricyclic compounds **2**, which were subjected to the thermolysis in MeCN, behave two, namely the 11-methyl and the 4,11-dimethyl derivative, **2a** and **2b**, respectively, distinctly different from the others in that they did not lead to the formation of the corresponding heptalene-dicarboxylates. Both gave, beside the expected azulenes **1a** and **1b**, respectively, the corresponding (*E*)-1-(azulen-1-yl)ethene-1,2-dicarboxylates **7a** and **7b**, and, in addition, the 3,4-ethano-bridged azulene-1,2-dicarboxylates **16a** and **16b**, respectively (*Scheme 4*). The (*Z*)-isomers of **7** were not observed. Neither (*E*)- or (*Z*)-**7** nor **16** (*e.g.* **16d**) or precursors of them were formed in the thermolysis of the other six tricyclic compounds in MeCN (*cf. Table 8*)[12]). The major products were the corresponding heptalene-dicarboxylates **6c–h**, accompanied by minor amounts of the starting azulenes **1c–h**.

Scheme 4



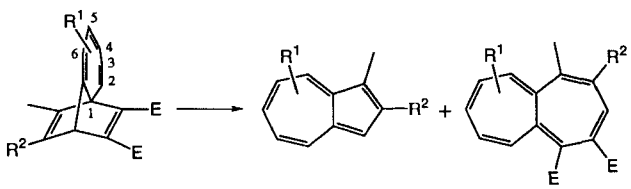
R = H : **2a**
R = Me : **2b**

1a (10%)
1b (19%)

(*E*)-**7a** (64%)
(*E*)-**7b** (63%)

16a (26%)
16b (18%)

Table 8. *Results of the Thermolysis of the Tricyclic Compounds* **2c–h** *in MeCN at 110°*



2c - 2h **1c - 1h** **6c - 6h**

Tricyclic compound **2**		Azulene **1**		Heptalene **6**[a])	
No.	R^1, R^2	No.	Yield [%]	No.	Yield [%]
2c	R^1 = 4,6-Me_2; R^2 = H	**1c**	30	**6c**	70
2d	R^1 = 3,5-Me_2; R^2 = H	**1d**	25	**6d**	75
2e	R^1 = 2,4,6-Me_3; R^2 = H	**1e**	27	**6e**	73
2f	R^1 = 2,4,6-Me_3; R^2 = Me	**1f**	24	**6f**	76
2g	R^1 = 3-(i-Pr), 6-Me; R^2 = H	**1g**	29	**6g**	71
2h	R^1 = 2,6-Me_2, 4-(*t*-Bu); R^2 = Me	**1h**	35	**6h**	65

[a]) Mixture of **6** and their DBS isomers, which were not separated under the applied HPLC conditions.

[12]) See, however, the thermolysis of **2g** in the presence of 1,8-bis(dimethylamino)naphthalene.

The thermolysis of the tricyclic compounds **2** in BuOH at 110° gave a completely different product pattern. The corresponding azulenes **1** were again formed as minor products (*Table 9*). However, instead of the heptalenes **6** and azulene-dicarboxylates **16** (in the case of **2a** and **2b**), (*E*)/(*Z*)-mixtures of **7** were obtained.

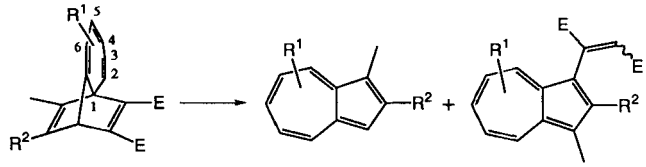


Table 9. *Results of the Thermolysis of the Tricyclic Compounds* **2** *in BuOH at 110°*

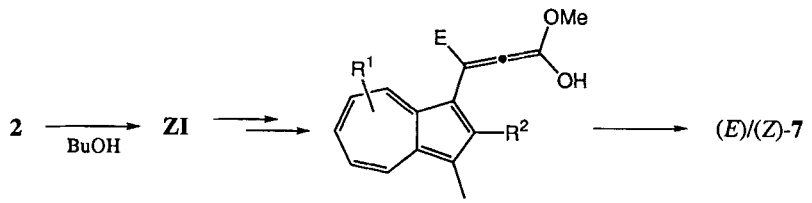
2 **1** (*E*)/(*Z*)-**7**

Tricyclic compound **2**		Azulene **1**		Ethene-dicarboxylates **7**		
No.	R^1, R^2	No.	Yield [%]	No.	Yield (*E*) [%]	Yield (*Z*) [%]
2a	$R^1 = R^2 = H$	**1a**	14	**7a**	46	40
2b	R^1 = 4-Me; $R^2 = H$	**1b**	21	**7b**	51	28
2c	$R^1 = 4,6\text{-}Me_2$; $R^2 = H$	**1c**	17	**7c**	45	38
2d	$R^1 = 3,5\text{-}Me_2$; $R^2 = H$	**1d**	7	**7d**	61	32
2e	$R^1 = 2,4,6\text{-}Me_3$; $R^2 = H$	**1e**	19	**7e**	43	38
2f	$R^1 = 2,4,6\text{-}Me_3$; R^2 = Me	**1f**	12	**7f**	33	55
2g	R^1 = 3-(i-Pr), 6-Me; $R^2 = H$	**1g**	22	**7g**	44	34
2h	$R^1 = 2,6\text{-}Me_2$, 4-(*t*-Bu); $R^2 = H$	**1h**	6	**7h**	37	57

A first survey of these results leads to the following picture: the thermolysis in MeCN give rise to an average amount of starting azulenes **1** of 28 ± 4% and of the heptalene-dicarboxylates **6** of 72 ± 4% with the exception of **2a** and **2b** (*vide infra*). The thermolysis in BuOH provide also the starting azulenes **1**. However, their average amount of 14.5 ± 6% is clearly smaller than in MeCN. This effect can be attributed to the higher E_T value of BuOH as compared with MeCN, *i.e.*, the heterolysis of the C(1)–C(10) bond in **2** is favored in BuOH. The thermolysis of **2a** and **2b** in BuOH is, in contrast to the results in MeCN, in line with the thermolysis of the other tricyclic compounds. If we compare the amounts of (*E*)- and (*Z*)-**7** formed in BuOH, we recognized for all azulenes **7**, which carry no Me group at C(2), a preponderance of the (*E*)-isomers (48.5 ± 6.5%) over the (*Z*)-forms (35.0 ± 4.5%) with an (*E*)/(*Z*) ratio of 1.4 ± 0.4. On the other hand, the two examples, where a Me group occupies C(2) in **7**, show evidently a higher amount of the (*Z*)-isomers (*ca.* 56%) in comparison to the (*E*)-isomers (*ca.* 35%; *i.e.*, (*E*)/(*Z*) ≈ 0.6). These observations indicate that the zwitterions **Z1** (*cf. Scheme 3*), arising from the heterolysis of the C(1)–C(10) bond in **2**, are protonated at the O-atom of the ketene-oxide substructure, followed by deprotonation to the corresponding ketenol structure **17**, which then gives (*E*)/(*Z*)-**7** by a prototopic shift (*Scheme 5*). The different (*E*)/(*Z*) ratios, found for R^2 = H and Me in **7**, reflect the change in the relative thermodynamic stability of the corresponding (*E*)/(*Z*) pairs of **7**, *i.e.*, the relative stability of (*Z*)-**7** increases with R^2 = Me in relation to (*E*)-**7**[13]). However, that the (*E*)/(*Z*) ratio is strongly dependent on

[13]) The equilibrium mixture of **7f** in toluene contains at 100° 14.7% of (*E*)-**7f** and 85.3% of (*Z*)-**7f**, whereas that of **7g**, having no Me group at C(2), consists of 67.2% of (*E*)-**7g** and 32.8% of (*Z*)-**7g**.

Scheme 5



17

Table 10. *Results of the Thermolysis of the Tricyclic Compound* **2g** *in Protic Solvents at 110°*

Solvent	E_T[a]) [kcal mol^{-1}]	Yields [%]		
		Azulene **1g**	(*E*)-**7g**	(*Z*)-**7g**
2-Methylbutan-2-ol	41.1	82	13	5
Pentan-2-ol	46.5	37	20	43
Pyrrolidin-2-one	48.3	39	39	22
2-Methylpropan-1-ol	48.6	25	31	44
3-Methylpentan-1-ol	49.0	25	44	31
Pentan-1-ol	49.1	21	45	34
BuOH	50.2	22	44	34
Benzyl alcohol	50.4	12	48	40
Diethyleneglycol	53.8	13	51	36
Formamide	56.6	n.o.[b])	57	43
2,2,2-Trifluoroethanol	59.8	n.o.	48	52

[a]) E_T Values according to [38].
[b]) n.o. = not observed.

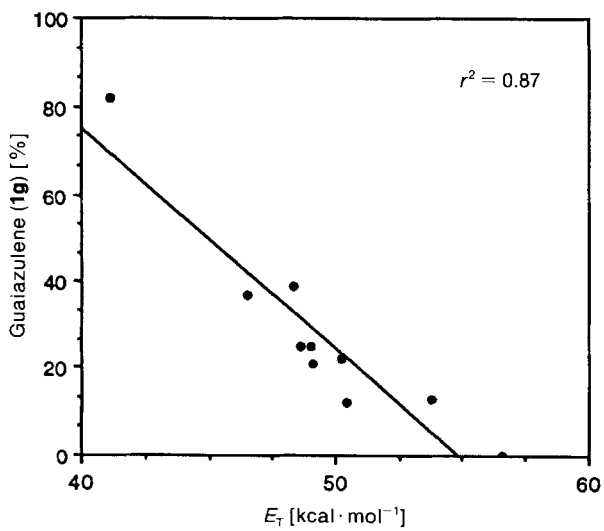


Fig. 3. *Correlation of the amount* [%] *of guaiazulene* (**1g**), *formed in the thermolysis of* **2g** *in protic solvents at 110°, and the corresponding* E_T *values of the solvents* (*cf. Table 10*)

the solvation of **ZI** and **17** shows the thermolysis of **2g** in different protic solvents (*Table 10*). The average (*E*)/(*Z*) ratio of **7g** is 1.3 ± 0.6 and still close to that found for all compounds **7**, carrying no substituent at C(2). The amount of guaiazulene (**1g**) formed in the different protic solvents is grossly linearly dependent on the E_T value of the protic solvent (*cf. Fig. 3*). The azulene formation is completely suppressed in formamide and 2,2,2-trifluoroethanol, *i.e.*, the heterolytic cleavage of the C(1)–C(10) bond in **2g** is strongly favored in these highly polar solvents in a way that the concerted and more or less apolar cleavage of the C(1)–C(10) and C(8)–C(9) bond, resulting in the formation of **1g**, and ADM can no longer compete with it.

Table 11 contains the already published data [1] together with some additional data of the thermolysis of **2g** in a number of aprotic solvents. Again, it can be seen that the azulene formation decreases in favor of the heptalene formation with an increase of the polarity of the solvents as expressed by their E_T values. We found comparable solvent effects for the thermolysis of the tricyclic compound **2e** (*cf.* Table 2 in [1]). *Fig. 4* shows the correlation of the amounts of guaiazulene (**1g**) that are formed from **2g** with the corresponding E_T values of the applied solvents. The correlation is anew grossly linear ([**1g**] (%) = 198.3 – 3.46 E_T). It shows that it is the polarity of the solvent and not its protic or aprotic nature that favors the heterolysis of the C(1)–C(10) bond in **2g** to lead to the zwitterion **ZI**. However, it is the nature of the solvent that determines the fate of the zwitterion **ZI**. It is quantitatively trapped by protonation in the protic solvents to yield finally (*E*)- and (*Z*)-**7** (*cf. Scheme 7*). In aprotic media, the zwitterion **ZI** seems to collapse to the precursors **5** of the heptalene-dicarboxylates **6** (*cf. Scheme 2*)[3]). However, in view of the results of the thermolysis of **2a** and **2b** in MeCN, which did not provide the corresponding heptalene-dicarboxylates **6a** and **6b**, respectively, the formation of the *Dewar* heptalenes **5** from the zwitterion **ZI** needs a closer inspection.

Table 11. *Results of the Thermolysis of the Tricyclic Compound* **2g** *in Aprotic Solvents at 110°*

Solvent	E_T[a]) [kcal mol^{-1}]	Yields [%]	
		Azulene **1g**	Heptalene **6g**[b])
Decane	31.0	100	n.o.
Decalin	31.2	100	n.o.
Tetrachloroethene	31.2	91	9
Et_3N	33.3 (32.1)	77	23
Toluene	33.9	70	30
t-BuOMe	35.5	65	35
Dioxane	36.0	47	53
AcOEt	38.1	58	42
Diglyme	38.6	69	31
1,2-Dichloroethane	41.3	63	37
PhCN	41.5	45	55
Isobutyronitrile	43.1	66	34
DMF	43.8	58	42
γ-Butyrolactone	44.3	55	45
DMSO	45.1	52	48
MeCN	45.6	29	71

[a]) E_T Values according to [38].
[b]) n.o. = not observed.

