110. Synthesis of an Isotopically Isomeric Mixture of 1,4,6,8-Tetramethyl[$^{13}C_2$]azulene and Its Thermal Reaction with Dimethyl Acetylenedicarboxylate

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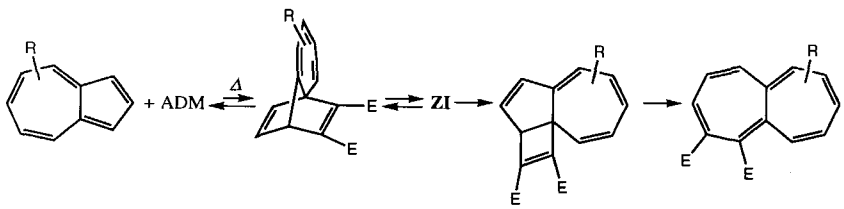
Sodium [1,3-$^{13}C_2$]cyclopentadienide in tetrahydrofuran (THF) has been prepared from the corresponding labelled [$^{13}C_2$]cyclopentadiene which was synthesized from $^{13}CO_2$ and (chloromethyl)trimethylsilane (*cf. Scheme 10*) according to an established procedure. It could be shown that the acetate pyrolysis of *cis*-cyclopentane-1,2-diyl diacetate (*cis*-**22**) at 550 ± 5° under reduced pressure (60 Torr) gives five times as much cyclopentadiene as *trans*-**22**. The reaction of sodium [1,3-$^{13}C_2$]cyclopentadienide with 2,4,6-trimethylpyrylium tetrafluoroborate in THF leads to the formation of the statistically expected 2:2:1 mixture of 4,6,8-trimethyl[1,3a-$^{13}C_2$]-, -[2,3a-$^{13}C_2$]-, and -[1,3-$^{13}C_2$]azulene (**20**; *cf. Scheme 7* and *Fig. 1*). Formylation and reduction of the 2:2:1 mixture [$^{13}C_2$]-**20** results in the formation of a 1:1:1:1:1 mixture of 1,4,6,8-tetramethyl[1,3-$^{13}C_2$]-, -[1,3a-$^{13}C_2$]-, -[2,3a-$^{13}C_2$]-, -[2,8a-$^{13}C_2$]-, and -[3,8a-$^{13}C_2$]azulene (**5**; *cf. Scheme 8* and *Fig. 2*). The measured $^2J(^{13}C,^{13}C)$ values of [$^{13}C_2$]-**20** and [$^{13}C_2$]-**5** are listed in *Tables 1* and *2*. Thermal reaction of the 1:1:1:1:1 mixture [$^{13}C_2$]-**5** with the four-fold amount of dimethyl acetylenedicarboxylate (ADM) at 200° in tetralin (*cf. Scheme 2*) gave 5,6,8,10-tetramethyl-[$^{13}C_2$]heptalene-1,2-dicarboxylate ([$^{13}C_2$]-**6a**; 22%), its double-bond-shifted (DBS) isomer [$^{13}C_2$]-**6b** (19%), and the corresponding azulene-1,2-dicarboxylate **7** (18%). The isotopically isomeric mixture of [$^{13}C_2$]-**6a** showed no $^1J(^{13}C,^{13}C)$ at C(5) (*cf. Fig. 3*). This finding is in agreement with the fact that the expected primary tricyclic intermediate [7,11-$^{13}C_2$]-**8** exhibits at 200° in tetralin only cleavage of the C(1)–C(10) bond and formation of a C(7)–C(10) bond (*cf. Schemes 6* and *9*), but no cleavage of the C(1)–C(11) bond and formation of a C(7)–C(11) bond. The limits of detection of the applied method is ≥ 96% for the observed process, *i.e.*, [1,3a-$^{13}C_2$]-**5** + ADM → [7,11-$^{13}C_2$]-**8** → [1,6-$^{13}C_2$]-**9** → [5,10a-$^{13}C_2$]-**6a** (*cf. Scheme 6*).

Introduction. – We have shown that the tricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-9,10-dicarboxylates **2**, which are the primary intermediates in the purely thermal [1] as well as in the Ru^{II}- [2] or Rh^{I}-catalyzed [3] reaction of azulenes **1** with dimethyl

Scheme 1[a])



1 **2** **3** **4**

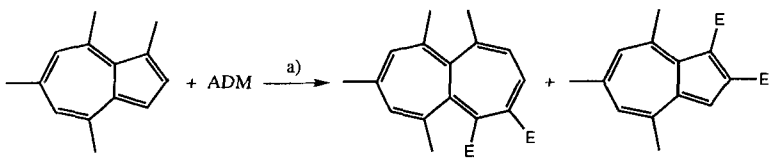
[a]) E = COOMe in this and the following schemes.

[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.

acetylenedicarboxylate (ADM), rearrange thermally, in polar aprotic media such as MeCN, DMF, or DMSO, *via* zwitterionic intermediates finally to heptalene-1,2-dicarboxylates **4a** [4] (see especially [5], *Scheme 1*)[2]).

In apolar media such as decane, the tricyclic compounds **2** undergo exclusively a *retro-Diels-Alder* reaction, yielding **1** and ADM [4] [5]. On the other hand, heating of **1** in the presence of an excess of ADM at 180–200° in hydrocarbons leads to the formation of heptalene-1,2-dicarboxylates **4a** and their DBS isomers **4b** as well as to the corresponding azulene-1,2-dicarboxylates (*cf.* **7** in *Scheme 2*; *cf.* [1] and lit. cit. there; see also [8]).

Scheme 2



5 **6a**[a]) **7**

a) The reaction, at 180–200° in tetralin [8] [9] or decalin [1], leads to the formation of up to 40% of a mixture **6a**/**6b** and a comparable percentage of **7**.

[a]) The equilibrium mixture **6a**/**6b** in tetralin amounts at 100° to 88.7% of **6a** and 11.3% of **6b** [10] (*cf.* also [11]).

An example is given in *Scheme 2*. It is specific in a way that the seven-membered ring of azulene **5** is symmetrically substituted. In such cases, the reactant-product correlation does not allow to distinguish between the reaction paths, leading to the heptalenes **6a**/**6b**, *via* cleavage of the C(1)–C(10) bond (**8** → **9**), *i.e.*, migration of the MeOCO-substituted C-atom, or *via* cleavage of the C(1)–C(11) bond (**8** → **10**), *i.e.*, migration of the Me-substituted C-atom (*cf. Scheme 3*).

The same is true for azulenes which are unsymmetrically substituted in the seven-membered ring, however, symmetrically in the five-membered ring. In such cases, a mixture of positionally isomeric heptalene-1,2-dicarboxylates and their DBS isomers are obtained. This can be interpreted as the result of the occurrence of positionally isomeric primary tricyclic intermediates or, alternatively, as the result of competing C–C cleavage reactions in these primary intermediates. Two examples are shown in *Scheme 4* [12] [13] (*cf.* also [8]). The appearance of two positionally isomeric azulene-1,2-dicarboxylates, **16** and **17**, in the reaction mixture at least indicates that the two isomeric tricyclic intermediates **12** and **13** must be formed in the primary addition step of ADM to **11** at 200°[3]). Since

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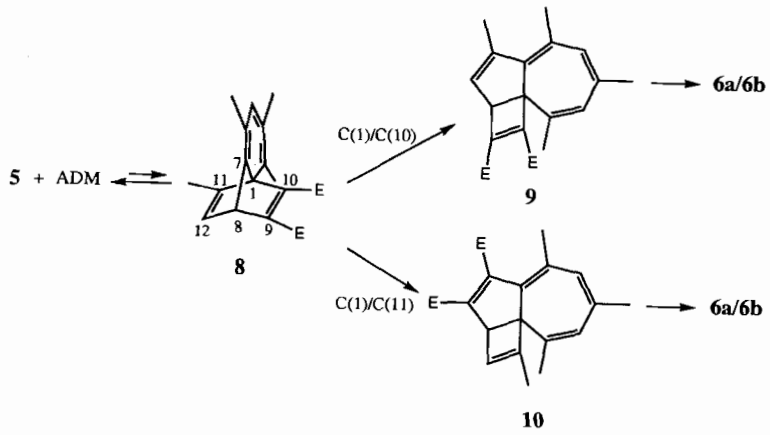
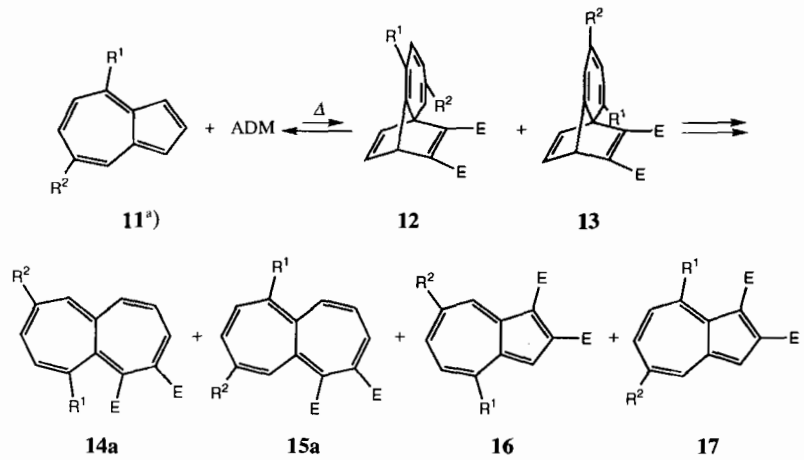
[2]) Indeed, the corresponding heptalene-4,5-dicarboxylates **4b**, the double-bond-shifted (DBS) isomers of **4a**, are also formed in the ring opening of the postulated tricyclic intermediates **3**. We will report on this observations in a later communication [6]. (For the nomenclature of the heptalenedicarboxylates used here, see Footnote 2 in [5].) Recently, we succeeded in the isolation of an intermediate of type **3** from the reaction mixture of 5,9-diphenylbenz[*a*]azulene and ADM [7].

[3]) The reaction of **11** ($R^1 = R^2 = Me$ or $R^1 = Me$, $R^2 = i\text{-Pr}$) with ADM, in MeCN and in the presence of $[RuH_2(PPh_3)_4]$ at 100°, leads to a 94:6 mixture **14a**/**15a**. The corresponding azulene-1,2-dicarboxylates **16** and **17** are not observed in this case [13].

Scheme 3



Scheme 4



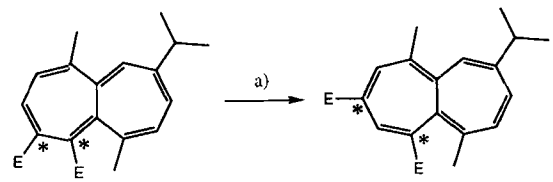
[a]) With $R^1 = R^2 = Me$, a 2:1 mixture **14a**/**15a** and a 1:1 mixture **16**/**17** are obtained at 200° in decalin [12]. Similar results are obtained for $R^1 = Me$ and $R^2 = i\text{-}Pr$ [12] (for $R^1 = Me$, $R^2 = H$, see [8]). Heptalenes **14a** and **15a** are accompanied by their DBS isomers **14b** and **15b**, respectively.

the C,C connectivity pattern will be changed by the two possible reaction paths of primary intermediates of type **8**, **12**, or **13** in apolar media at 200°, we investigated the thermal reaction of [$^{13}C_2$]-labelled **5** with ADM to give the labelled heptalene-1,2-dicarboxylate **6a**. We report here on the results of our experiments.

2. Results and Discussions. – Earlier outcomes of the synthesis and thermal rearrangement of the [1,2-$^{13}C_2$]heptalene-1,2-dicarboxylate **18** into the corresponding [3,5-$^{13}C_2$]-heptalene-3,5-dicarboxylate **19** [14] as well as of the photochemically induced DBS isomerization of [1,2-$^{13}C_2$]-**6a** into [4,5-$^{13}C_2$]-**6b** [10] had shown that $^1J(^{13}C,^{13}C)$ value, within the heptalene skeleton, amounts to 61 to 74 Hz, depending on the fact whether the

coupling occurs across a C–C ([1,2-$^{13}C_2$]-**6a**) or a C=C bond ([4,5-$^{13}C_2$]-**6b**). On the other hand, $^2J(^{13}C,^{13}C)$ value is too small to be measurable under normal conditions (*cf. Scheme 5*). Therefore, we decided to synthesize an azulene **5** with a 1,3-positional relation of two ^{13}C-atoms, *e.g.* [1,3a-$^{13}C_2$]-**5**, which would allow to follow the rearrangement into **6a** by a change in the $^{13}C,^{13}C$-coupling pattern (see *Scheme 6*). The expected reaction path, *via*

Scheme 5

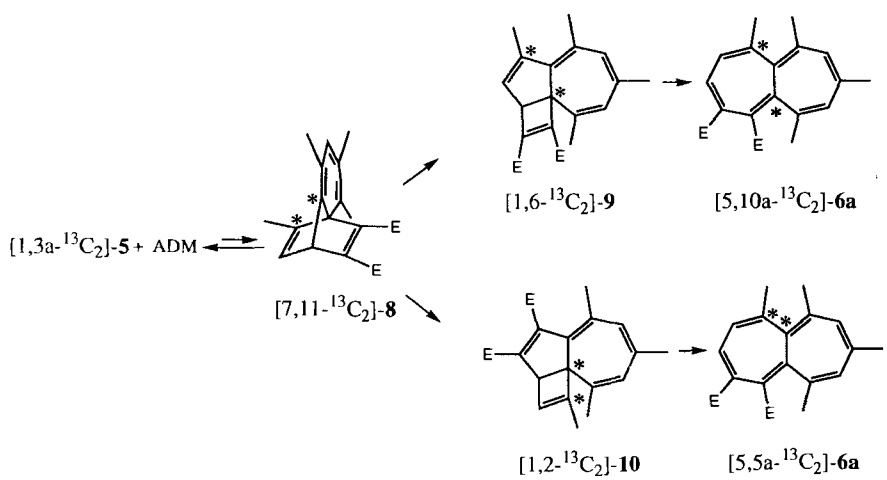


18[a]) **19**[b])

a) Tetralin, 210° [14]; * = ^{13}C label.

[a]) $^1J(^{13}C,^{13}C) = 61.4$ Hz.
[b]) $^2J(^{13}C,^{13}C) < 1$ Hz.

Scheme 6

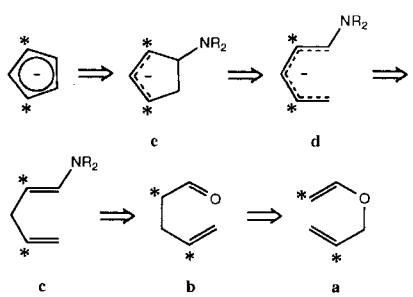


migration of C(10) of [7,11-$^{13}C_2$]-**8**, would lead to the formation of [5,10a-$^{13}C_2$]-**6a** with an unchanged 1,3-positional relation of the ^{13}C labels, whereas the second reaction path, *via* migration of C(11) of [7,11-$^{13}C_2$]-**8**, would yield [5,5a-$^{13}C_2$]-**6a** with a 1,2-positional relation of the ^{13}C labels. The second migration mode should be indicated by a $^{13}C,^{13}C$ coupling in the order of 61 Hz, *i.e.*, clearly distinguishable from the first one which should give rise to no observable $^{13}C,^{13}C$ coupling.

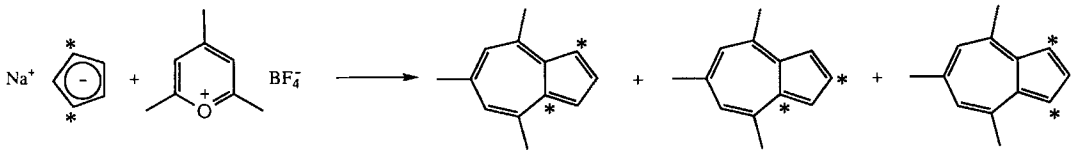
Synthesis of an Isotopically Isomeric Mixture of 1,4,6,8-Tetramethyl[$^{13}C_2$]azulene. In recent years, several azulenes, specifically labelled with ^{13}C-atoms, have been synthesized, mainly to study the mechanism of the azulene-naphthalene and azulene-azulene rearrangements (*cf.* [15] [16] and lit. cit. there). However, to our knowledge, no syntheses of azulenes, doubly labelled with ^{13}C-atoms, have so far been published. Most of the known azulene syntheses (*cf.* [15]) would be suitable for the specific introduction of two ^{13}C-atoms in position 1 and 3a of the azulene skeleton (*cf. Scheme 6*). However, the synthesis of the desired ^{13}C-labelled precursors would be lengthy and not unequivocal with respect to the ^{13}C label in all cases. Therefore, we decided to synthesize 4,6,8-trimethyl-[$^{13}C_2$]azulene ([$^{13}C_2$]-**20**) according to the established procedure of *Hafner* and *Kaiser* [17]; however, starting with 2,4,6-trimethylpyrylium tetrafluoroborate and sodium [1,3-$^{13}C_2$]-cyclopentadienide in THF. This should result in the formation of a 2:2:1 mixture [1,3a-$^{13}C_2$]-**20**/[2,3a-$^{13}C_2$]-**20**/[1,3-$^{13}C_2$]-**20** (*Scheme 7*), *i.e.*, the statistical yield of the suitable isotopomer [1,3a-$^{13}C_2$]-**20** would be 40%. The established formylation/reduction procedure (*cf.* [18]) for the introduction of a Me group at C(1) of the azulene skeleton will further reduce the statistical amount of the desired compound [1,3a-$^{13}C_2$]-**5** by a factor of two (*Scheme 8*). The synthesis of [1,3a-$^{13}C_2$]-**5**, starting with 2,4,6-trimethylpyrylium tetrafluoroborate and sodium [1,3-$^{13}C_2$]cyclopentadienide, therefore, will lead to a statistical distribution of 1:1:1:1:1 for the isotopomers of [$^{13}C_2$]-**5** shown in *Scheme 8*. However, it is only [1,3a-$^{13}C_2$]-**5** in this mixture of isotopomers that will yield, on thermal reaction with ADM, tricycle [7,11-$^{13}C_2$]-**8**, which, on migration of C(11), leads to the formation of a heptalene, namely [5,5a-$^{13}C_2$]-**6a**, that carries the two ^{13}C-atoms attached to each other (*cf. Scheme 6*). All other heptalenes that will be formed from the other isotopomers, by migration of C(10) or C(11), carry the two ^{13}C labels in a 1,3- or a 1,4-positional relation, *i.e.*, these heptalenes will show no ^{13}C,^{13}C coupling (> 1 Hz; *cf. Scheme 9*).