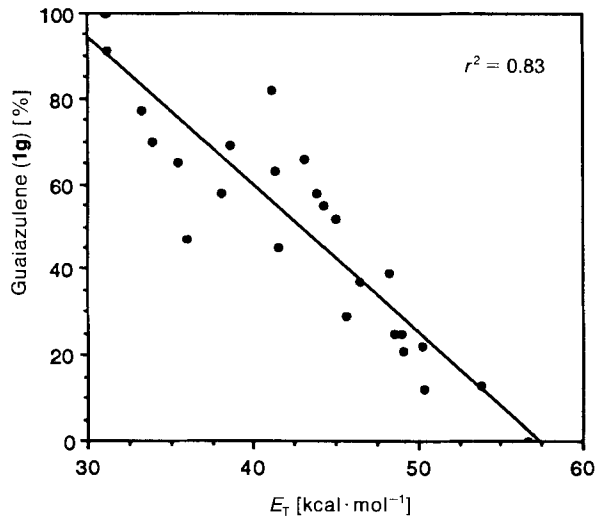
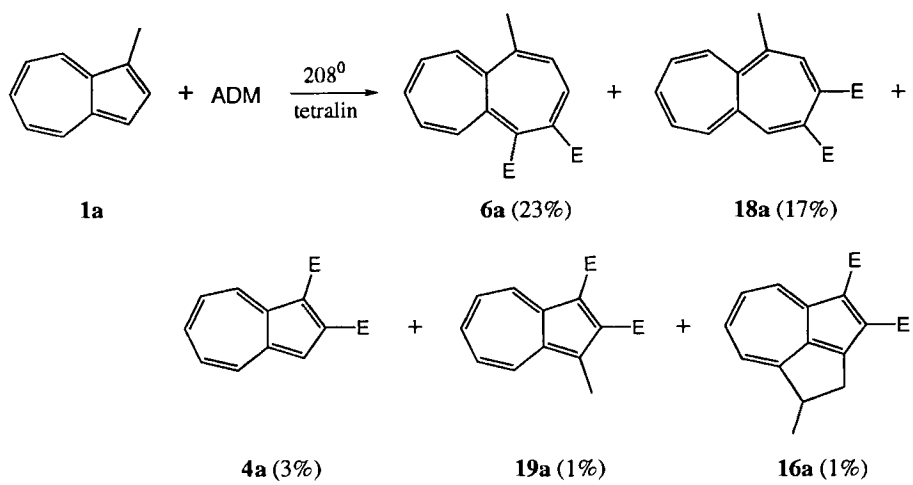


Fig. 4. *Correlation of the amount* [%] *of guaiazulene* (**1g**), *formed in the thermolysis of* **2g** *in protic and aprotic solvents at 110°, and the corresponding* E_T *values of the solvents* (*cf. Tables 10* and *11*)

Hafner et al. investigated the thermal behavior of azulene **1a** in the presence of an excess of ADM in tetralin at 208° and found that heptalene-dicarboxylate **6a** was formed together with its positional isomer **18a** (*Scheme 6*) [13]. In addition, small amounts of the two azulene-dicarboxylates **4a** and **19a** as well as **16a** are also formed. Compounds **4a**, **6a**, **16a**, and **18a** must arise from the tricyclic compound **2a** and its corresponding zwitterion **ZI** (*Scheme 7*). On the other hand, azulene-dicarboxylate **19a** must be the *retro-Diels-Alder* product of a constitutionally isomeric tricyclic compound to **2a**, which carries the Me substituent at C(8) instead of C(11) (see also the discussion in [5]). We

Scheme 6

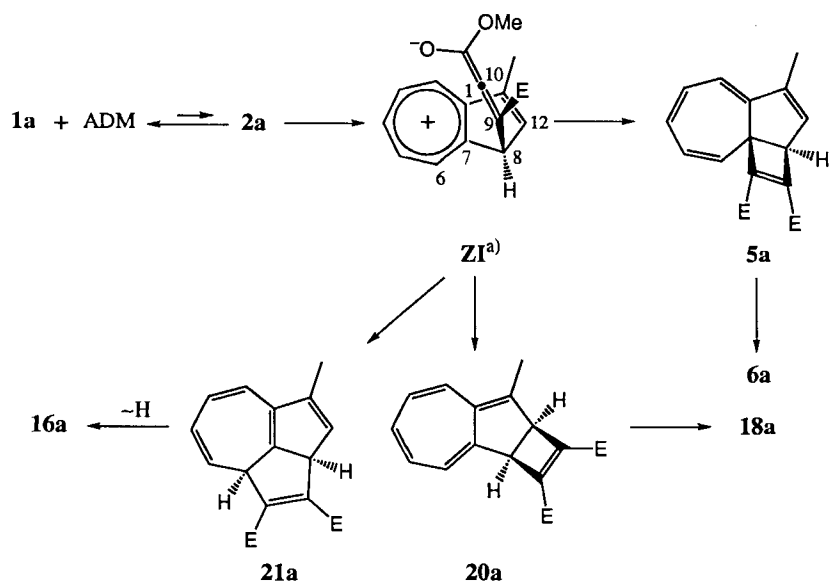


1a **6a** (23%) **18a** (17%)

4a (3%) **19a** (1%) **16a** (1%)

assume that the zwitterion **ZI** (*Scheme 7*) has a limited rotational mobility in tetralin at 208° due to the opposite charges in **ZI** and the low polarity of the solvent. When it rotates counter-clockwise around the C(8)–C(9) bond (with respect to the shown (8*S*)-configuration of the zwitterion **ZI** in *Scheme 7*), it will first meet C(7), which allows charge compensation by formation of **5a**, the precursor of **6a**. On the other hand, if rotation around the C(8)–C(9) bond occurs in a clockwise sense, charge compensation can take place *via* bond formation with C(12). This leads to **20a**, the precursor of the heptalene-3,4-dicarboxylate **18a** (and its DBS isomer). However, whereas the formation of **5a** needs a turn around the C(8)–C(9) bond of less than 36° within the potential of the delocalized positive charge of the tropylium ion to bring C(10) in bonding distance to C(7), the generation of **20a** requires a turn around the C(8)–C(9) bond of more than 70° against the potential of the tropylium ion to bring C(10) and C(12) in a distance for bond formation[14]). It seems, therefore, that the formation of the heptalene-1,2-dicarboxylates **6** from the tricyclic compounds **2** follows in apolar media at temperatures > 180° the 'principle of least motion' that favors the formation of the *Dewar*-heptalene structures **5**. The

Scheme 7[a])



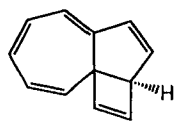
[a]) Results according to *Hafner et al.* [13].

calculated ΔH_f° values (in kcal mol^{-1}; according to MM3) for the three possible parent structures that can arise from the zwitterion **ZI** (for **15**, see also *Table 2*) are given below. The *Dewar*-heptalene structure **22** that corresponds to **5a** is by more than 10 kcal mol^{-1} less stable than its isomeric structure **23** that is adequate to **18a**. However, the most stable structure is **24** that corresponds to **21a** (*Scheme 7*) and must be the precursor of **16a**. If

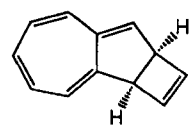
[14]) We estimated the necessary turn angles around the C(8)–C(9) bond by assuming a regular pentagon, the 108° angle of which is divided by a line passing through this and the opposite angle. This yields angles of 36 and 72°.

there would be a more or less free rotation around the C(8)–C(9) bond in the zwitterion **ZI** in apolar media, one would expect a predominant formation of compounds of type **16**, followed by the formation of the heptalene-3,4-dicarboxylates of type **18**. Yet, compounds of type **16** are found in amounts of only 1% in the thermal reaction mixtures of appropriately substituted azulenes (*i.e.*, with unoccupied C(3) and C(4)) and ADM in tetralin (*cf.* [13])[15]). The formation of heptalene-3,4-dicarboxylates in competition ot the heptalene-1,2-dicarboxylates has sporadically been observed. The impetus for their formation is not quite clear at the moment[16]).

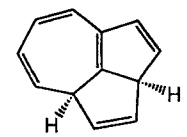
15 (113.9)



22 (119.5)



23 (108.3)



24 (82.9)

The situation changes in polar aprotic media such as MeCN. The much better stabilization of the zwitterion **ZI** by solvation allows the formation of the most stable tricyclic structures **21a** and **21b** in the case of the reaction of **2a** and **2b**, respectively. It means that the zwitterionic rearrangement of **2a** and **2b** follows in polar aprotic media no longer the 'principle of least motion' due to the better charge stabilization.

It is a relevant question, how the internal redox process **21a, b** → **16a, b** takes place. In principle, sigmatropic [1,5]-H shifts in corresponding cyclopentadiene substructures may induce this redox process, since it is known that [1,5]-H shifts in cyclopentadienes occur quite easily (see *e.g.* [41]). *Scheme 8* shows some of the possible parent structures that might be involved in such concerted H-shifts. Their calculated ΔH_f° values clearly indicate that only the peripheral path *via* **25** and **26** should be realizable on grounds of the expected ΔH_f° differences[17]). The last step **26** → **27** cannot occur concertedly for steric reasons[18]). Nevertheless, the H-atom at C(4) may be shifted concertedly to C(6) in **27** or

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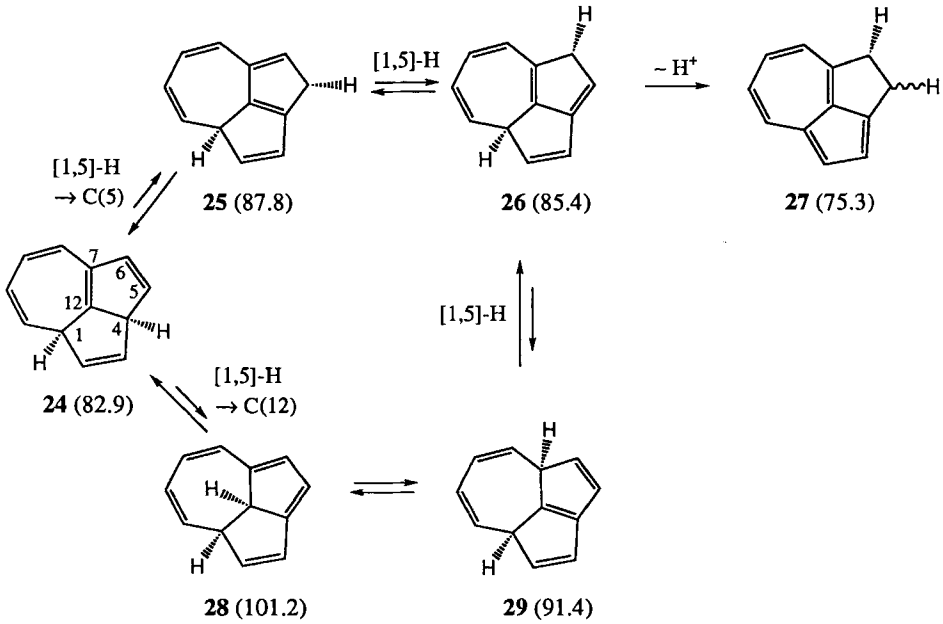
[15]) Indeed, the Et_2AlCl-catalyzed reaction of azulenes with ADM in toluene at 0° leads exclusively to product type **21a** as primary intermediate [20] [39] [40].

[16]) *Hafner et al.* observed the formation of heptalene-3,4-dicarboxylates in competition to heptalene-1,2-dicarboxylates at 208° in tetralin with azulenes that carried an alkyl group at C(1) or at C(1) and C(8) [13]. We made similar observations; *e.g.* the thermal reaction of 1,6,8-trimethylazulene with ADM in decalin at 200° leads in low yield to the formation of a 1:1 mixture of dimethyl 5,6,8-trimethylheptalene-1,2-dicarboxylate and dimethyl 1,8,10-trimethylheptalene-3,4-dicarboxylate [20]. The structure of the latter compound was confirmed by an X-ray crystal-structure analysis (*cf.* Table 3 in [5]). It seems that an alkyl substituent at C(10) in the zwitterion **ZI** (*cf. Scheme 7*) is necessary to allow an efficient charge separation by rotation around the C(8)–C(9) bond, thus leading to bond formation between C(10) and C(12), which finally leads to heptalenes **18**.

[17]) If we assume that the free enthalpy difference ($\Delta\Delta G_f^\circ$) of **25** is similar to the corresponding enthalpy difference of 4.9 kcal mol^{-1}, we find that *ca.* 0.2% of **25** should be in thermal equilibrium with **24**; *i.e.*, the thermodynamic prerequisites are given for the formation of **27**, the parent structure of **16**.