The 2:2:1 mixture of [$^{13}C_2$]cyclopentadienes, labelled in 1,3-positions, had been synthesized as depicted in *Scheme 10* by *Schwarz* and coworkers [19] in small amounts for mass-spectrometric investigations. Despite the fact that the pyrolysis of the diacetates **22** affords, according to *Schwarz* and coworkers, the 2:2:1 mixture of [$^{13}C_2$]cyclopentadienes only in a yield of *ca.* 5%, we also chose this synthesis[4]). It could be improved at several steps, because we had to work with larger amounts of materials (cf. *Exper. Part*). We

[4]) Originally, we developed an – as we felt – attractive retrosynthetic scheme for the formation of [1,3-$^{13}C_2$]cyclopentadienide which resulted in a *Claisen* rearrangement of an appropriately ^{13}C-labelled allyl vinyl ether or allyl acetate. Electrocyclization reactions of the type **d** → **e** have been realized, at least with 2,4-diazapentadienides [20]. However, we did not succeed in the electrocyclization of deprotonated enamines **d**, neither thermally nor photochemically (for details, see *Footnote 1*).



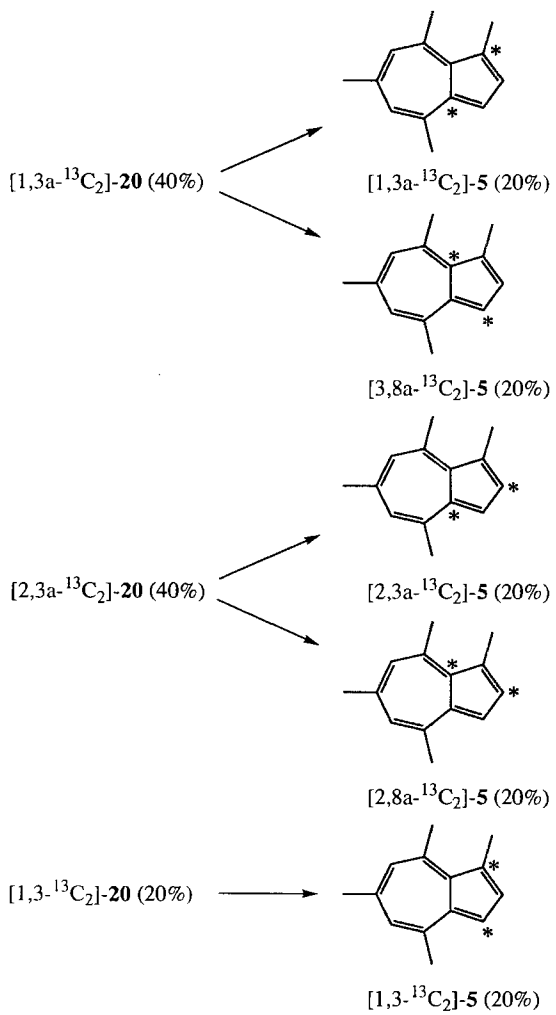
Scheme 7



[1,3a-$^{13}C_2$]-**20**[a]) [2,3a-$^{13}C_2$]-**20** [1,3-$^{13}C_2$]-**20**

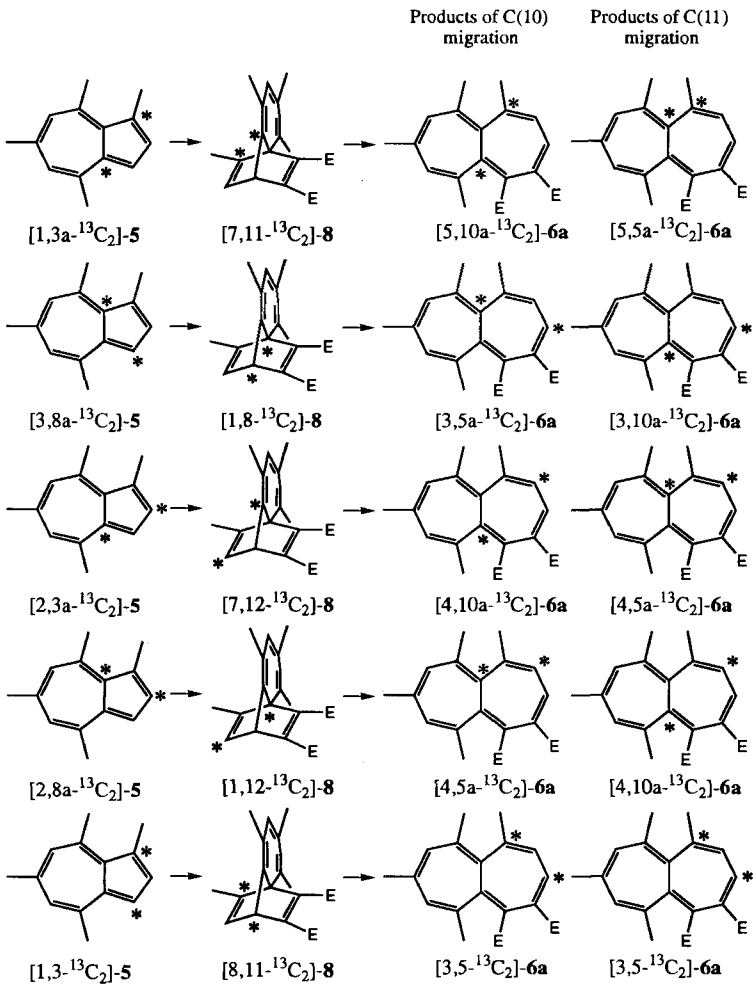
[a]) Neglecting kinetic isotope effects, the statistical ratio of the three [$^{13}C_2$]-isotopomers will be 2:2:1.

Scheme 8



[a]) Neglecting kinetic isotope effects in the envisaged formylation reaction, a statistical 1:1:1:1:1 ratio of the shown isotopomers of [$^{13}C_2$]-**5** is to be expected.

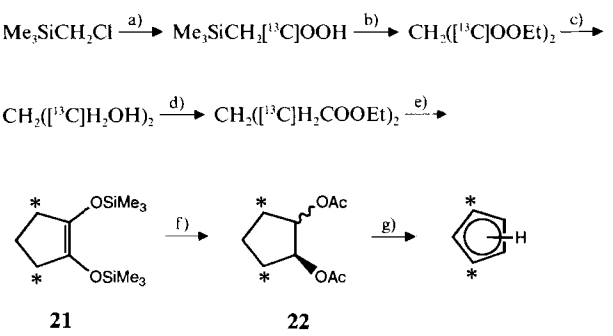
Scheme 9



[a]) Only the heptalene-1,2-dicarboxylates [$^{13}C_2$]-**6a** are shown which preponderate in the thermal equilibrium with their DBS isomers [$^{13}C_2$]-**6b**.

started with $Ba^{13}CO_3$ with a ^{13}C content of 98%. At the stage of 1,3-dibromo[1,3-$^{13}C_2$]propane, 75% of non-labelled material was added. 1,2-Bis(trimethylsilyloxy)cyclopent-1-ene (**21**) turned out to be not very stable. Therefore, it was just hydrogenated in the presence of Rh(5%)/Al_2O_3 and a small amount of PtO_2, followed by acetylation with AcCl. Under these conditions, cyclopentane-1,2-diyl diacetate (**22**) was obtained in yields of 93% and with a content of the *cis*-compound of up to 80%. A high content of this stereoisomer in the product was crucial. Preliminary pyrolysis experiments with pure *cis*- and *trans*-stereoisomers of **22** (synthesized according to [21] and [22], resp.) had shown that the yield of 4,6,8-trimethylazulene (**20**), obtained with the pyrolysate of *cis*-**22** (5%), was appre-

Scheme 10



[a]) 1. Mg/THF; 2. $^{13}CO_2$ liberated from $Ba^{13}CO_3$; content of ^{13}C: 98%.
[b]) 1. LDA/THF; 2. $^{13}CO_2$; 3. EtOH/$CHCl_3$, TsOH, reflux.
[c]) $LiAlH_4/Et_2O$.
[d]) 1. HBr/H_2SO_4, reflux; 2. KCN/MeCN, 18-crown-6; 3. NaOH/H_2O/EtOH, reflux; 4. EtOH/$CHCl_3$, TsOH, reflux.
[e]) Na/toluene, 110°; Me_3SiCl.
[f]) 1. H_2, Rh/Al_2O_3 (5%) + PtO_2/cyclohexane, 100° and 105 bar. 2. AcCl, 25°.
[g]) Continuous gas-phase pyrolysis at 550 ± 5° in a stream of N_2.

ciably higher than with the pyrolysate of *trans*-**22** (1%)[5]). We found no hydrogenation procedures of **21** that gave more than 80% of *cis*-**22** in the mixture with *trans*-**22**. Decreasing the reaction temperature or the H_2 pressure reduced the amount of *cis*-**22** in the mixture with *trans*-**22**.

The [$^{13}C_2$]-labelled cyclopentadiene (*cf.* [19]), obtained after pyrolysis in a N_2 stream under reduced pressure in a quartz tube (*cf.* [25] and *Exper. Part*), was not characterized. The pyrolysate was chromatographed over basic Al_2O_3 with THF to remove AcOH formed and then directly treated with dispersed Na in THF. The formed sodium [$^{13}C_2$]cyclopentadienide was reacted with 2,4,6-trimethylpyrylium tetrafluoroborate according to [17] (*cf. Scheme 7*). The yield of the 2:2:1 mixture [1,3a-$^{13}C_2$]-**20**/[2,3a-$^{13}C_2$]-**20**/[1,3-$^{13}C_2$]-**20** amounted to 4.7% in the 'hot' experiment. The ^{1}H- and ^{13}C-NMR data of **20** are shown in *Table 1* (*cf.* also [26] [27]). The ^{13}C-signals of C(1,3), C(2), and C(3a,8a) are clearly separated. *Fig. 1* shows the regions of the highly resolved signals of these C-atoms. The signal of C(1,3) in the symmetrically labelled [1,3-$^{13}C_2$]-**20** appears as the dominant *s* at 115.960 ppm. The slightly down-field shifted *s* at 115.963 ppm is due to C(1,3) of [1-^{13}C]-**20** of natural abundance. The remaining *d* at 115.963 ppm with J = 10.1 Hz must be caused by C(1,3) in [1,3a-$^{13}C_2$]-**20**. The intensities of 1:1 of the inner *s* and the outer *d*

[5]) Taking into account that the pyrolysis of cyclopentyl acetates give average yields of cyclopentenes of *ca.* 30% (*cf.* [23]), and that the yield of 4,6,8-trimethylazulene (**20**) also amounts to *ca.* 30%, the observed yield of 5% for **20** corresponds to about half of the expected yield. The definitely lower yield of 1% of **20**, starting from *trans*-**22**, shows that the yield of cyclopentadiene from the pyrolysis reaction must also be significantly lower as compared to the pyrolysis reaction of *cis*-**22**. We assume that, in the case of *trans*-**22**, the thermal *syn*-elimination of AcOH preferably occurs to the side of the other AcO group, thus leading mainly to the formation of cyclopent-1-en-1-yl acetate. On further pyrolysis, the latter compound may undergo a *retro*-ene reaction to give ketene and cyclopentanone (*cf.* [24]).

Table 1. *^1H- and ^{13}C-NMR Data* ($CDCl_3$) *of 4,6,8-Trimethylazulene* (**20**)[a]) *and Its Doubly ^{13}C-Labelled Isotopomers*[b])

Atom	δ [ppm][c])	Signal multiplicities and coupling constants [Hz]	
		A[d])	B[e])
C(1,3)	115.96[f])	*ddd*, $^1J(H) = 166.4$, $^2J(H-C(2)) = 4.7$, $^3J(H-C(3,1)) = 7.9$	*d*, $^2J(C(3a)) = 10.1$
H–C(1,3)	7.365	*d*, $^3J(H-C(2)) = 3.9$	*d*, $^1J(C(1,3)) = 166.4$
C(2)	132.31[g])	*dt*, $^1J(H) = 162.5$, $^2J(H-C(1,3)) = 4$	*d*, $^2J(C(3a)) = 4.0$
H–C(2)	7.670	*t*, $^3J(H-C(1,3)) = 3.9$	*d*, $^1J(C(2)) = 162.5$
C(3a,8a)	136.05[h])	narrow *m*	$d + d$, $^2J(C(1)) = 10.0$, $^2J(C(2)) = 4.0$
C(4,8)	145.41	*q*, $^2J(CH_3) = 5.6$	
CH_3–C(4,8)	24.97	*qd*, $^1J(H) = 127.6$, $^3J(H-C(5,7)) = 7.0$	
CH_3–C(4,8)	2.893	*s*	
C(5,7)	126.95	*d*, *sept.*-like; $^1J(H) = 151.8$	
H–C(5,7)	7.079	*s*	
C(6)	146.00	*q*, $^2J(CH_3) = 5.9$	
CH_3–C(6)	28.63	*qt*, $^1J(H) = 126.3$, $^3J(H-C(5,7)) = 6.2$	
CH_3–C(6)	2.644	*s*	

[a]) For reported data and assignment, see also [26] [27].
[b]) ^{1}H-NMR at 300 MHz; ^{13}C-NMR at 150 MHz.
[c]) $\delta(^{13}C)$ from **20** with natural abundance of ^{13}C.
[d]) ^{13}C-NMR Multiplicities and coupling constants from **20** with natural abundance of ^{13}C.
[e]) ^{1}H and ^{13}C multiplicities and coupling constants from the 2:2:1 mixture [1,3a-$^{13}C_2$]-**20**/[2,3a-$^{13}C_2$]-**20**/[1,3-$^{13}C_2$]-**20**.
[f]) δ(C(1,3)) of [1,3-$^{13}C_2$]-**20**: 115.960 ppm; δ(C(1,3)) of [1,3a-$^{13}C_2$]-**20** and of [1-^{13}C]-**20**: 115.963 ppm.
[g]) δ(C(2)) of [2,3a-$^{13}C_2$]-**20**: 132.316 ppm; δ(C(2)) of [2-^{13}C]-**20**: 132.314 ppm.
[h]) δ(C(3a)) of [1,3a-$^{13}C_2$]-**20**: 136.064 ppm; δ(C(3a)) of [2,3a-$^{13}C_2$]-**20**: 136.066 ppm; δ(C(3a)) of [3a-^{13}C]-**20**: 136.069 ppm.

signals is in perfect agreement with the expected statistical 1:2 ratio of [1,3-$^{13}C_2$]-**20**/[1,3a-$^{13}C_2$]-**20**. In the region of C(2), one can recognize the *d* of [2,3a-$^{13}C_2$]-**20** at 132.316 ppm with $J = 4.0$ Hz. Between the *d* lines appears the *s* of [2-^{13}C]-**20** of natural abundance. The slightly unsymmetric position of this *s* at 132.314 ppm is again due to a small isotope effect of the chemical shift of C(2) in [2,3a-$^{13}C_2$]-**20** and [2-^{13}C]-**20**. The region of C(3a,8a) can unequivocally be interpreted as the superposition of the *d* of equal intensities of C(3a) of [1,3a-$^{13}C_2$]-**20** (^2J(C(1),C(3a)) = 10.0 Hz) and of [2,3a-$^{13}C_2$]-**20** (^2J(C(2),C(3a)) = 4.0 Hz). The slightly unsymmetrically placed *s* at 136.069 ppm at the center of the two *d* belongs to C(3a,8a) of [3a-^{13}C]-**20** of natural abundance. The isotopic shifts of C(3a) in [1,3a-$^{13}C_2$]-**20** and [2,3a-$^{13}C_2$]-**20** amount to −0.005 and −0.003 ppm, respectively (*cf. Table 1*). The equal intensities of the *d* for C(3a) show that the two isotopomers [1,3-$^{13}C_2$]-**20** and [2,3-$^{13}C_2$]-**20** occur in the mixture in an equal amount, *i.e.*, the statistically expected 2:2:1 ratio fo all three isotopomers is reflected in the signal intensities of their labelled ^{13}C-atoms. The mass-spectrometrically determined content of [$^{13}C_2$]-**20** in **20** amounted to 25.5% in very good agreement with the three-fold dilution, carried out at the stage of 1,3-dibromo[1,3-$^{13}C_2$]propane.

The *Vilsmeier* formylation of the 2:2:1 mixture gave the corresponding 4,6,8-trimethyl[$^{13}C_2$]azulene-1-carbaldehydes (*cf.* [9]) in 90% yield. The mixture of aldehydes was not further characterized but just reduced with B_2H_6 to the isotopically isomeric

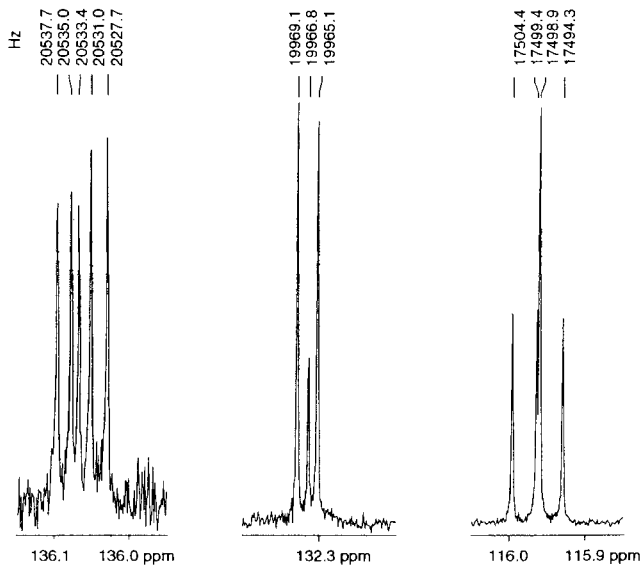


Fig. 1. *^{1}H-Decoupled ^{13}C-NMR spectrum* (150.904 MHz; $CDCl_3$) *of the 2:2:1 mixture [1,3a-$^{13}C_2$]-***20***/[2,3a-$^{13}C_2$]-***20***/[1,3-$^{13}C_2$]-***20**. Regions: from right to left: C(1,3), C(2), and C(3a,8a).

mixture of 1,4,6,8-tetramethyl[$^{13}C_2$]azulenes ([$^{13}C_2$]-**5**; *cf. Scheme 8*). The ^{1}H- and ^{13}C-NMR data of **5** and the observed $^2J(^{13}C,^{13}C)$ values, taken from the 1:1:1:1 mixture of the isotopomers of [$^{13}C_2$]-**5**, are presented in *Table 2*. *Fig. 2* shows the expanded regions of C(1), C(2), C(3), C(3a), and C(8a) in the highly resolved and ^{1}H-decoupled ^{13}C-NMR spectrum of this mixture. The unsymmetric substitution of **5** causes for its isotopomers in all five labelled positions almost 1:1 superpositions of *d*. ^2J(C(1),C(3)) value of 1.2–1.3 Hz is as expected very small, and in the region of C(1) and C(3) one of the *d* lines coincides with the signal of [1-^{13}C]-**5** and [3-^{13}C]-**5**, respectively, of natural abundance. In the regions of C(2), C(3a), and C(8a) (*cf. Fig. 2*), the central *s* is caused by the corresponding signals of [2-^{13}C]-**5**, [3a-^{13}C]-**5**, and [8a-^{13}C]-**5** of natural abundance. All *d* exhibit an almost equal intensity according to the statistical 1:1:1:1 ratio of the said isotopomers. In all cases, small isotopic shifts in the order of (0.003 ± 0.001) ppm (*cf. Footnotes* in *Table 2*) are observed, well recognizable by the slightly unsymmetrical position of the *s* of the corresponding C-atoms of natural abundance (*cf. Fig. 2*). The mass-spectrometric analysis of the mixture of the [$^{13}C_2$]-**5** isotopomers gave an average ^{13}C content of 17–20%[6]).