[18]) Other intermediate tricycles that may be formed, for example, by a [1,5]-H shift to C(2) in **25** (locants as in **24**), would finally lead to the formation of parent tricyclic structures, which carry the two indicated H-atoms at C(4) and C(5), *i.e.*, the last step to yield **27** would be a non-concerted 1,3-H shift in such a case.

Scheme 8[a])

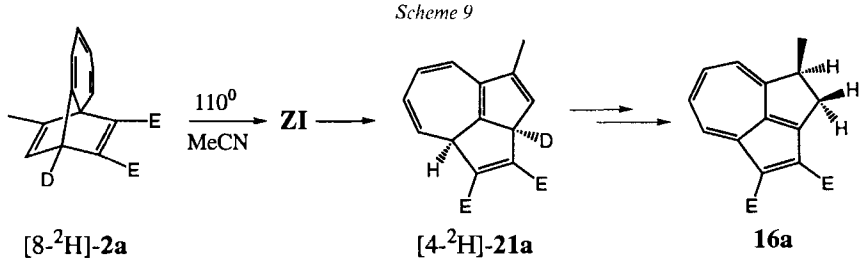


[a]) In parenthesis $\Delta H_f°$ values [kcal mol^{-1}] according to MM3 calculations.

C(5), if the prototropic non-concerted H-shift, resulting in **27**, takes place already at the stage of structure **25**.

We tried to answer the question of concerted H-shifts in compounds of type **21** by the thermolysis of [8-^{2}H]-**2a** in MeCN at 110° (*Scheme 9*)[19]). The isolated azulene-1,2-dicarboxylate **16a** showed no ^{2}H incorporation, neither at C(3) nor at C(4) or any other position. This result speaks for the fact that the rearrangement **21a** → **16a** is induced by intermolecular H$^+$-shifts, which allow an easy H/D exchange with the medium[20]).

Scheme 9



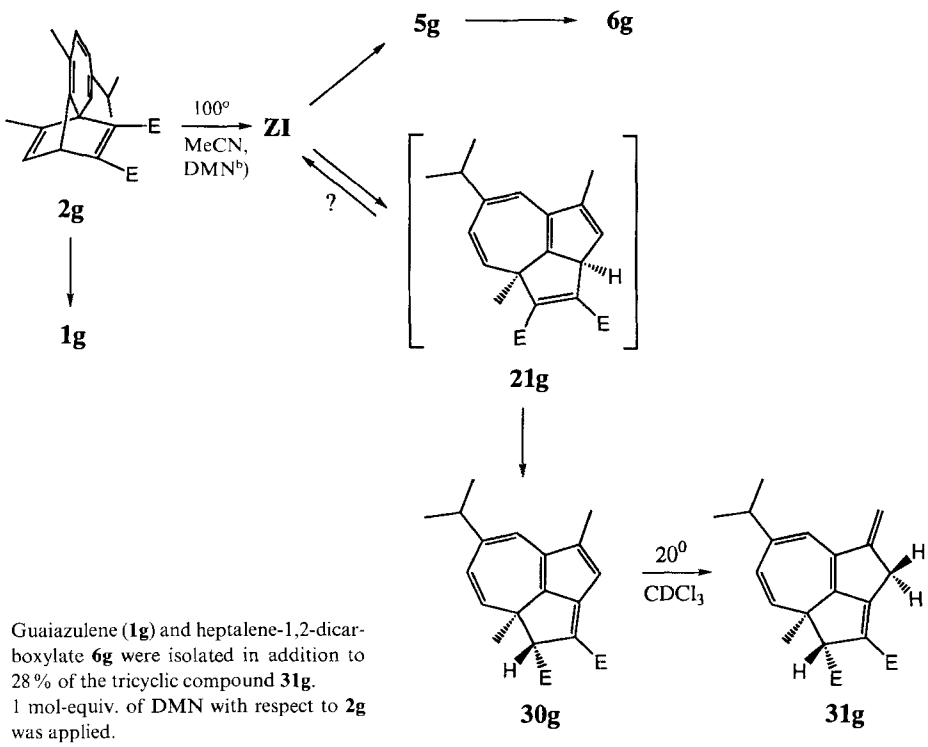
[19]) Compound [3-^{2}H]-**1a**, the precursor of [8-^{2}H]-**2a** (*cf. Scheme 1*), was easily available by deuteration of **1a** with 50% [$^2H_2$]SO_4 at 20° (*cf. Exper. Part*).

[20]) In principle, an amount of < 0.1% H_2O in MeCN would have been sufficient for a complete H/D exchange. On the other hand, we have not proved whether MeCN itself is the proton source.

The formation of > 60% of (*E*)-**7a** and (*E*)-**7b** in the thermolysis reaction of **2a** and **2b**, respectively, in MeCN indicates a protonation of the corresponding zwitterion **ZI** (*cf. Scheme 7*). The expected structure of the **ZI** would allow a direct C-protonation of the ketenolate part only from 'outside', since its inner sphere is completely shielded by the tropylium part of the **ZI**. The exclusive formation of (*E*)-**7a** and (*E*)-**7b**, respectively, can, therefore, be explained in terms of an irreversible C-protonation of the zwitterion **ZI** by any proton source present in the medium. The proton source will be regenerated in the final step, *i.e.*, the deprotonation of protonated **ZI** at C(8) leading to (*E*)-**7a** and (*E*)-**7b**, respectively. It means that the protonated **ZI** could itself play the part of the involved proton source, or, in other words, the formation of (*E*)-**7a** and (*E*)-**7b** can be regarded as an autocatalytic transformation of **21a** and **21b**, respectively.

The appearance of **21a** and **21b** in the course of the thermolysis of **1a** and **1b**, respectively, in MeCN leads to the question[21]), whether this type of intermediates or their follow-up products may also play a rôle in the thermal reactions of the other tricyclic compounds **2c–h** in MeCN or other polar aprotic media. We found no indication for the presence of such type of compounds in all other cases (*cf. Tables 8* and *11*). A reason for this finding might be that the zwitterion **ZI**, derived from the other tricyclic compounds,

Scheme 10[a])



[a]) Guaiazulene (**1g**) and heptalene-1,2-dicarboxylate **6g** were isolated in addition to 28% of the tricyclic compound **31g**.

[b]) 1 mol-equiv. of DMN with respect to **2g** was applied.

[21]) Compounds **16a** and **16b** are also formed in small amounts (*ca.* 5%) in the $[RuH_2(PPh_3)_4]$-catalyzed reaction of **1a** and **1b**, respectively, with ADM in MeCN at 100° [7].

with the exception of **2d**, carry a Me substituent at C(6) (*cf. Scheme 7*). This means that the energetically favorable, 'down-hill' redox reaction to the corresponding 3,4-ethano-bridged azulene-1,2-dicarboxylates **16** is not possible, or, in other words, the thermodynamically unfavorable equilibrium of type **24**⇌**25** (*cf. Scheme 8*) cannot alter the situation, and the formation of compounds of type **21** from the zwitterion **ZI** may become reversible.

We can support these considerations with at least one additional experiment. When the tricyclic compound **2g** was heated in MeCN in the presence of 1 mol-equiv. of the 'proton sponge' 1,8-bis(dimethylamino)naphthalene (DMN), we isolated, beside the expected guaiazulene (**1g**) and heptalene-1,2-dicarboxylate **6g**, the tricyclic compound **30g** as a red oil in a yield of 28% (*Scheme 10*). There is little doubt that **21g** is the precursor of **30g**[22])[23]). The formation of **30g** must be induced by deprotonation of **21g** at C(4) through DMN, followed by reprotonation at C(2). However, **30g** was not observed in the thermolysis reaction of **2g** in Et_3N as solvent. Therefore, it must be the higher basicity of DMN that is responsible for the formation of **30g**. Heating of **30g** in MeCN at 100° for several hours did not lead to heptalene **6g** or guaiazulene (**1g**)[24]). It seems, therefore, that the formation of **21g** from **ZI** is under neutral or weakly basic conditions (Et_3N) fully reversible[23]).

On the other hand, we observed that the red solution of **30g** in $CDCl_3$ turned green, on standing at −20° for several days, as a result of an almost quantitative formation of the new compound **31g** (*Scheme 10*). Compound **31g** was only characterized by its ^{1}H-NMR spectrum and by corresponding ^{1}H-NOE measurement (*cf. Exper. Part*).

2.3.2. *Kinetics of the Thermolysis of* **2** *in Different Solvents.* The kinetics of the thermolysis of the tricyclic compounds **2** were measured in *ca.* $3 \cdot 10^{-3}$ M solutions of the different solvents in a temperature range of 59–80°. The temperature variations of the thermostate were less than ±0.1°. The reference temperature for all compounds **2** was 74.8 ● 0.1°, and MeCN was chosen as reference solvent. As a rule, 7 time intervals were chosen for the HPLC measurements. The decrease of the concentration of all tricyclic compounds followed first-order kinetics with correlation coefficience $r^2 > 0.994$.

The kinetic data of the thermolysis of the eight tricyclic compounds **2** in MeCN at 74.8° are presented in *Table 12*. Neglecting k_T(**2c**)[25]), we observe a steady increase of k_T(**2**) with the number of alkyl substituents in the tricyclic compounds. Indeed, the correlation of ln k_T(**2**) with the number of Me groups, whereby the i-Pr and *t*-Bu groups are approached by three Me groups, is mainly linear (*Fig. 5*). The incremental augmentation of ln k_T(**2**) with the number of Me groups is a convincing argument that the rate-deter-

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[22]) We observed compounds of type **30** also in the thermal reaction of 5,9-diphenylbenz[*a*]azulene with ADM in MeCN in the presence of $[RhCl(PPh_3)_3]$ [10].

[23]) At the moment, we cannot exclude the possibility that the formation of **30g** takes place without the involvement of **21g**. If we assume that DMN has the ability to deprotonate the zwitterion **ZI**, derived from **2g**, at C(8) (*cf. Scheme 7*), we will end up with a guaiazulene derivative, substituted at C(1) with a ketenolate function. Intramolecular addition of the ketenolate function at C(8) will then generate an anion, which, on protonation, yields **30g**. The intramolecular-addition process could also be interpreted as a charge-driven 8e-electrocyclization reaction.

[24]) MM3 Calculations of the parent structure of **30g** show that it is by 7 kcal mol^{-1} less stable than the parent structure **24** of **21g**.

[25]) According to the linear correlation of ln k_T(**2**) with the number of Me substituents (*Fig. 5*), k_T(**2c**) would be too large. Unfortunately, we did not have enough material of **2c** for a repetition of the kinetic measurements of **2c**.

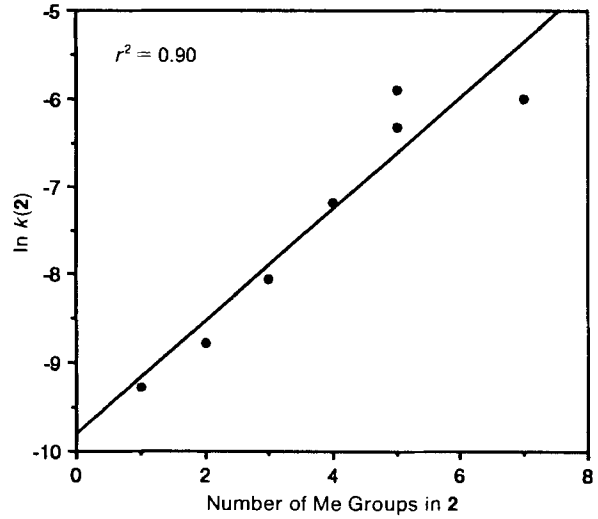


Fig. 5. *Correlation of ln* k_T **(2)** *of the thermolysis of* **2** *in MeCN at 74.8° with the number of Me groups in* **2**

Table 12. *Kinetic Data of the Thermolysis of the Tricyclic Compounds* **2** *in MeCN at 74.8°* [a])

Compound	$k_T \cdot 10^4$ [s^{-1}]	$\tau_{1/2}(T) \cdot 10^{-2}$ [s]	k_{rel}
2a	0.942	73.6	1.00
2b	1.54	45.0	1.63
2c	12.5	5.56	13.3
2d	3.17	21.9	3.37
2e	7.54	9.19	8.00
2f	27.5	2.52	29.2
2g	17.8	3.89	18.9
2h	24.6	2.81	26.1

[a]) k_T = Rate constant of the decrease of the tricycles.

Table 13. *Kinetic Data of the Thermolysis of Tricyclic Compound* **2g** *in Different Solvents at 74.8°*

Solvent	E_T[a]) [kcal mol^{-1}]	$k_T \cdot 10^4$ [s^{-1}]	$\tau_{1/2}(T) \cdot 10^{-2}$ [s]
Decane	31.0	0.891	77.8
Bu_2O	33.0	2.07	33.5
AcOEt	38.1	5.21	13.3
1,2-Dichloroethane	41.3	11.0	6.30
MeCN	45.6	17.8	3.89
EtOH	51.9	31.5	2.20

[a]) E_T Values according to [38].

mining step of the main reaction (72 ± 4%) in the thermolysis of **2** in MeCN is the formation of a vinyl-substituted tropylium ion, whose charge is stabilized additively by the number of its Me substituents.