Thermal Reaction of the Isotopically Isomeric Mixture of 1,4,6,8-Tetramethyl-[$^{13}C_2$]azulene with ADM. It was performed as reported in [9]. The isotopically isomeric mixture of [$^{13}C_2$]-**5** was heated in 0.05M solution in dry tetralin with a four-fold molar amount of ADM for 2 h at 200°. The chromatographic workup by prep. TLC on silica gel with hexane/Et_2O 1:1 gave 19% of the heptalene-4,5-dicarboxylate **6b**, 22% of the heptalene-1,2-dicarboxylate **6a**, and, finally, 18% of the corresponding azulene-1,2-dicarboxylate **7** (*cf. Scheme 2*). The dicarboxylate **6a** was recrystallized from Et_2O/hexane

[6]) Unfortunately, the mass spectra of **5** and its isotopomeric mixture were not recorded under identical experimental conditions. Therefore, the found ^{13}C content represents only an approximate value.

and further investigated by mass and NMR spectroscopy. The analysis of the $M^{+\cdot}$, $[M - Me]^+$, and $[M - Me - MeOH]^+$ regions in the mass spectrum gave in comparison to non-labelled **6a** [9] an average $[^{13}C_2]$ content of 23%, in good agreement with the 1:3 dilution of the synthesized 1,3-dibromo[1,3-$^{13}C_2$]propane (*cf. Scheme 10*) as well as of the measured $[^{13}C_2]$ content of $[^{13}C_2]$-**20** and $[^{13}C_2]$-**5**.

Table 2. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$) *of 1,4,6,8-Tetramethylazulene* (**5**)[a]) *and Its Doubly ^{13}C-Labelled Isotopomers*[b])

Atom	δ [ppm][c])	Signal multiplicities and coupling constants [Hz]	
		A[d])	B[e])
C(1)	126.81[f])	narrow *m*, $^2J(Me) \approx 6$	$d + d$, $^2J(C(3)) = 1.3$, $^2J(C(3a)) = 10.7$
CH_3–C(1)	19.67	br. *q*, $^1J(H) = 126.3$, $^2J(H{-}C(2)) \leq 4$	
CH_3–C(1)	2.557	*s*	
C(2)	136.53[g])	br. *d*, $^1J(H) = 160.9$	$d + d$, $^2J(C(3a)) = 3.6$, $^2J(C(8a)) = 5.7$
H–C(2)	7.438	*d*, $^3J(H{-}C(3)) = 3.9$	
C(3)	114.65[h])	*dd*, $^1J(H) = 166.6$, $^2J(H{-}C(2)) = 3.7$	$d + d$, $^2J(C(1)) = 1.2$, $^2J(C(8a)) = 9.1$
H–C(3)	7.251	*d*, $^3J(H{-}C(2)) = 3.9$	
C(3a)	136.73[i])	narrow *m*, $^3J(H{-}C(5)) \approx 7.5$, $^3J(Me{-}C(4)) \leq 4$	$d + d$, $^2J(C(1)) = 10.7$, $^2J(C(2)) = 3.6$
C(4)	145.01	br. *s*, $^2J(Me) \leq 7$	
CH_3–C(4)	25.42	*qd*, $^1J(H) = 127.2$, $^3J(H{-}C(5)) = 6.3$	
CH_3–C(4)	2.813	*s*	
C(5)	125.73	*dm*[j]), $^1J(H) = 151.7$, $^3J(H{-}C(7)) \leq 7$	
H–C(5)	6.86[k])	*s*	
C(6)	145.85	narrow *m*, $^2J(Me) \leq 7.5$	
CH_3–C(6)	28.44	*qt*, $^1J(H) = 126.9$, $^3J(H{-}C(5,7)) \leq 6$	
CH_3–C(6)	2.560	*s*	
C(7)	127.75	*dm*[j]), $^1J(H) = 150.7$, $^3J(H{-}C(5)) \leq 7$	
H–C(7)	6.864[k])	*s*	
C(8)	147.16	narrow *m*, $^2J(Me) \leq 7.5$	
CH_3–C(8)	27.66	*qd*, $^1J(H) = 127.3$, $^3J(H{-}C(7)) = 6.6$	
CH_3–C(8)	3.022	*s*	
C(8a)	132.93[l])	narrow *m*, $^3J(H{-}C(2,3,7)) \leq 7$, $^3J(Me{-}C(1,8)) \leq 5$	$d + d$, $^2J(C(2)) = 5.7$, $^2J(C(3)) = 9.1$

[a]) See also [28].

[b]) ^{1}H-NMR at 300 MHz; ^{13}C-NMR at 150 MHz.

[c]) $\delta(^{13}C)$ from **5** with natural abundance of ^{13}C.

[d]) ^{13}C-NMR Multiplicities and coupling constants from **5** with natural abundance of ^{13}C.

[e]) ^{13}C-NMR Multiplicities and coupling constants from the ^{1}H-decoupled spectrum of the 1:1:1:1:1 mixture [1,3-$^{13}C_2$]-**5**/[1,3a-$^{13}C_2$]-**5**/[2,3a-$^{13}C_2$]-**5**/[2,8a-$^{13}C_2$]-**5**/[3,8a-$^{13}C_2$]-**5**.

[f]) δ(C(1)) of [1,3-$^{13}C_2$]-**5**: 126.810 ppm; δ(C(1)) of [1,3a-$^{13}C_2$]-**5**: 126.812 ppm; δ(C(1)) of [1-$^{13}C_2$]-**5**: 126.814 ppm.

[g]) δ(C(2)) of [2,3a-$^{13}C_2$]-**5**: 136.531 ppm; δ(C(2)) of [2,8a-$^{13}C_2$]-**5**: 136.534 ppm; δ(C(2)) of [2-^{13}C]-**5**: 136.530 ppm.

[h]) δ(C(3)) of [1,3-$^{13}C_2$]-**5**: 114.649 ppm; δ(C(3)) of [3,8a-$^{13}C_2$]-**5**: 114.652 ppm; δ(C(3)) of [3-^{13}C]-**5**: 114.653 ppm.

[i]) δ(C(3a)) of [1,3a-$^{13}C_2$]-**5**: 136.726 ppm; δ(C(3a)) of [2,3a-$^{13}C_2$]-**5**: 136.727 ppm; δ(C(3a)) of [3a-^{13}C]-**5**: 136.729 ppm.

[j]) Narrow *m* lines.

[k]) Taken from the ^{1}H,^{13}C long-range correlated spectrum at 600 MHz. The ^{1}H-NMR spectra show a br. *s* for H–C(5,7).

[l]) δ(C(8a)) of [2,8a-$^{13}C_2$]-**5**: 132.931 ppm; δ(C(8a)) of [3,8a-$^{13}C_2$]-**5**: 132.928 ppm; δ(C(8a)) of [8a-^{13}C]-**5**: 132.933 ppm.

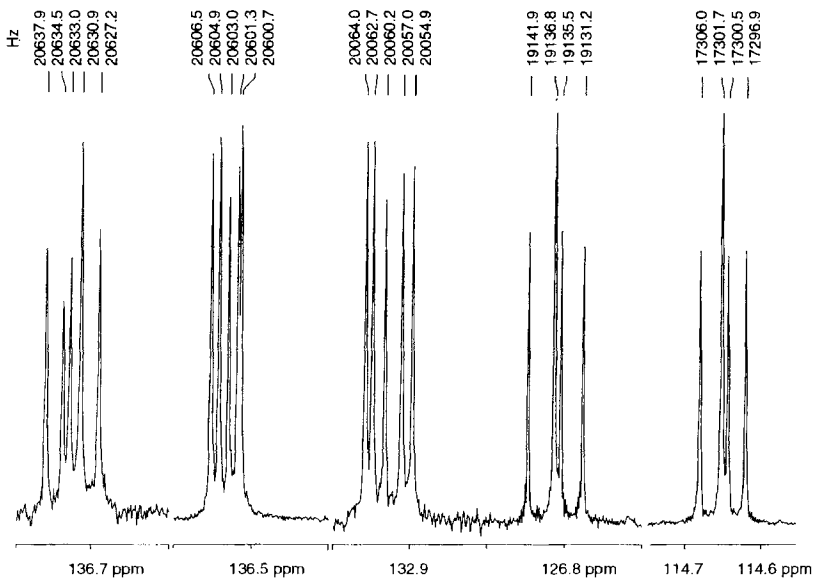


Fig. 2. *^{1}H-Decoupled ^{13}C-NMR spectrum* (150.904 MHz; $CDCl_3$) *of the 1:1:1:1:1 mixture [1,3-$^{13}C_2$]-**5**/[1,3a-$^{13}C_2$]-**5**/[2,3a-$^{13}C_2$]-**5**/[2,8a-$^{13}C_2$]-**5**/[3,8a-$^{13}C_2$]-**5***.
Regions: from right to left: C(3), C(1), C(8a), C(2), and C(3a).

The ^{1}H-NMR spectrum of [$^{13}C_2$]-**6a** was identical with that of unlabelled **6a** (*cf. Table 3* and [9]). However, the ^{1}H-decoupled ^{13}C-NMR spectrum of [$^{13}C_2$]-**6a** showed clearly enhanced signal intensities for C(3), C(4), C(5), C(5a), and C(10a) as compared to unlabelled **6a** (*cf. Table 3* and [29]). *Fig. 3* shows the range of 146–138 ppm, wherein C(6),

Table 3. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$) *of Dimethyl 5,6,8,10-Tetramethylheptalene-1,2-dicarboxylate* (**6a**)[a])

Atom	δ [ppm][b])	Signal multiplicities and coupling constants [Hz][c])
C(1)	122.32	*d*, $^3J(H-C(3)) = 9.3$
MeO*C*O–C(1)	167.75	*q*-like, $^3J(MeO-CO) \approx 3.9$
*C*H$_3$OCO–C(1)	52.03	*q*, $^1J(H) = 147.0$
CH$_3$OCO–C(1)	3.691	*s*
C(2)	131.31	*d*, $^3J(H-C(4)) = 7.8$
MeOCO–C(2)	167.55	*quint.*-like, $^3J(MeO-CO) = {}^3J(H-C(3)) \approx 7$
*C*H$_3$OCO–C(2)	51.90	*q*, $^1J(H) = 146.7$
CH$_3$OCO–C(2)	3.706	*s*
C(3)	139.18	*d*, $^1J(H) = 158.6$
H–C(3)	7.525	*dq*, $^3J(H-C(4)) = 5.9$, $^5J(Me-C(5)) = 1$
C(4)	125.94	*dq*, $^1J(H) = 159.0$, $^3J(Me-C(5)) = 5.9$
H–C(4)	6.269	*dq*, $^3J(H-C(3)) = 5.9$, $^4J(Me-C(5)) = 1.4$
C(5)	143.12	*quint.*-like, $^2J(Me-C(5)) \approx {}^3J(H-C(3)) \approx 7$[d])
*C*H$_3$–C(5)	23.48	*dq*, $^1J(H) = 127.9$, $^3J(H-C(4)) \approx 6.0$
CH$_3$–C(5)	2.002	*t*-like, $^4J(H-C(4)) \approx {}^5J(H-C(3)) \approx 1$
C(5a)	130.43[e])	*m*
C(6)	145.64	*dq*
*C*H$_3$–C(6)	18.35	*qd*, $^1J(H) = 127.9$, $^3J(H-C(7)) \approx 3.5$
CH$_3$–C(6)	1.744	*s*

Table 3 (cont.)

Atom	δ [ppm][b])	Signal multiplicities and coupling constants [Hz][c])
C(7)	130.21	*d*, *sext.*-like, $^1J(H) = 159.0$, $^3J(H-C(9)) \approx {}^3J(Me-C(8))$
H–C(7)	6.145	br. *s*
C(8)	125.49	*quint.*-like, $^2J(H-C(9)) \approx {}^2J(Me-C(8)) \approx 6$
CH_3–C(8)	25.07	*qd*, $^1J(H) = 127.9$, $^3J(H-C(7)) \approx 7$, $^3J(H-C(9)) \approx 3.5$
CH_3–C(8)	1.962	*d*-like, $^4J(H-C(7)) \approx 1.3$
C(9)	129.13	*dquint.*-like, $^1J = 159.0$, $^3J(Me-C(10)) \approx {}^3J(H-C(7))$
H–C(9)	6.010	br. *s*
C(10)	139.47	*q*, $^2J(Me-C(10)) = 6.1$
CH_3–C(10)	22.03	*qd*, $^1J(H) = 127.9$, $^3J(H-C(9)) \approx 7$
CH_3–C(10)	2.043	*d*-like, $^4J(H-C(9)) \approx 1.2$
C(10a)	130.46[e])	*m*

[a]) ^{1}H-NMR at 400 MHz [9]; ^{13}C-NMR at 150 MHz (see also [28]).

[b]) $\delta(^{13}C)$ from **6a** with natural abundance of ^{13}C.

[c]) ^{13}C-NMR Multiplicities and coupling constants from the H-coupled spectrum of **6a** with ^{13}C of natural abundance.

[d]) Selective irradiation of Me–C(5) at 2.002 ppm causes for C(5) a *d* with $^3J(H-C(3)) = 7.7$ Hz.

[e]) δ for C(5a) and C(10a) may be interchanged.

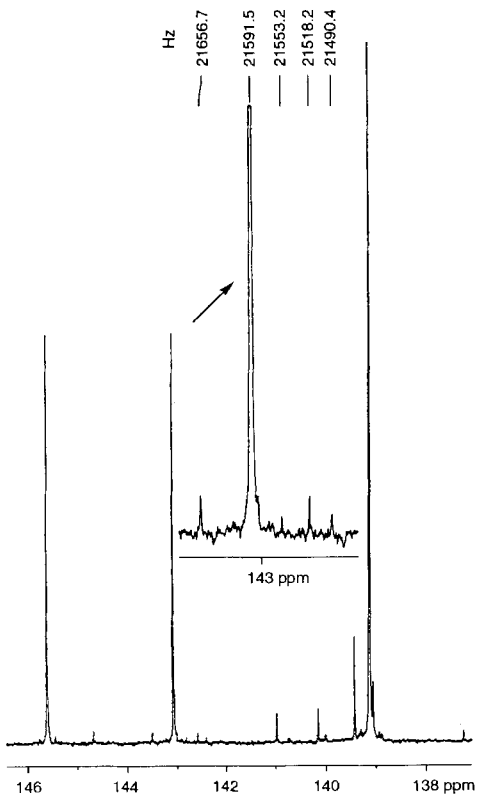


Fig. 3. *^{1}H-Decoupled ^{13}C-NMR spectrum* (150.904 MHz; $CDCl_3$) *of the isotopically isomeric mixture of [$^{13}C_2$]-***6a**: *range of C(6), C(5), C(10), and C(3).* The insert shows the enhanced signal of C(5).

C(5), C(10), and C(3) appear, and the insert of the enhanced signal of C(5) which emerges in the ^{1}H-coupled ^{13}C-NMR spectrum as a *quint.*-like signal at 143.08 ppm. It couples with Me–C(5) and H–C(3). Selective irradiation of Me–C(5) at 2.002 ppm reduces the signal of C(5) to a *d* with $^3J(H–C(3)) = 7.7$ Hz, *i.e.*, the signal of C(5) is unequivocally assignable in the ^{13}C-NMR spectrum of **6a**. The insert of the enhanced signal of C(5) shows that there are no lines of a *d* recognizable in a distance of 30 Hz, on the left and right from the *s* at 21591.5 Hz (143.081 ppm). Therefore, a *d* with $^1J(^{13}C,^{13}C) \approx 60$ Hz, which would be indicative for the presence of [5,5a-$^{13}C_2$]-**6a** (*cf. Scheme 9*) in the mixture of isotopomers of [$^{13}C_2$]-**6a**, can at best be buried in the noise of the spectrum. Since the signal/noise ratio of the enhanced C(5) region is ≥ 100, and because there are only two isotopomers in the mixture, which carry ^{13}C-atoms in position 5, namely [3,5-$^{13}C_2$]-**6a** and [5,10a-$^{13}C_2$]-**6a**, the migratory ratio of C(10)/C(11) in the primary tricyclic intermediate [7,11-$^{13}C_2$]-**8** must be > 25 (*cf. Scheme 6*). In other words, the upper limit for the presence of [5,5a-$^{13}C_2$]-**6a** in the mixture of isotopomers of [$^{13}C_2$]-**6a** is 4% under the applied analytical conditions, *i.e.*, the migration of C(11) in the tricyclic intermediates **2** plays no role in the formation of the heptalene precursors **3** at 200° in tetralin (*cf. Scheme 1*).