The rate of thermolysis of the tricyclic compound **2g** at 74.8 ± 0.1° was followed in six different solvents. The data are collected in *Table 13*. Again, we recognize a clear dependence for the rates of the thermolysis on the E_T values of the solvents. The ln $\tau_{1/2}$(T) values exhibit, with the exception of that in decane (see later), a nearly perfect linear correlation with the corresponding E_T values of the solvents, which cover a change of polarity of nearly 20 kcal mol^{-1} as expressed in ΔE_T. That ln $\tau_{1/2}$(T) for decane does not fit into the linear correlation with the E_T values shows that the transition state of the *retro-Diels-Alder* reaction of **2g** in decane, yielding **1g** and ADM, is characterized by almost no charge separation, *i.e.*, the zwitterion **ZI** is not responsible for the formation of **1g** and ADM. To support this finding, we determined the activation parameters of the

thermal decomposition of **2g** in decane in the temperature range of 59–80°. The calculated values are collected in *Table 14*. The values derived from the rates of decomposition (k_T) of **2g** and from the rates of formation (k_A) of guaiazulene (**1g**) are the same within the range of experimental error. Moreover, *Table 15*, containing the already published activation parameters for the thermolysis of **2g** in MeCN [1] and the corresponding average figures of **2g** in decane, demonstrates that the formation of gaiazulene (**1g**) exhibits no solvent effect, in full agreement with the concertedness of the cleavage of C(1)–C(10) and C(8)–C(9) bonds in **2g** and the generation of a transition state of little polarity.

Table 14. *Activation Parameters for the Thermolysis of* **2g** *in Decane at 59–80°*

Activation parameters	From k_T(**2g**)[a])	From k_A(**2g**)[a])	Average
E_a (kcal mol^{-1})	27.4	26.0	26.7
ln A	29.9	32.7	31.3
$\Delta H^{\#}_{298}$ (kcal mol^{-1})	26.5	25.4	26.0
$\Delta S^{\#}_{298}$ (cal deg^{-1} mol^{-1})	–1.1	4.3	1.6
$\Delta G^{\#}_{298}$ (kcal mol^{-1})	26.8	24.1	25.5

[a]) Margins of error less than ± 3%; k_T = rate constant of the decomposition of **2g**; k_A = rate constant of the formation of **1g**.

Table 15. *Comparison of the Activation Parameters for the Thermolysis of* **2g** *in MeCN and Decane in the Temperature Range of 59–80°* [a])

Activation parameters	For k_H[b]) in MeCN	For k_A in MeCN	For $k_{av.}$[c]) in decane
E_a (kcal mol^{-1})	22.5	26.9	26.7
ln A	25.6	31.6	31.3
$\Delta H^{\#}_{298}$ (kcal mol^{-1})	21.9	26.3	26.0
$\Delta S^{\#}_{298}$ (cal deg^{-1} mol^{-1})	–9.7	2.4	1.6
$\Delta G^{\#}_{298}$ (kcal mol^{-1})	24.8	25.6	25.5

[a]) Parameters for MeCN taken from [1].
[b]) k_H = Rate constant of heptalene formation; margins of error less than ± 3%.
[c]) *Cf. Table 14.*

Quite typical for transition states of *retro-Diels-Alder* reactions in rigid tricyclic systems are also the comparably large ln A values, which correspond to $\Delta S^{\#}$ figures close to zero due to the small difference in the rigidity of the ground and transition state. Examples are the gas-phase thermolysis of *endo*-dicyclopentadiene (ln A = 29.9) [42], norbornene (ln A = 31.8) [43], and bornylene (ln A = 32.5) [44], which exhibit activation energies in the range of 33–46 kcal mol^{-1} [26]).

Last but not least, it is worth mentioning that the clearly negative $\Delta S^{\#}$ value for heptalene formation supports the deduction of the heterolysis of the C(1)–C(10) bond in **2** as the rate-determining step in the heptalene-forming reaction, since the generation of a zwitterion **ZI** needs a higher degree of ordered solvation in the transition state as compared with the more or less apolar ground state. The observed $\Delta S^{\#}_{298}$ = –9.7 cal deg^{-1} mol^{-1} for heptalene formation in the thermolysis of **2g** in MeCN falls well within the

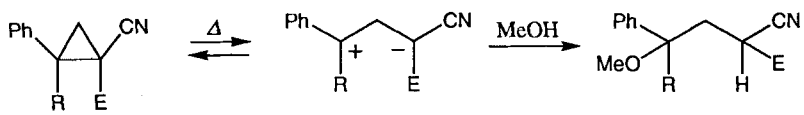
[26]) For further examples, see *e.g.* [45].

range of $\Delta S^{\#}$ values of other reactions leading to zwitterions (*cf.* [46] as well as *Table 16* in *Chapt. 3*).

3. General Considerations and Concluding Remarks. – The heterolysis of C–C bonds has already been observed or at least invoked or postulated for a number of other reactions and has most thoroughly been studied by *Huisgen*, *Cram*, *Arnett* and others, and theoretically enlightened by *Salem* and *Rowland* (*cf. e.g.* [47]).

Cram and coworkers found that donor-acceptor-substituted cyclopropane derivatives react thermally to corresponding zwitterions **ZI** which may be intercepted by protic solvents such as MeOH, or may cause stereoisomerization of the cyclopropane derivatives by intramolecular rotation and again ring closure [46]. Typical examples from *Cram*'s work are shown in *Scheme 11*. Both compounds, **32** and **33**, undergo in MeOH at 126–150° solvolysis to the corresponding MeOH derivatives **34** and **35**, respectively. In the case of **35**, inversion of configuration is observed at the Ph-substituted C-atom. The rate of racemization of optically active **32** is strongly solvent-dependent. *Table 16* contains some of the activation parameters that have been published by *Cram* and coworkers [46a, b][27]). The observed $\Delta S^{\#}$ values are in the same range as we have found for the thermolysis of **2g** in MeCN (*cf. Table 15*). In contrast to these findings stand the activation parameters for the *trans,cis*-isomerization of the methyl cyclopropanecarboxylate **36** in MeOH [46]. The observed $\Delta S^{\#}$ value of -0.7 ± 1.2 cal deg^{-1} mol^{-1} is in agreement with the intervention of an apolar 1,3-diradical in its singlet state (*Scheme 12*). The example demonstrates how substituent effects can move the relative energies of zwitterions **ZI** and their corresponding singlet diradical counterparts on the hypersurface correlating reactants and products[28]).

Scheme 11



R = Ph: **32**[a])
R = H: **33**[b])

ZI

34
35

[a]) See [46a, b]. [b]) See [46a, c].

Table 16. *Solvent Dependence of the Racemization of (+)- and (−)-***32** *at 126.0–149.2°* [a])

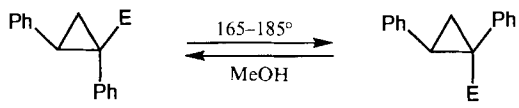
Solvent	$\Delta H^{\#}$ [kcal mol^{-1}]	$\Delta S^{\#}$ [cal deg^{-1} mol^{-1}]
Benzene	30.4 ± 0.2	−7.6 ± 0.6
DMF	27.7 ± 0.3	−11 ± 1
MeOH	25.5 ± 0.3	−14 ± 1

[a]) Data from [46b] are calculated for 126.0°.

[27]) The thermolysis and rearrangement of donor-acceptor-substituted cyclopropanes have found in the meantime broad application in organic synthesis as has been shown by *Reissig* [48].

[28]) The work of *Hixson* should be mentioned in this context, who showed that cyclopropanes, which react in the ground state *via* singlet diradicals, undergo singlet photoreactions *via* zwitterionic states (*cf.* [49]), in full agreement with the predictions of *Salem* and *Rowland* (*cf.* [47]).

Scheme 12[a])



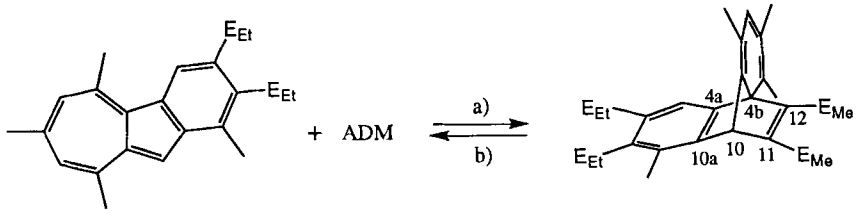
cis -**36** *trans* -**36**

$\Delta H^{\neq}(cis \rightarrow trans) = 37.4 \pm 0.5$ kcal mol^{-1}
$\Delta S^{\neq}(cis \rightarrow trans) = -0.7 \pm 1.2$ cal deg^{-1} mol^{-1}

[a]) Data from [46e] calculated for 184.4°.

That subtle substituent effects govern also the thermal behavior of tricyclic compounds of type **2** is demonstrated by the following experiment. The Rh^{I}-catalyzed reaction of the benz[*a*]azulene-dicarboxylate **37**, the synthesis of which we have recently described [50], leads in MeCN at 100° to the benzo-annelated tricyclic compound **38** (*Scheme 13*). Whereas tricyclic compounds of type **38**, having no substituent at the benzo ring, can successfully be rearranged to the corresponding benzo[*a*]heptalene-6,7-dicarboxylates (*cf.* [6] [7] [10]), the thermal reaction of **38**, with the two strong π- and σ-acceptor substituent at the benzo ring, gave only the starting materials as *retro-Diels-Alder* products. It seems that, in this case, the heat of formation of the transition of the corresponding zwitterion **ZI** is, also in polar media, too high to compete with the heat of formation of the transition state of the concerted *retro-Diels-Alder* reaction, which may be interpreted as a concerted homolysis of the C(4b)–C(12) and C(10)–C(11) bond.

Scheme 13



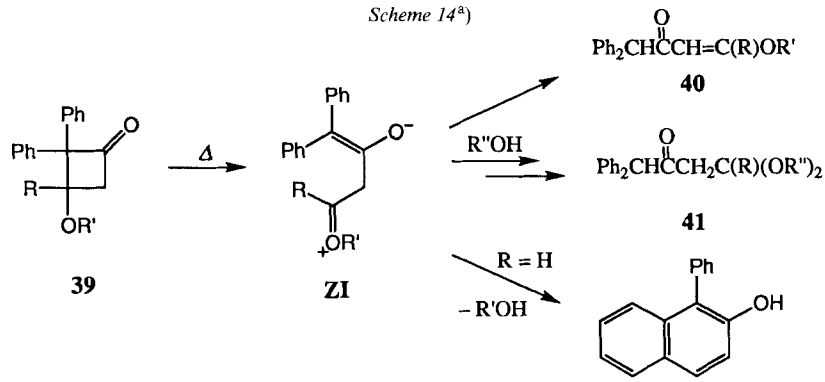
37 **38** (26%)

a) 2 mol-% [$RhH(PPh_3)_4$] in MeCN, 100°, 14 h. b) MeCN or DMF, 150°, quant.

The similar strain energies of three- and four-membered ring systems result in a similar behavior with respect to C–C bond heterolysis. *Huisgen et al.* reported already in 1969 that the cycloaddition products of diphenylketene and enol ethers undergo thermal ring opening at the C(2)–C(3) bond under formation of corresponding 1,4-zwitterions **ZI** (*Scheme 14*) [51]. The formed zwitterions **ZI** may undergo a 1,3-prototropic shift (→ **40**), addition of R″OH (→ **41**), or ring closure, followed by loss of R′OH (→ **42**). The ring opening of **39** is solvent-dependent [51]. Similar observations were also made with diphenylketene and enamines [52]. Other examples can be found in *Huisgen*'s compre-

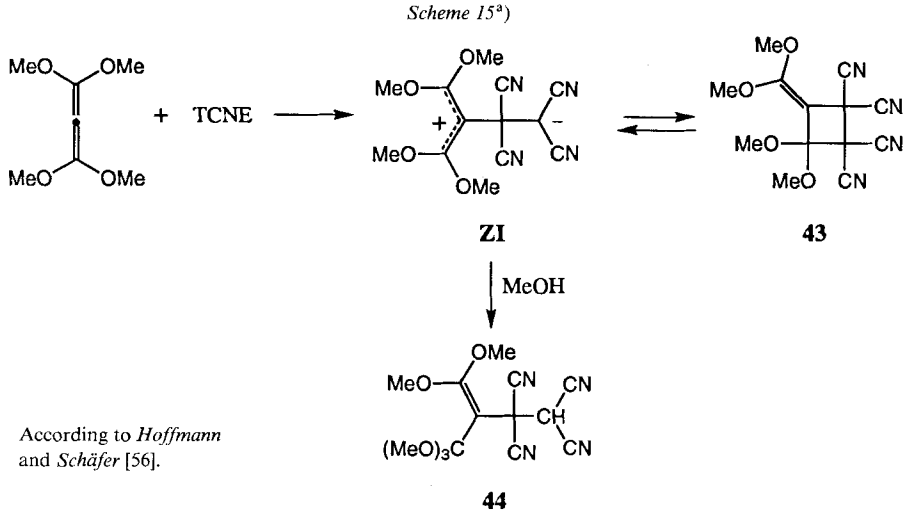
hensive work on (2+2) cycloadditions *via* 1,4-zwitterions **ZI** (see *e.g.* [53]). The cycloadducts for alkyl *trans*- and *cis*-propenyl ethers and tetracyanoethylene (TCNE), for example, undergo stereoisomerization at room temperature in MeCN, but not in benzene [54]. In other cases, the trapping of zwitterions **ZI** from the TCNE-enol-ether adducts and alcohols was observed [55]. *Hoffmann* and *Schäfer* found that the cycloadduct of tetramethoxyallene and TCNE reacts in MeOH *via* its corresponding zwitterion **ZI** that is trapped by the solvent (*Scheme 15*) [56].