Indeed, a concerted migration of C(10) or C(11) to C(7) in the tricyclic intermediates of type **2** would correspond to a sigmatropic [1,7]-C shift which would be thermally 'allowed' only in the [1a,7s] mode. However, the *a* mode of C(10) or C(11) in a geometric 1,2 migration is impossible in the perfectly flat cycloheptatriene substructure [4] [5] due to steric reasons. The complete cleavage of the involved C(1)–C(10) or C(1)–C(11) bond has, therefore, to occur before bond formation between C(7)–C(10) or C(7)–C(11) can take place. We have already shown (see [4] as well as [5]) that the heterolysis of the C(1)–C(10) bond, which is strongly favored by the MeOCO substituent at C(10), has to compete with the apolar homolysis of the C(1)–C(10) bond, which induces the concomitant homolysis of the C(8)–C(9) bond, *i.e.*, the concerted *retro-Diels-Alder* reaction to the starting materials **1** and ADM (*cf. Scheme 1*). An H-atom or an alkyl substituent at C(11) will at best favor the homolysis of the C(1)–C(11) bond in **2** which, in turn, will prompt the concomitant cleavage of the C(8)–C(12) bond, *i.e.*, again a concerted *retro-Diels-Alder* reaction that leads, in this case, to the formation of the corresponding azulene-1,2-dicarboxylates. The formation of azulene-1,2-dicarboxylates always accompanies the purely thermal (*e.g. Scheme 2*) or transition-metal-catalyzed (*cf.* [2]) formation of heptalene-dicarboxylates from azulenes and ADM and may become dominant in cases, where the C(1)–C(11) bond is weakened by sterically overcrowded substituents (*cf.* [2]) or radical-stabilizing substituents at C(11) [29]. The situation will be discussed in more detail in a later communication [5].

We thank Prof. *M. Hesse* and his coworkers for mass spectra, Prof. *W. von Philipsborn* and his coworkers for NMR support, especially in memory of the late Dr. *R. Hollenstein* who measured the high-resolution ^{13}C-NMR spectra. The financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. See [4] [30].

1. Synthesis of the 2:2:1 Mixture of 4,6,8-Trimethyl[1,3a-$^{13}C_2$]-, -[2,3a-$^{13}C_2$]-, and -[1,3-$^{13}C_2$]azulene ([1,3a-$^{13}C_2$]-20, [2,3a-$^{13}C_2$]-20, and [1,3-$^{13}C_2$]-20). – 1.1. *2-(Trimethylsilyl)-[1-^{13}C]acetic Acid* (*cf.* [19]). (Chloromethyl)trimethylsilane (12.32 g, 0.100 mol) and activated Mg (2.55 g, 0.107 mol[7]) were reacted in THF (250 ml) to

yield the corresponding *Grignard* reagent. After 3 h stirring at 25°, the *Grignard* soln. was cooled with liquid N_2. In a closed apparatus, $^{13}CO_2$ (liberated from 20.20 g (0.101 mol) $Ba^{13}CO_3$[8]) with conc. H_2SO_4 (100 ml) and passed through basic Al_2O_3) was condensed on the surface of the *Grignard* soln. The carboxylation starts, when the reaction mixture is warmed up to 25°. The cooling and warm-up procedure was repeated twice in the closed apparatus. Thereafter, the mixture was poured on to chopped ice (50 g) and carefully neutralized with 1N HCl until the pH value reached 4.5[9]). The neutralized mixture was extracted with Et_2O (3 × 40 ml). The combined Et_2O phases were dried ($MgSO_4$). Et_2O was removed and the residue dried at 0.04 Torr over P_2O_5 during 18 h. 2-(Trimethylsilyl)[1-^{13}C]acetic acid (8.97 g; 67% with respect to $Ba^{13}CO_3$) was obtained in colorless, in the air liquifying crystals. IR ($CHCl_3$): 3000 (very br., OH), 1670 (sh), 1646, 922. ^{1}H-NMR ($CDCl_3$): 9.21 (br. *s*, OH); 1.88 (*d*, $^2J(H,^{13}C) = 7.1$, CH_2); 0.12 (*s*, Me_3Si).

1.2. *Diethyl [1,3-$^{13}C_2$]Malonate* (*cf.* [19]). At 0°, BuLi in hexane (116 ml of a 1.47M solution; 0.170 mol) was added to $(i\text{-}Pr)_2NH$ (LDA; 17.8 g, 0.183 mol) in THF (50 ml). This LDA soln. was passed through a cannula into a soln. of 2-(trimethylsilyl)[1-^{13}C]acetic acid (8.97 g, 0.097 mol) in THF (250 ml). The presence of Ph_3CH as indicator guaranteed for a stoichiometric reaction. On reaction with LDA, the soln. of the acid in THF became first milky, then transparent, and finally reddish. The soln. was stirred for 3 h at 25° to complete the formation of the bislithio derivative of the acid. The carboxylation of this derivative with $^{13}CO_2$ (liberated from 13.34 g (0.067 mol) $Ba^{13}CO_3$ with conc. H_2SO_4 (100 ml)) was performed as described (see *1.1*). The mixture was poured on to ice (100 g), acidified (pH 1) with 15% HCl, saturated with NaCl, and continuously extracted with Et_2O during 25 h. Et_2O was removed, and the yellow residue dissolved in dry EtOH (25 ml). After addition of a catalytic amount of TsOH and $CHCl_3$ (500 ml), the soln. was heated under reflux in a water separator during 30 h. The excess of EtOH and $CHCl_3$ was distilled off and the residue subjected to a bulb-to-bulb distillation (100°/0.04 Torr) to give pure diethyl [1,3-$^{13}C_2$]malonate (4.31 g; 40%with respect to $Ba^{13}CO_3$). IR (film): 1706, 1696 (sh). ^{1}H-NMR ($CDCl_3$): 4.20 (*dq*, $^3J(CH_2CH_3) = 7.1$, $^3J(CH_2O,^{13}C) = 3.2$, 2 MeCH_2O); 3.36 (*t*, $^2J(CH_2,^{13}C) = 7.5$, CH_2); 1.28 (*t*, $^3J(CH_2CH_3) = 7.1$, 2 $MeCH_2O$).

1.3. *[1,3-$^{13}C_2$]Propane-1,3-diol* (*cf.* [19] [31]). A soln. of diethyl [1,3-$^{13}C_2$]malonate (4.31 g, 0.027 mol) in Et_2O (150 ml) was dropped within 1 h into a soln. of $LiAlH_4$ (4.6 g, 0.114 mol) in Et_2O (600 ml). Thereafter, the mixture was heated for 3 h at reflux and then hydrolyzed in the following manner (see [31] [32]): after cooling to 0°, the mixture was treated with H_2O (4.6 ml), 15% NaOH (4.6 g), and again, H_2O (13.8 ml). The white precipitate was extracted with CH_2Cl_2 for 30 h in a *Soxhlet* apparatus. The CH_2Cl_2 was distilled off and the residue combined with the Et_2O phase of the hydrolyzed reaction mixture. After removal of the solvent (r.e.), the residue was subjected to bulb-to-bulb distillation (100°/0.08 Torr): 1.23 g (60%) of [1,3-$^{13}C_2$]propane-1,3-diol. ^{1}H-NMR ($CDCl_3$): 3.83 (*dtd*, $^1J(H,^{13}C) = 114.5$, $^3J(H,H) = 5.5$, $^3J(H,^{13}C) = 4.0$, $CH_2(1,3)$); 3.0 (br. *s*, 2 OH); 1.80 (*quint.t*, $^3J(H,H) = 5.5$, $^2J(H,^{13}C) = 4.0$, $CH_2(2)$).

1.4. *1,3-Dibromo[1,3-$^{13}C_2$]propane* (*cf.* [19]). To a mixture of 48% HBr (6.74 g, 40 mmol) and conc. H_2SO_4 (2.05 g) was added slowly [1,3-$^{13}C_2$]propane-1,3-diol (1.23 g, 16.2 mmol), followed by conc. H_2SO_4 (3.25 g). The dark mixture was heated for 6 h at reflux. Thereafter, the dibromo compound was distilled off over 2 h and at a bath temp. of 170°. The org. phase of the distillate was separated from the aq. phase, washed with H_2O (2 ml), conc. H_2SO_4 (2 ml), and 5% aq. Na_2CO_3, and then dried ($CaCl_2$). The dried dibromopropane was taken up in CH_2Cl_2, the $CaCl_2$ washed with CH_2Cl_2, and CH_2Cl_2 removed by distillation. The residue was purified by bulb-to-bulb distillation (100°/20 Torr) to yield 2.54 g (78%) of the dibromo compound. ^{1}H-NMR ($CDCl_3$): 3.57 (*dt*, $^1J(H,^{13}C) = 152.4$, $^3J(H,H) = 6.2$, $CH_2(1,3)$); 2.36 (*quint.t*, $^3J(H,H) = 6.2$, $^2J(H,^{13}C) = 3.7$, $CH_2(2)$).

1.5. *[2,4-$^{13}C_2$]Glutarodinitrile* (*cf.* [19]). 1,3-Dibromo[1,3-$^{13}C_2$]propane (2.06 g) was diluted with unlabelled material (6.11 g) and the whole amount (40.4 mmol) dissolved in MeCN (50 ml). 18-Crown[6] (0.10 g) and KCN (11.0 g, 169 mmol; dried in high vacuum) were added, and the mixture was heated at 83° for 27 h under strong stirring. The mixture was filtered and H_2O (30 ml) added. The aq. phase was extracted with CH_2Cl_2 (3 × 15 ml). The org. layers were combined and dried ($CaCl_2$). Evaporation of the solvents gave crude dinitrile which was subjected to bulb-to-bulb distillation (70°/0.04 Torr) to yield the pure compound (3.75 g; 93%). ^{1}H-NMR ($CDCl_3$): 2.51 (*dtd*, $^1J(H,^{13}C) = 134.8$, $^3J(H,H) = 7.0$, $^2J(H,^{13}C) = 5.5$, 0.25 H, $CH_2(2,4)$); 2.51 (*t*, $^3J(H,H) = 7.0$, 0.75 H, $CH_2(2,4)$); 1.99 (*quint.t*, $^3J(H,H) = 7.0$, $^2J(H,^{13}C) = 5.5$, 0.25 H, $CH_2(3)$); 1.99 (*quint.*, $^3J(H,H) = 7.0$, 0.75 H, $CH_2(3)$).