Scheme 14[a])



[a]) According to *Huisgen et al.* [51].

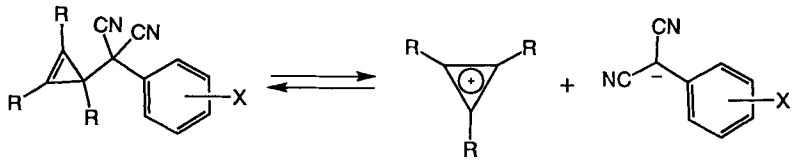
Scheme 15[a])



[a]) According to *Hoffmann* and *Schäfer* [56].

In all these cited cases, strained $C(sp^3)$–$C(sp^3)$ bonds in three- and four-membered ring systems are prone to heterolysis in polar aprotic or protic media. *Arnett* and *Molter* showed that, with the right set-up of substituents, also open-chain compounds may undergo $C(sp^3)$–$C(sp^3)$-bond heterolysis to carbanions and carbocations (*Scheme 16*) [24]. In MeCN at room temperature, an equilibrium between the neutral forms **45**, and

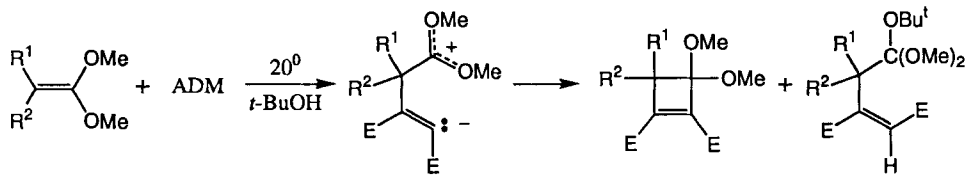
Scheme 16[a])



45[b]) **46** **47**

[a]) According to *Arnett* and *Molter* [24]. [b]) See also *Footnote 6*.

Scheme 17[a])



ZI **48** (55%) **49** (16%)

[a]) According to *Graziano et al.* [58]; yields for R^1 = Me, R = H.

the ions **46** and **47** is established. Also the design of specifically substituted *Cope* systems by *Wigfield et al.* allows rearrangements, possibly *via* heterolytic cleavage of the central σ bond [57]. However, there are, to the best of our knowledge, no examples where C(sp^3)–C(sp^2) bonds are heterolytically cleaved. Recently, *Graziano et al.* showed that the (2+2) cycloaddition of 1,1-dimethoxyalkenes and ADM possibly involves corresponding zwitterions **ZI** (*Scheme 17*) [58]. In MeCN, only the cycloadducts **48** are formed in yields of 30–60%. However, in *t*-BuOH the alcohol adduct **49** (R^1 = Me, R^2 = H) of the corresponding zwitterion **ZI** is obtained in addition to the cycloadduct **48**. On the other hand, cyclobutene **48** (R^1 = Me, R^2 = H) was stable, when dissolved in *t*-BuOH and kept at room temperature over 4 h. These experiments reveal that heterolytic cleavage of a C(sp^3)–C(sp^2) bond does not occur as easy as the heterolytic rupture of a similarly substituted C(sp^3)–C(sp^3) bond, despite the fact the strain energy of cyclobutene derivatives are larger than that of cyclobutanes.

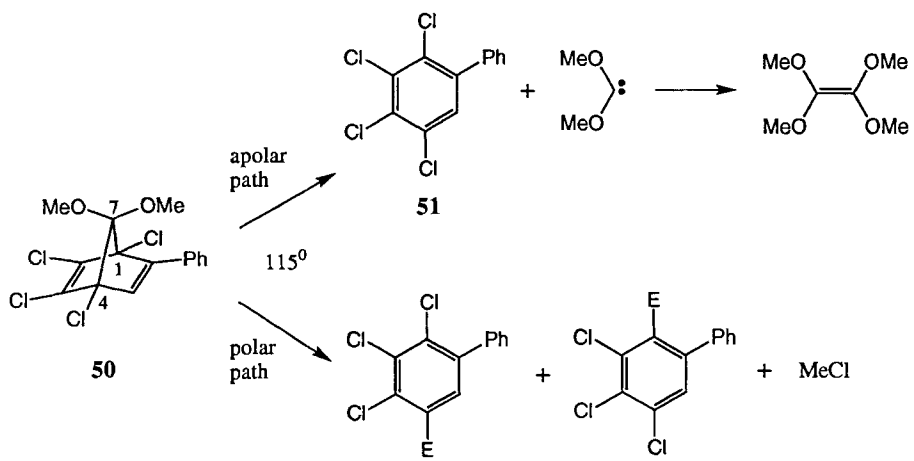
Therefore, it seems that the heterolytic cleavage of a C(sp^3)–C(sp^3) bond as described in this work is unique. Our experiments document that, under suitable structural prerequisites, an ester group, linked to a C(sp^2)-atom, can as efficiently stabilize a developing negative charge as two ester or CN groups, attached to a C(sp^3)-atom. This is understandable with respect to *Arnett*'s finding that the heat of heterolysis (ΔH_{het}) in polar solvents such as PhCN is linearly proportional to the pK_a of the corresponding carbanion precursors [24]. Thus, if we compare the α-CH acidities of carboxylic esters (p$K_a \approx 24$[29])) with that of malonates (p$K_a \approx 13$), we observe an appreciable acidity jump, *i.e.*, a substantial gain in stability of the corresponding carbanions. This increase in stability is partially

[29]) pK_a Values from [59]. In principle, for our discussion, kinetic acidities should be taken as references.

compensated by the increase in acidity, when we change from a sp^3-hybridized (C_2H_6: $pK_a \approx 50$) to a sp^2-hybridized C-atom (C_2H_4: $pK_a \approx 44$), and may be further equaled by σ-acceptor substituents (*e.g.* MeOCO) at the neighbor C(sp^2)-atom. We already mentioned that, in the case of the tricyclic compounds **2**, stereoelectronic factors may also contribute to facilate the heterolytic cleavage of the C(1)–C(10) bond due to the fact that the energetically most favorable conformation of the MeOCO group at C(10) is its orthogonal arrangement with respect to the C(9)=C(10) bond. The uptake of the developing negative charge in the course of the heterolysis by a ketenolate substructure will thus be optimal. The X-ray crystal structures of **2f** and **2g** support this idea (*cf. Fig. 1*). That the formation of a tropylium structure is enhancing C–C bond heterolysis is well established by the work of *Takahashi et al.* (*cf.* [60] and lit. cit. there; see also *Okamoto et al.* [61]).

There is a last point left for discussion. It is the fact that in a molecule the same C–C bond takes competitively part in a heterolytic and in a concerted homolytic, *i.e.*, apolar, bond cleavage. To the best of our knowledge, we can cite only one comparable process. It is the thermal extrusion of dialkoxycarbenes from 7,7-dialkoxynorbornadienes that has been thoroughly studied specifically by *Lemal et al.* [62] and, in general, by *Hoffmann et al.* [63]. *Lemal et al.* observed that product formation in the thermolysis of the norbornadienone dimethylacetal **50** is strongly solvent-dependent (*Scheme 18*). Whereas heating as

Scheme 18[a])



[a]) According to *Lemal et al.* [62].

Table 17. *Product Distribution of the Thermolysis of Acetal* **50** *in Different Solvents at 115°* [a])

Solvent	Biphenyl **51** [wt.-%]	Carboxylate **52** [wt.-%]	Carboxylate **53** [wt.-%]	**51**/(**52** + **53**)
Cyclohexane	91.8	6.5	0.8	12.6
MeCN	12.5	67.4	20.1	0.143
MeOH	23.2	58.4	16.2	0.311

[a]) *Cf. Scheme 18*; data taken from [62].

a melt or in apolar solvents such as cyclohexane mainly leads to the formation of the biphenyl derivative **51** and dimethoxycarbene, which dimerizes to tetramethoxyethene, in polar solvents such as MeCN or MeOH, the formation of the methyl biphenyl-carboxylates **52** and **53** and of MeCl is strongly favored (*cf. Table 17*). The formation of the esters **52** and **53** and of MeCl is a clear indication for the occurrence of zwitterions **ZI**, formed by heterolytic cleavage of the C(1)–C(7) bond (→**53**). The further fate of the zwitterions **ZI** is the loss of Cl^-, followed by demethylation of the dimethoxycarbenium part due to the nucleophilic attack of Cl^-. On the other hand, the formation of the biphenyl derivative **51** is in accord with a homolysis of the C(1)–C(7) and/or C(4)–C(7) bond, followed by the loss of dimethoxycarbene in the singlet state[30]). However, nothing speaks in this case against a concerted, surely not synchronous, cleavage of the C(1)–C(7) and C(4)–C(7) bonds in the sense of a linear cheletropic reaction with a transition state of low polarity, which is strongly favored under apolar condition (*cf. Table 17*). If we see the observed thermal apolar and polar reaction path of the tricyclic compounds **2** and the norbornadiene derivatives of type **50** in relation to fundamental vibrational modes of the basal parent structure, *i.e.*, norbornadiene, the apolar (homolytic and concerted) paths correspond to symmetric skeletal vibrations (*e.g.* synchronous elongation of the C(1)–C(2) and C(3)–C(4) bonds by concomitant shortening of the C(1)–C(6) and C(4)–C(5) bonds or simultaneous elongation of the C(1)–C(7) and C(4)–C(7) bonds) and the polar (heterolytic) paths to asymmetrical skeletal vibrations (*e.g.* synchronous elongation of the C(1)–C(2) and C(4)–C(5) bonds by concomitant shortening of the C(3)–C(4) and C(1)–C(6) bonds or simultaneous elongation of the C(1)–C(7) bond and shortening of the C(4)–C(7) bond and *vice versa*) of comparable vibrational energy[31]).

We thank Dr. *A. Linden* for the X-ray crystal-structures analyses, Prof. *M. Hesse* and his coworkers for mass spectra, Prof. *W. von Philipsborn* and his coworkers for NMR support and ^{1}H-NOE measurments, *H. Frohofer* for elemental analyses, and *P. Uebelhart* for help with HPLC problems. Special thanks are due to *K. Hochreutner* and *W. Eisele* for technical adaption of the high-pressure apparatus from *NOVA SWISS* in accordance to our wishes. The financial support of this work by the *Swiss National Science Foundations* is gratefully acknowledged.

Experimental Part

General. See [1]. The modified high-pressure autoclave (reaction volume *ca.* 20 ml) from *NOVA SWISS* has already been described in [1]. A more detailed description can be found in [64]. However, one point is worth mentioning. The *Kynar* tube, recommended by *NOVA SWISS* for the essential inner reaction chamber, withstood the applied maximum liquid pressure of 7 kbar, but often burst in the pressure relaxation phase, leading to an uncontrolled intermixture of the goods of the reaction chamber and the pressure-transducing liquid (kerosine). *W. Eisele* solved this problem by a reconstruction of the reaction chamber with a stainless steel bellow tube (inner diameter 10 mm, outer diameter 16 mm, length 100 mm), welded to the corresponding gaskets. This system worked perfectly up to 7 kbar.

1. Synthesis of Dimethyl Tricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylates 2. All pressure reactions were performed in 12 ml of hexane at 30° (for details, see *Table 1*). Chromatographic separations (CC) were performed on silica gel, pretreated with 1% of Et_3N, and with hexane/Et_2O (mostly 1:1) mixtures as eluants. Where necessary, the tricyclic compounds **2** were further purified by reverse-phase HPLC (C_{18} column, MeCN/H_2O 9:1).

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[30]) For a more detailed discussion of the thermal behavior of norbornadienes, see [63c].

[31]) Of course, the discussed vibrational modes are accompanied by corresponding compensating bond-angle changes. We thank Dipl.-Chem. *A. Gelessus* (research group of Prof. *W. Thiel*) for the calculation of the fundamental vibrational modes of norbornadiene.

1.1. *Dimethyl 11-Methyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**2a**). *1-Methylazulene* (**1a**; 0.210 g, 1.48 mmol) [65] gave **2a** (0.186 g), after CC and HPLC, as a dark-green oil, which crystallized from hexane at −20°. The crystals melted, however, at r.t. R_f(hexane/Et_2O 1:1): 0.29. ^{1}H-NMR (300 MHz, C_6D_6): 5.95 (*sext.*-like, $^3J(8,12) = 3.4$, ^4J(Me−C(11),12) = 1.9, H−C(12)); 5.91 (*d*, $^3J(3,2) = 12.35$, H−C(2)); 5.83 (*ddd*, $^3J(2,3) = 12.35$, $^3J(4,3) = 7.3$, $^4J(5,3) = 1.0$, H−C(3)); 5.48 (*ddt*, $^3J(5,4) = 11.8$, $^3J(3,4) = 7.3$, $^4J(6,4) \approx {}^4J(2,4) = 1.0$, H−C(4)); 5.40 (*ddt*, $^3J(4,5) = 11.8$, $^3J(6,5) = 7.3$, $^4J(3,5) \approx {}^5J(2,5) = 1.0$, H−C(5)); 4.63 (*dd*, $^3J(5,6) = 7.3$, $^4J(4,6) = 1.1$, H−C(6)); 4.16 (*d*, $^3J(12,8) = 3.4$, H−C(8)); 3.42, 3.29 (2*s*, 2 MeOOC); 1.78 (*d*, ^4J(12,Me−C(11) = 1.8, Me−C(12)).

1.2. *Dimethyl 11-Methyl[8-^{2}H]tricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* ([8-^{2}H]-**2a**).

1.2.1. *1-Methyl[3-^{2}H]azulene* ([3-^{2}H]-**1a**). A soln. of **1a** (0.30 g) in Et_2O (3 ml) was slowly added at 0° to a mixture of D_2O (99.8 atom-% D; 2.5 ml) and D_2SO_4 (96%; 99.5 atom-% D, 2.0 ml). The mixture was stirred for 1 h at r.t. and then diluted with D_2O (8 ml). After neutralization with K_2CO_3, the heavy H_2O phase was extracted twice with Et_2O (20 ml). [3-^{2}H]-**1a** was dried during 8 h under high vacuum and r.t.: quant. yield. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.24 (*d*, $^3J(5,4) \approx {}^3J(7,8) = 9.6$, 2.0 H, H−C(4,8)); 7.76 (*s*, 1.0 H, H−C(2)); 7.53 (*t*, $^3J(5,6) \approx {}^3J(7,6) = 9.7$, 1.0 H, H−C(6)); 7.08 (*t*, $^3J(6,5) \approx {}^3J(4,5) = 9.6$, 1.0 H, H−C(5)); 7.05 (*t*, $^3J(6,7) \approx {}^3J(8,7) = 9.6$, 1.0 H, H−C(7)); 2.69 (*s*, 3.0 H, Me−C(1)). No recognizable signal at 7.21 ppm (H−C(3)).

1.2.2. *Pressure Reaction.* The reaction of [3-^{2}H]-**1a** (0.20 g, 1.40 mmol) led to [8-^{2}H]-**2a** (0.100 g) after two CC. R_f(hexane/Et_2O 1:1): 0.29. ^{1}H-NMR (300 MHz, C_6D_6): Identical with that of **2a** with the exception that H−C(12) at 5.95 appeared as *q* (^3J(Me−C(11),12) = 1.8) and the integral of the signal of H−C(8) at 4.16 indicated only 0.04 H.

1.3. *Dimethyl 4,11-Dimethyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**2b**). *1,6-Dimethylazulene* (**1b**; 0.165 g, 1.15 mmol) [66] [67] gave, after CC and HPLC, **2b** (0.035 g) as a brownish oil, which did not crystallize from hexane. R_f(hexane/Et_2O 1:1): 0.30. ^{1}H-NMR (300 MHz, C_6D_6): 6.02 (*sext.*-like, $^3J(8,12) = 3.4$, ^4J(Me−C(11),12) = 1.8, H−C(12)); 5.97 (*d*, $^3J(3,2) = 12.45$, H−C(2)); 5,75 (*dd*, $^3J(2,3) = 12.45$, $^4J(5,3) = 1.5$, H−C(3)); 5.28 (*dsext.*-like, $^3J(6,5) = 7.8$, $^4J(3,5) \approx {}^4J$(Me−C(6),5) = 1.5, H−C(5)); 4.62 (*d*, $^3J(5,6) = 7.8$, H−C(6)); 4.20 (*d*, $^3J(12,8) = 3.4$, H−C(8)); 3.44, 3.31 (2*s*, 2 MeOOC); 1.82 (*d*, ^4J(12,Me−C(11)) = 1.8, Me−C(11)); 1.60 (*d*, ^4J(5,Me−C(6)) = 1.4, Me−C(6)).

1.4. *Dimethyl 4,6,11-Trimethyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**2c**). *1,4,6-Trimethylazulene* (**1c**; 0.110 g, 0.65 mmol) [20] gave, after CC and HPLC, **2c** (0.011 g) as a pale-brown oil, which could not be crystallized from hexane. R_f(hexane/Et_2O 1:1): 0.37. ^{1}H-NMR (300 MHz, C_6D_6): 6.06 (*sext.*-like, $^3J(8,12) = 3.5$, ^4J(Me−C(11),12) = 1.8, H−C(12)); 6.02 (*d*, $^3J(3,2) = 12.3$, H−C(2)); 5.75 (*dd*, $^3J(2,3) = 12.3$, $^4J(5,3) = 1.5$, H−C(3)); 5.26 (*m*, H−C(5)); 4.53 (*d*, $^3J(12,8) = 3.5$, H−C(8)); 3.46, 3.31 (2*s*, 2 MeOOC); 1.84 (*d*, ^4J(12,Me−C(11)) = 1.8, Me−C(11)); 1.62 (*d*, ^4J(5,Me−C(4)) = 1.4, Me−C(4)); 1.45 (*s*, Me−C(6)).

1.5. *Dimethyl 3,5,11-Trimethyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**2d**). *1,5,7-Trimethylazulene* (**1d**; 0.50 g, 2.93 mmol) [31] gave after two CC, **2d** (0.122 g) as a brownish oil, which could not be crystallized from hexane. R_f(hexane/Et_2O 1:1): 0.32. ^{1}H-NMR (300 MHz, C_6D_6): 6.05 (*sext.*-like, $^3J(8,12) = 3.4$, ^4J(Me−C(11),12) = 1.6, H−C(12)); 5.78 (*m*, H−C(2)); 5.35 (*d*, $^4J(6,4) = 1.35$, H−C(4)); 4.55 (*d*, $^4J(4,6) = 1.35$, H−C(6)); 4.15 (*d*, $^3J(12,8) = 3.5$, H−C(8)); 3.47, 3.34 (2*s*, 2 MeOOC); 1.84 (*d*, ^4J(12,Me−C(11)) = 1.65, Me−C(11)); 1.75 (br. *s*, Me−C(5)); 1.54 (br. s, Me−C(3)).

1.6. *Dimethyl 2,4,6,11-Tetramethyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**2e**). See [1]. An improved workup protocol gave **2e** (0.256 g, 41.3%), (*E*)-**7e** (0.033 g, 5.3%), and (*Z*)-**7e** (0.020 g, 3.2%).

Data of Dimethyl (Z)-1-(3,4,6,8-Tetramethylazulen-1-yl)ethene-1,2-dicarboxylate ((*Z*)-**7e**): brown oil. R_f(hexane/Et_2O 1:1): 0.51. UV (hexane): λ_{max} 400 (3.78), 338 (sh, 4.07), 328 (4.08), 295 (4.41), 289 (sh, 4.37), 247 (4.35); λ_{min} 271 (4.04), 313 (4.03), 368 (3.58). IR (film): 2951, 2925, 2874, 1735/1717*s* (COOR), 1607, 1579, 1553, 1511, 1436, 1407, 1375, 1334, 1305, 1250, 1194, 1159, 1111, 1083, 1051, 1023, 981, 928, 871, 839, 785, 754. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.49 (br. *s*, H−C(2)); 6.92 (br. *s*, H−C(5,7)); 5.64 (*s*, C*H*COOMe), 3.90, 3.77 (2*s*, 2 MeOOC); 2.96, 2.82 (2*s*, Me−C(4,8)); 2.76 (*s*, Me−C(3)); 2.52 (*s*, Me−C(6)). EI-MS: 326 (87, $M^{+\cdot}$), 311 (21, [M − Me]$^+$), 279 (6, [M − Me − MeOH]$^+$), 267 (100, [M − MeOOC]$^+$), 253 (13), 252 (13), 251 (7), 208 (38), 207 (50), 193 (65), 192 (14), 191 (12), 189 (8).

1.7. *Dimethyl 2,4,6,11,12-Pentamethyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**2f**). See [1]. Anal. calc. for $C_{21}H_{24}O_4$ (340.62): C 74.09, H 7.11; found: C 74.01, H 7.30.

1.8. *Dimethyl 3-Isopropyl-6,11-dimethyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**2g**). See [1]. For ^{13}C-NMR data, see also *Table 6*. An optimized workup protocol gave from 0.30 g (1.50 mmol) of **1g** the tricyclic compound **2g** (0.256 g; 61.7% with respect to the turnover of **1g**), (*E*)-**7g** (0.039 g, 9.1%), (*Z*)-**7g** (0.025 g, 5.8%), and **6g** (0.032 g, 7.5%), beside 0.050 g (17%) of guaiazulene (**1g**).

Additional Data of **2g**: ^{1}H-NMR (300 MHz, $CDCl_3$; *cf. Table 5*): 6.28 (*sext.*-like, $^3J(8,12) = 3.4$, ^4J(Me–C(11),12) = 1.8, H–C(12)); 5.57 (br. *s*, H–C(2)); 5.53 (*dd*, $^3J(5,4) = 12.6$, $^4J(2,4) = 1.6$, H–C(4)); 5.46 (*dd*, $^3J(4,5) = 12.6$, $^5J(2,5) = 1.1$, H–C(5)); 4.38 (*d*, $^3J(12,8) = 3.4$, H–C(8)); 3.82, 3.74 (2*s*, 2 MeOOC); 2.32 (*sept.*, Me_2CH); 1.91 (*d*, ^4J(12,Me–C(11)) = 1.8, Me–C(11)); 1.64 (*s*, Me–C(6)); 1.06, 1.02 (2*d*, Me_2CH).

*Data of Dimethyl (*E*)-1-(5-Isopropyl-3,8-dimethylazulen-1-yl)ethene-1,2-dicarboxylate* ((*E*)-**7g**): See [1].

*Data of (*Z*)-***7g***:* Green oil. R_f(hexane/Et_2O 1:1): 0.44. UV (hexane): λ_{max} 399 (br., 3.85), 325 (br., 3.96), 306 (4.02), 289 (4.35), 260 (sh, 4.08), 244 (4.22); λ_{min} 358 (3.52), 313 (3.95), 304 (4.04). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.18 (*d*, $^4J(6,4) = 2.0$, H–C(4)); 7.68 (br. *s*, H–C(2)); 7.46 (*dd*, $^3J(7,6) = 11.0$, $^4J(4,6) = 2.0$, H–C(6)); 7.12 (*d*, $^3J(6,7) = 11.0$, H–C(7)); 5.68 (*s*, *CH*COOMe); 3.90, 3.72 (2*s*, 2 MeOCO); 3.08 (*sept.*, Me_2CH); 2.68 (*s*, Me–C(8)); 2.60 (*s*, Me–C(3)); 1.36 (*d*, Me_2CH).

When (*E*)- resp. (*Z*)-**7g** (each 0.015 g) were heated in toluene (5 ml) in the presence of traces of I_2 at 100° an equilibrium mixture was formed, which consisted, after 25 h, of 67.2% of (*E*)-**7g** and 32.8% of (*Z*)-**7g**.

Data of Dimethyl 7-Isopropyl-5,10-dimethylheptalene-1,2-dicarboxylate (**6g**): m.p. 143–144° (hexane/Et_2O; [68]: 141–142.5° (tetralin)). All spectral data are identical with those reported in [68].

1.9. *Dimethyl 4-(*tert*-Butyl)-2,6,11,12-tetramethyltricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylate* (**2h**). *6-(*tert*-Butyl)-1,2,4,8-tetramethylazulene* (**1h**; 0.061 g, 0.254 mmol) [69] gave, after two CC, pure **2h** (0.035 g) beside a fraction which contained (*E*)- and (*Z*)-**7h** (HPLC and ^{1}H-NMR). Compound **2h** crystallized from hexane at –20° in small colorless crystals, m.p. 135° (melt turned blue). TLC proved the presence of azulene **1h** and **6h**. R_f(hexane/Et_2O 1:1): 0.35. ^{1}H-NMR (300 MHz, C_6D_6): 6.23 (*m*, H–C(3)); 5.45 (br. *s*, H–C(5)); 4.29 (*s*, H–C(8)); 3.49, 3.31 (2*s*, MeOOC); 2.05 (br. *s*, Me–C(2)); 1.68, 1.65 (2 *q*-like, Me–C(11,12)); 1.27 (*s*, Me–C(6)); 1.07 (*s*, *t*-Bu).

1.10. *2,3-Diethyl 11,12-Dimethyl 1,5,7,9-Tetramethyl-4b,10-etheno-10*H*-benz[*a*]azulene-2,3,11,12-tetracarboxylate* (**38**). *Diethyl 1,5,7,9-Tetramethylbenz[*a*]azulene-2,3-dicarboxylate* (**37**; 0.11 g, 0.29 mmol) [50], ADM (0.25 g, 1.76 mmol), and $[RhH(PPh_3)_4]$ (0.013 g, 0.011 mmol) were dissolved in MeCN (4.0 ml) and heated in a sealed flask at 100° for 14 h. CC on silica gel (pre-treated with 1% of Et_3N; (hexane/Et_2O 1:1)) gave **38** in the first fraction, which was recrystallized from Et_2O/hexane (0.040 g, 26%).

Data of **38**: yellow crystals. M.p. 141–142°. R_f(hexane/Et_2O 1:1): 0.10. UV (hexane): λ_{max} 337 (3.46), 298 (sh, 3.62), 280 (sh, 3.74), 247 (4.36), 206 (4.62); λ_{min} 316 (3.40), 232 (4.34). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.78 (*s*, H–C(4)); 5.82 (br. *s*, H–C(8)); 5.18 (br. *s*, H–C(6)); 4.87 (*s*, H–C(10)); 4.40, 4.31 (2*q*, $J = 7.1$, 2 CH_3CH_2OCO); 3.80, 3.76 (2*s*, 2 MeOOC); 2.42 (*s*, Me–C(1)); 2.17 (*s*, Me–C(5)); 1.79 (*s*, Me–C(7)); 1.62 (*s*, Me–C(9)); 1.38, 1.34 (2*t*, $J = 7.1$, 2 CH_3CH_2OCO). EI-MS: 520 (12, M^+), 505 (12, $[M - Me]^+$), 461 (22, $[M - MeOOC]^+$), 378 (100, $[M - ADM]^{+\cdot}$), 303 (19), 111 (20), 59 (68).

Heating of **38** in MeCN or DMF at temp. up to 150° led exclusively to **37**. No other products could be detected.

2. Thermolyses of the Tricyclic Compounds 2. *Ca.* 10^{-3} M solns. of the compounds were prepared in 1.0 ml of the solvent. The solns. were heated in 5-ml flasks, sealed with a septum, in an oil bath for 1 h at 110 ± 1°. The rearranged products were analyzed by HPLC and UV detection at 290 nm. 20 µl were injected for each analysis. The products were identified on the basis of their retention times and characteristic UV spectra (210–450 nm) in comparison with authentic probes.

2.1. *Comparative Thermolysis in MeCN.* Calibration curves were established for the products, namely **1e** and **1g** as well as **6e** [32] and **6g** [68] of the thermolysis of **2e** and **2g**, resp. The calibration curves were also applied for the determination of the yields of the thermolysis of the other tricyclic compounds. The data are collected in *Scheme 4* and in *Table 8*.

2.1.1. *Thermolysis of* **2a**. Compound **16a** was isolated and spectroscopically characterized.

*Data of Dimethyl 3,4-Dihydro-4-methylcyclopent[*cd*]azulene-1,2-dicarboxylate* (**16a**) (*cf.* [7]): blue oil. R_f(hexane/Et_2O 2:3): 0.26. UV (HPLC, MeCN): λ_{max} 299. ^{1}H-NMR (300 MHz, $CDCl_3/C_6D_6$): 8.90/9.09 (*d*, $^3J(7,8) = 10.1$, H–C(8)); 7.69/7.00 (*t*, $^3J(5,6) \approx {}^3J(7,6) = 9.9$, H–C(6)); 7.28/6.70 (*t*, $^3J(6,7) \approx {}^3J(8,7) = 10.0$, H–C(7)); 7.24/6.50 (*d*, $^3J(6,5) = 9.9$, H–C(5)); 3.96, 3.95/3.74, 3.73 (2*s*, 2 MeOOC); 3.71–3.63/3.40–3.30 (*m*, 2 H); 3.01/2.75 (*dd*, $J_{gem} = 16.3/15.1$, $^3J(4,3) = 2.3$, H–C(3)); 1.52/0.94 (*d*, ^3J(4,Me–C(4)) = 7.3/7.2, Me–C(4)). CI-MS: 285 (100, $[M + 1]^+$), 253 (7, $[(M + 1) - MeOH]^+$).

*Data of Dimethyl (*E*)-(3-Methylazulen-1-yl)ethene-1,2-dicarboxylate* ((*E*)-**7a**): UV (HPLC, MeCN): λ_{max} 341, 281, 236; λ_{min} 255, 223.

2.1.2. *Thermolysis of [8-^{2}H]-***2a**. The tricyclic compound (0.040 g, 0.14 mmol) was dissolved in MeCN (10 ml) and heated for 1 h at 100°. CC yielded traces of [3-^{2}H]-**1a**, **16a** (0.010 g, 25%), and (*E*)-**7a** (0.025 g, 63%). ^{1}H-NMR ($CDCl_3$) of **16a** showed that no ^{2}H was present at C(3) and/or C(4) or at any other position in amounts of > 0.03 H.

2.1.3. *Thermolysis of* **2b**. Compound **16b** was isolated and spectroscopically characterized.

Data of Dimethyl 3,4-Dihydro-4,7-dimethylcyclopent[cd]azulene-1,2-dicarboxylate (**16b**): blue oil. R_f(hexane/Et_2O 2:3): 0.26. UV (HPLC, MeCN): λ_{max} 301. ^{1}H-NMR (C_6D_6): 0.14 (br. *s*, H–C(8)); 6.99 (*d*, $^3J(5,6) = 10.35$, H–C(6)); 6.49 (*d*, $^3J(6,5) = 10.35$, H–C(5)); 3.76, 3.75 (2*s*, 2 MeOOC); 3.4–3.3 (*m*, 2 H); 2.77 (*d*, $J_{gem} = 15.1$, H–C(3)); 2.13 (*s*, Me–C(7)); 0.99 (*d*, $^3J(4,Me–C(4)) = 7.1$, Me–C(4)).

*Data of Dimethyl (*E*)-1-(3,6-Dimethylazulen-1-yl)ethene-1,2-dicarboxylate* ((*E*)-**7b**): UV (HPLC, MeCN): λ_{max} 348 (sh), 287, 236; λ_{min} 258, 223.

2.1.4. *Thermoylsis of* **2c**. *Dimethyl 5,8,10-trimethylheptalene-1,2-dicarboxylate* (**6c**) was identified by comparison with an authentic probe [20].

2.1.5. *Thermolysis of* **2d**. *Dimethyl 5,7,9-trimethylheptalene-1,2-dicarboxylate* (**6d**) was formed and identified by its UV (HPLC, MeCN): λ_{max} 352 (sh), 284, 250, 211; λ_{min} 263, 230, in comparison with that of dimethyl 7,9-dimethyl-heptalene-1,2-dicarboxylate. UV (hexane): λ_{max} 343 (3.70), 276 (4.31), 206 (4.47); λ_{min} 317 (3.59), 237 (4.20) [20].

2.1.6. *Thermoylsis of* **2f**. *Dimethyl 4,5,6,8,10-pentamethylheptalene-1,2-dicarboxylate* (**6f**) was identified by comparison with an authentic probe [5].

2.1.7. *Thermolysis of* **2h**. *Dimethyl 8-(*tert*-Butyl)-4,5,6,10-tetramethylheptalene-1,2-dicarboxylate* (**2h**) was formed and identified by its UV (HPLC, MeCN): λ_{max} 292, 233, 211; λ_{min} 264, 230, in comparison with that of **2f** [5].

2.1.8. *Thermolysis of* **2g** *in the Presence of 1,8-Bis(dimethylamino)naphthalene (DMN).* The tricyclic compound (0.12 g, 0.35 mmol) and DMN (0.085 g, 0.35 mmol) were dissolved in MeCN (3.0 ml) and heated in a sealed flask for 30 min at 100°. The yellow color of the mixture had turned to green. The formed *guaiazulene* (**1g**) was removed with a first CC on silica gel (hexane/Et_2O 1:1). The orange colored second fraction was subjected to a second CC on silica gel (hexane/Et_2O 3:1), which delivered a red fraction containing **30g** (0.034 g, 28%), followed by a yellow fraction that consisted of **6g**. Compound **30g** was further purified by rapid distillation in high vacuum (100°).

*Data of Dimethyl (1*RS,2SR*)-9-Isopropyl-1,6-dimethyltricyclo[5.4.1.0^{4,12}]dodeca-3,5,7(12),8,10-pentaene-2,3-dicarboxylate* (**30g**): red oil. R_f(hexane/Et_2O 3:1): 0.35. UV (hexane): λ_{max} 311 (4.19), 280 (4.24), 236 (4.28), 202 (4.50); λ_{min} 300 (4.17), 261 (4.18), 233 (4.28). ^{1}H-NMR (300 MHz, $CDCl_3$): 6.39 (br. *s*, H–C(8)); 6.08 (*q*-like, ^4J(Me–C(6),5) = 1.6, H–C(5)); 6.00 (*d*, $^3J(10,11) = 10.8$, H–C(11)); 5.91 (*d*, $^3J(11,10) = 10.8$, H–C(10)); 4.27 (*s*, H–C(2)); 3.81, 3.76 (2*s*, 2 MeOOC); 2.56 (*sept.*, $J = 6.9$, Me_2CH); 2.15 (*t*-like, $^4J(5,Me–C(6)) = 1.3$, Me–C(6)); 1.14, 1.13 (2*d*, $J = 6.9$, 6.8, Me_2CH); 0.84 (*s*, Me–C(1)). EI-MS: 340 (31, $M^{+\cdot}$), 325 (46, $[M - Me]^+$), 293 (39, $[M - Me - MeOH]^+$), 281 (100, $[M - MeOOC]^+$), 266 (38, $[M - Me - MeOOC]^+$), 249 (47, $[M - MeOOC - MeOH]^+$), 239 (24), 221 (22), 207 (60, $[M - 2\,MeOOC - Me]^+$), 195 (14), 192 (18), 191 (27), 189 (17), 180 (14), 179 (33), 178 (19), 165 (29).

When the red soln. of **30g** in $CDCl_3$ was stored for 1 week at −20°, it had turned green and **31g** had quantitatively been formed.

*Data of Dimethyl (1*RS,2SR*)-9-Isopropyl-1-methyl-6-methylidenetricyclo[5.4.1.0^{4,12}]dodeca-3,7(12),8,10-tetraene-2,3-dicarboxylate* (**31g**): ^{1}H-NMR (300 MHz, $CDCl_3$): 6.48 (*s*, H–C(8)); 6.00 (*AB*, $^3J_{AB} \approx 12$, H–C(10,11)); 5.16 (*t*-like, $^4J(5,H_Z–CH=C(6)) \approx {}^2J(H_E,H_Z) \approx 2$, H_Z–CH=C(6)); 5.00 (*t*-like, $^4J(5,H_E–CH=C(6)) < {}^2J(H_Z,H_E) \approx 2$, H_E–CH=C(6)); 4.19 (*t*, $^5J(H_A–C(5),2) \approx {}^5J(H_B–C(5),2) = 2.1$, H–C(2)); 3.76, 3.75 (2*s*, 2 MeOOC); 3.51 (*dq*-like, $^2J(H_B,H_A) = 21.0$, $^4J(H_Z–CH=C(6),H_A–C(5)) \approx {}^4J(H_E–CH=C(6),H_A–C(5)) \approx {}^5J(2,H_A–C(5)) \approx 1.8$, H_A–C(5)); 3.44 (*dq*-like, $^2J(H_A,H_B) = 21.0$, $^4J(H_Z–CH=C(6),H_B–C(5)) \approx {}^4J(H_E–CH=C(6),H_B–C(5)) \approx {}^5J(2,H_B–C(5)) \approx 1.9$, H_B–C(5)); 2.56 (*sept.*, $J = 6.9$, Me_2CH); 1.15, 1.14 (2*d*, $J = 6.9$, 6.8, Me_2CH); 0.87 (*s*, Me–C(1)). ^{1}H-NOE (400 MHz, $CDCl_3$): 6.48 (H–C(8))→5.16 (*m*, H_Z–CH=C(6)); 2.56 (*m*, Me_2CH); 1.15, 1.14 (*w*, Me_2CH); 4.19 (H–C(2))→6.00 (*m*, H–C(11)); 0.87 (Me–C(1))→6.00 (*m*, H–C(11)).

2.2. *Comparative Thermolyses in BuOH.* Since all products represented azulene derivatives with comparable extinction coefficients at 290 nm, no calibration curves were established. The thermolysis data are collected in *Table 9*.

2.2.1. *Thermolysis of* **2a**. (*E*)-**7a**: See *2.1.1.* (*Z*)-**7a**: Identified by its UV (HPLC, MeCN): λ_{max} 400, 318, 285, 231; λ_{min} 359, 298, 263, 211.

2.2.2. *Thermolysis of* **2b**. (*E*)-**7b**: See *2.1.2.* (*Z*)-**7b**: Identified by its UV (HPLC, MeCN): λ_{max} 400, 328, 290, 235; λ_{min} 365, 305, 264, 211.

2.2.3. *Thermolysis of* **2c**. (*E*)- and (*Z*)-**7c** were isolated.

*Data of Dimethyl (*E*)-1-(3,6,8-Trimethylazulen-1-yl)ethene-1,2-dicarboxylate* ((*E*)-**7c**): green oil. R_f(hexane/Et_2O 1:1): 0.35. UV (HPLC, MeCN): λ_{max} 350, 293, 236; λ_{min} 260, 223. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.05 (*d*,

$^3J(5,4) = 10.3$, H–C(4)); 7.30 (*s*, H–C(2)); 7.08 (*s*, C*H*COOMe); 6.95 (*d*, $^3J(4,5) = 10.3$, H–C(5)); 6.93 (br. *s*, H–C(7)); 3.90, 3.53 (2*s*, 2 MeOCO); 2.87 (*s*, Me–C(3)); 2.58 (*s*, Me–C(8)); 2.56 (*s*, Me–C(6)).

*Data of (Z)-***7c**: brown-greenish oil. R_f(hexane/Et_2O 1:1): 0.34. UV (HPLC, MeCN): λ_{max} 400, 336, 293, 236; λ_{min} 360, 264, 212. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.00 (*d*, $^3J(5,4) = 9.9$, H–C(4)); 7.49 (*s*, H–C(2)); 6.97 (br. *s*, H–C(7)); 6.95 (*d*, $^3J(4,5) = 10.3$, H–C(5)); 5.61 (*s*, C*H*COOMe); 3.80, 3.64 (2*s*, 2 MeOCO); 2.76 (*s*, Me–C(3)); 2.52 (*s*, Me–C(6)); 2.46 (*s*, Me–C(8)).

2.2.4. *Thermolysis of* **2d**. (*E*)- and (*Z*)-**7d** were identified by their UV. (*E*)-**7d**: UV (HPLC, MeCN): λ_{max} 345 (sh), 287, 241; λ_{min} 261, 231. (*Z*)-**7d**: UV (HPLC, MeCN): λ_{max} 400, 327, 305, 293, 237, 211; λ_{min} 366, 318, 300, 277, 216.

2.2.5. *Thermolysis of* **2e**. Authentic probes of (*E*)- and (*Z*)-**7e** were available. See [1] and *1.6*.

2.2.6. *Thermolysis of* **2f**. Authentic probes of (*E*)- and (*Z*)-**7f** were synthesized (see below).

2.2.6.1. *Dimethyl (*E*)- and (Z)-1-(2,3,4,6,8-Pentamethylazulen-1-yl)ethene-1,2-dicarboxylate* ((*E*)- and (*Z*)-**7f**). *1,2,4,6,8-Pentamethylazulene* (**1f**; 0.147 g, 0.742 mmol) [50] and ADM (0.160 g, 1.11 mmol) were dissolved in Et_2O (30 ml) and stirred at r.t. in the presence of $ZnBr_2$ (0.168 g, 0.742 mmol) for 15 min and then for 2 h at reflux temp. CC on silica gel (hexane/Et_2O 1:1) gave in a first fraction unreacted **1f** (0.045 g, 31%) and, in a second fraction, the mixture of (*E*)/(*Z*)-**7f**. The latter two compounds were separated in a second CC (silica gel; hexane/Et_2O 7:3), yielding crystalline (*E*)-**7f** (0.061 g, 42%) and (*Z*)-**7f** (0.041 g, 28%).

*Data of (*E*)-***7f**: black-shining crystals, which dissolved in $CDCl_3$ with dark-red color. M.p. 105–106° (hexane). R_f(hexane/Et_2O 7:3): 0.27. UV (hexane): λ_{max} 444 (2.75), 361 (3.62), 346 (3.57), 301 (4.69), 297 (sh, 4.67), 249 (4.38), 218 (4.17); λ_{min} 390 (2.59), 353 (3.54), 333 (3.51), 266 (3.78), 225 (4.18). IR (KBr): 2958*m*, 2923*m*, 2852*m*, 1734/1717*s* (COOR), 1627*m*, 1578*m*, 1556*m*, 1511*m*, 1454*m*, 1436*s*, 1378*m*, 1313*s*, 1260*s*, 1198*m*, 1105*m*, 1023*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.20 (*s*, C*H*COOMe); 6.81 (*s*, H–C(5)); 6.76 (*s*, H–C(7)); 3.75, 3.51 (2*s*, 2 MeOOC); 2.99 (*s*, Me–C(4)); 2.72 (*s*, Me–C(3)); 2.66 (*s*, Me–C(8)); 2.47 (Me–C(6)); 2.20 (*s*, Me–C(2)). ^{1}H-NOE (400 MHz, $CDCl_3$): 2.20 (Me–C(2))→2.72 (*s*, Me–C(3)); 2.47 (Me–C(6))→6.81, 6.76 (*s*, H–C(5), H–C(7)); 2.66 (Me–C(8))→6.76 (*s*, H–C(7)); 2.72 (Me–C(3))→2.99 (*s*, Me–C(4)), 2.20 (*s*, Me–C(2)); 2.99 (Me–C(4))→6.81 (*s*, H–C(5)), 2.72 (*s*, Me–C(3)). CI-MS: 341 (100, $[M + 1]^+$), 327 (1), 311 (1), 293 (1), 281 (3), 267 (1), 250 (1). Anal. calc. for $C_{21}H_{24}O_4$ (340.42): C 74.09, H 7.11; found: C 74.05, H 7.21.

*Data of (Z)-***7f**: black-shining crystals, which dissolved in $CDCl_3$ with a pale-brown color. M.p. 138–139° (hexane). R_f(hexane/Et_2O 7:3): 0.22. UV (hexane); λ_{max} 397 (3.17), 362 (3.81), 346 (3.86), 301 (4.86), 293 (sh, 4.80), 250 (4.55), 217 (4.30); λ_{min} 383 (3.12), 337 (3.86), 266 (3.85), 225 (4.27), 208 (4.28). IR (KBr): 2952*w*, 2922*w*, 1732/1720*s* (COOR)[32]), 1633*m*, 1580*m*, 1509*m*, 1437*m*, 1405*m*, 1334*s*, 1264*m*, 1243*s*, 1196*m*, 1165*s*, 1093*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.87 (*s*, H–C(5,7)); 5.99 (*s*, C*H*COOMe); 3.82, 3.77 (2*s*, 2 MeOOC); 3.00 (*s*, Me–C(4)); 2.92 (*s*, Me–C(3)); 2.70 (*s*, Me–C(8)); 2.50 (*s*, Me–C(6)); 2.40 (*s*, Me–C(2)). CI-MS: Identical with those of (*E*)-**7f**.

Heating (*E*)-**7f** (0.002 g) in toluene (0.7 ml) in the presence of traces of I_2 at 100° gave slowly within 63 to 88 h an equilibrium mixture of 14.7% of (*E*)-**7f** and 85.3% of (*Z*)-**7f**.

2.2.7. *Thermolysis of* **7g**. Authentic probes of (*E*)- and (*Z*)-**7g** were available. See [1] and *1.8*.

2.2.8. *Thermolysis of* **7h**. (*E*)- and (*Z*)-**7h** were identified by their UV and HPLC retention times, which are close to those of (*E*)- and (*Z*)-**7f**. (*E*)-**7h**: UV (HPLC, MeCN): λ_{max} 345 (sh), 300, 249; λ_{min} 325, 265, 230. (*Z*)-**7h**: UV (HPLC, MeCN): λ_{max} 350, 300, 249; λ_{min} 325, 265, 230.

2.3. *Thermolysis of* **2g** *in Different Protic and Aprotic Solvents*. The thermolyses were performed at 110 ± 1° as described for BuOH and MeCN and analyzed by HPLC by use of the established calibration curves. The data are collected in *Tables 10* and *11*.

2.3.1. *Kinetics of the Thermolysis of* **2** *in MeCN at 74.8°*. The dara are collected in *Table 12*.

2.3.2. *Kinetics of the Thermolysis of* **2g** *in Different Solvents at 74.8°*. The data are collected in *Table 13*.

2.3.3. *Kinetics of the Thermolysis of* **2g** *in Decane in the Range of 60–80°*. The measured k values, obtained from the decrease of **2g** (k_T) and increase of **1g** (k_A) are collected in *Table 18*; for the calculated activation parameters, see *Table 14*.

2.3.4. *Kinetics of the Thermolysis of* **2g** *in MeCN in the Range of 60–80°*. See Table 3 in [1]. Further details can be found in [64].

2.4. *Kinetic Measurements*. 1.5 ml of *ca.* $3 \cdot 10^{-3}$ M solns. were distributed (0.1 ml each) over 12 ampoules (total volume 0.5 ml) and heated in a water thermostat (temp. constancy ±0.1°). At given time intervals, two ampoules were crosswise removed and chilled with chopped ice and immediately analyzed by HPLC using the established

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[32]) The band intensities at 1732/1720 are just opposite to those at 1734/1717 of (*E*)-**7f**. In the latter isomer, the second band is more intense than the first one.

Table 18. *Rate Constants of the Thermolysis of* **2g** *in Decane at 60–80°* [a])

Temperature [°]	$k_T \cdot 10^5$ [s^{-1}]	$k_A \cdot 10^5$ [s^{-1}]	
59.4	1.43	1.35	
64.5	2.51	2.30	
69.4	4.63	3.89	
74.8	8.91	7.84	[a]) Margins of error
79.9	15.2	12.7	$< \pm 3\%$.

calibrating curves for **2e** and **2g**[33]). The decrease of the tricyclic compounds **2** were followed at 230 nm. Therefore, only solvents could be used in UV quality (*Fluka AG*), showing no own absorption at 230 nm.

3. X-Ray Crystal-Structure Determinations. Atomic coordinates, and bond lengths and angles for **2f** and **2g** have been deposited with the *Cambridge Crystallographic Data Center*, 12 Union Road, Cambridge CB2 1EZ, England. For crystallographic data of **2f** and **2g** see *Table 19*.

Table 19. *Crystallographic Data for the Tricyclic Compounds* **2f** *and* **2g**

Parameter	**2f**	**2g**
Crystallized from	hexane	hexane
Empirical formula	$C_{21}H_{24}O_4$	$C_{21}H_{24}O_4$
Formula weight	340.42	340.42
Crystal color, habit	pale, yellow, prisms	colorless, prisms
Crystal temp. [K]	173 (1)	213 (1)
Crystal dimensions [mm]	0.15 × 0.20 × 0.42	0.36 × 0.38 × 0.46
Crystal systems	monoclinic	triclinic
Lattice parameters		
Reflections for cell determination	22	25
2θ range [°]	$24 < 2\theta < 37$	
a [Å]	14.6538 (8)	8.139 (2)
b [Å]	7.253 (1)	8.805 (2)
c [Å]	17.321 (1)	13.907 (3)
α [°]	90	108.87 (2)
β [°]	100.465 (5)	91.21 (2)
γ [°]	90	98.67 (2)
V [Å^3]	1810.2 (4)	92.97 (4)
Space group	$P2_1/c$	$P\bar{1}$
Z	4	2
D_x [g·cm^{-3}]	1.249	1.216
Absorption coefficient μ (MoK_α) [cm^{-1}]	0.800	0.776
Absorption correction min, max	–	–
2θ (max) [°]	60	55
Total reflections measured	5859	4571
Symmetry independent reflections	5663	4270
Reflections observed ($I > 3\sigma(I)$)	3426	3192
Variables	323	322
Final R	0.0449	0.0432
R_w [a])	0.0414	0.0561
Goodness fit s	1.833	2.357
Final Δ_{max}/σ	0.003	0.0001
$\Delta\rho$ (max, min) [eÅ^{-3}]	0.28, –0.23	0.29, –0.22

[a]) Function minimized $\Sigma w(|F_o| - |F_c|)^2$; $1/w = \sigma^2(F_o) + (0.005\,F_c)^2$.

[33]) Since single and double analyses showed no significant variations, we performed in later phases of the work only single analyses, allowing to increase the number of time intervals.

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