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[7]) Activated with $C_2H_4Br_2$.

[8]) *ICN*; ^{13}C content: 98%.

[9]) Preliminary experiments with non-labelled CO_2 had shown that the best yields of (trimethylsilyl)acetic acid were obtained at pH 4.5 and not at pH 6 [31].

1.6. *Diethyl [2,4-$^{13}C_2$]Glutarate* (*cf.* [19]). The labelled dinitrile (3.75 g, 39.8 mmol) was heated with NaOH (6.08 g, 148 mmol) in EtOH/H_2O (5 ml/18.5 ml) at 100° for 12 h. Workup and extraction with Et_2O (3 × 20 ml) gave, after removal of Et_2O, the glutaric acid (3.19 g, 61%) in colorless crystals (IR ($CHCl_3$): 3000 (very br. OH), 1712). The acid was dissolved in EtOH/$CHCl_3$ (10 ml/300 ml) and heated at reflux in the presence of a catalytic amount (0.03 g) of TsOH in a water separator. The solvents were removed by distillation and the residue purified by bulb-to-bulb distillation (140°/20 Torr) to yield 3.36 g (74%) of the glutarate. ^{1}H-NMR ($CDCl_3$): 4.13 (*q*, $J(CH_2CH_3) = 7.2$, 2 MeCH_2O); 2.36 (*dtd*, $^1J(H,^{13}C) = 128.0$, $^3J(H,H) = 7.4$, $^3J(H,^{13}C) = 4.3$, 0.25 H, CH_2(2,4)); 2.36 (*t*, $^3J(H,H) = 7.5$, 0.75 H, CH_2(2,4)); 1.94 (*quint.t*, $^3J(H,H) = 7.4$, $^2J(H,^{13}C) = 4.5$, 0.25 H, CH_2(3)); 1.94 (*quint.*, $^3J(H,H) = 7.4$, 0.75 H, CH_2(3)); 1.25 (*t*, $J(CH_2CH_3) = 7.2$, 2 *Me*CH_2O). CI-MS: 191 (22, $[M + 3]^+$), 192 (11, $[M + 2]^+$), 189 (95, $[M + 1]^+$), 163 (7), 162 (3), 161 (28), 147 (2), 146 (2), 145 (23), 144 (9), 143 (100), 117 (5), 116 (3), 114 (4), 89 (2), 88 (1), 87 (7).

1.7. *1,2-Bis(trimethylsilyloxy)[3,5-$^{13}C_2$]cyclopent-1-ene* (**21**) (*cf.* [19]). Na (1.85 g, 80 mmol) was finely dispersed in toluene (100 ml) at 115° under O_2-free N_2. At this temp., a mixture of the glutarate (3.36 g, 17.9 mmol) and Me_3SiCl (10.63 g, 98 mmol) in toluene (20 ml) was added dropwise under strong stirring. The mixture was heated for 5 h at 115°. After 2 h, the color of the mixture became blue-violet. After cooling, salts were removed by filtration and washed with toluene. The toluene was removed by distillation and the residue purified by bulb-to-bulb distillation (100–102°, 20 Torr) to yield a strong smelling yellow liquid (3.30 g, 76%). Since **21** decomposed rapidly, it was just hydrogenated and acetylated (see *1.8*). IR ($CHCl_3$) of a non-labelled probe of **21**: 1750, 1713, 1624. ^{1}H-NMR ($CDCl_3$) of a non-labelled probe of **21**: 2.25 (*t*, $^3J(H,H) = 7.0$, CH_2(3,5)); 1.77 (*quint.*, $^3J(H,H) = 7.0$, CH_2(4)); 0.20 (*s*, 2 Me_3SiO).

1.8. *[3,5-$^{13}C_2$]Cyclopentane-1,2-diyl Diacetate* (**22**) (*cf.* [19]). Cyclopentene **21** (3.30 g, 13.5 mmol) was hydrogenated in cyclohexane (50 ml) at 100°/105 bar for 24 h in the presence of Rh(5%)/Al_2O_3 (0.227 g) and PtO_2 (0.01 g). The catalysts were removed by filtration, AcCl (25 ml) was added and the mixture stirred for 60 h at 25°. Cyclohexane, excess of AcCl and the formed Me_3SiCl were removed by distillation and the residue subjected to a bulb-to-bulb distillation (150°, 40 Torr). Compound **22** was obtained as a colorless liquid (2.34 g, 93%) and in a 4:1 ratio (see ^{1}H-NMR) of the *cis*- and the *trans*-form. Non-labelled probes of *cis*-**22** and *trans*-**22** were synthesized according to [21] and [22], resp. ^{1}H-NMR ($CDCl_3$) of the 4:1 mixture of labelled *cis*-**22** and *trans*-**22**: 5.11 (*m*, H–C(1,2) of *cis*-**22**); 5.02 (*m*, H–C(1,2) of *trans*-**22**); 2.02 (*s*, 2 MeOCO of *cis*-**22** and *trans*-**22**); 2.4–1.6 (*m*, CH_2(3,4,5) of *cis*-**22** and *trans*-**22**).

1.9. *Pyrolysis of* **22**. 1.9.1. *General Procedure. Principle:* Continuous gas-phase pyrolysis in an N_2 stream under reduced pressure in a quartz tube (*cf.* [25]). *Construction and Dimensions of the Apparatus:* Horizontal quartz tube of 430-mm length and 16-mm diameter, filled with short quartz tube cuts (length: 4–7 mm, diameter: 4–6 mm), and placed in a cylindrical oven (length: 300 mm, inner diameter: 18 mm) with open ends. The temp. was measured and regulated automatically (temp. variations: ±5° at 550°). A constant N_2 stream of 5–6 ml/min was secured by an appropriately dimensioned glass capillary. *Pyrolysis Procedure:* The substance is placed in an open ampoule in the cold part of the pyrolysis tube. The apparatus is closed and flushed with N_2. The two cooling traps at the exit of the oven are immersed in liquid N_2 and the apparatus evacuated, until the wanted pyrolysis pressure is attained. To allow and, as much as possible constant evaporation of the substance, the cold end of the quartz tube is warmed with a heating tape. After pyrolysis, the apparatus is flushed with N_2 and the content of the warmed-up cooling traps dissolved in the appropriate solvent.

1.9.2. *Example of a Pyrolysis of* **22**. The diacetate **22** (2.34 g, 12.6 mmol) was placed in an ampoule in the cold part of the quartz tube. After a constant N_2 pressure of 60 Torr was attained the oven was heated to 550 ± 5°. Heating of **22** in the cold end of the quartz tube to 150° led to a gentle evaporation of **22** within 1 h through the filled tube. The pyrolysate was collected in two cooling traps, connected in series and immersed in liquid N_2. The cooling traps were warmed to r.t. and the content dissolved and washed out with THF. The THF soln. was passed over a column, filled with basic Al_2O_3, in order to remove H_2O and the formed AcOH. The so prepared THF soln. of cyclopentadiene was used for the formation of sodium cyclopentadienide.

1.10. *Reaction of Sodium [1,3-$^{13}C_2$]Cyclopentadienide with 2,4,6-Trimethylpyrylium Tetrafluoroborate.* The purified pyrolysate of the 4:1 mixture of *cis*- and *trans*-[3,5-$^{13}C_2$]-**22** (2.34 g, 12.6 mmol) in THF (40 ml) was dropped to a Na suspension (0.27 g, 11.7 mmol; from Na suspension (45%) in paraffin oil, after washing with hexane) in THF (30 ml) within 15 min. Stirring at 25° was continued for 40 min. The color of the mixture became light-brown. It was warmed to 42°. 2,4,6-Trimethylpyrylium tetrafluoroborate (0.97 g, 4.63 mmol) [17] was added under an intense stream of N_2 within 5 min. The azulene formation was at once recognizable by the change of the color from brown to deep blue. After additional stirring for 20 min at 25°, most of the THF was removed by distillation. MeOH (5 ml) and H_2O (15 ml) were added, and the aq. phase was extracted 3 times with hexane (in total 50 ml). The combined blue hexane phases were washed with H_2O (5 × 5 ml) and dried ($CaCl_2$). Hexane was

evaporated and the residue of [$^{13}C_2$]-**20** dried during 16 h at 0.04 Torr. Yield: 0.100 g (4.7% with respect to **22**). ^{1}H-NMR ($CDCl_3$; 300 MHz; *cf. Table 1*): 7.69 (*dt*, $^1J(H,^{13}C) = 162.6$, $^3J(2,1/3) = 3.9$, *ca.* 0.2 H, H–C(2)); 7.69 (*t*, $^3J(2,1/3) = 3.9$, *ca.* 0.8 H, H–C(2)); 7.38 (*dd*, $^1J(H,^{13}C) = 166.4$, $^3J(1/3,2) = 3.9$, *ca.* 0.44, H–C(1,3)); 7.38 (*d*, $^3J(1/3,2) = 3.9$, *ca.* 1.6 H, H–C(1,3)); 7.04 (br. *s*, H–C(5,7)); 2.90 (*s*, Me–C(4,8)); 2.66 (*s*, Me–C(6)). ^{13}C-NMR ($CDCl_3$; 150 MHz, ^{1}H-decoupled; *cf. Table 1* and *Fig. 1*): 147.10 (*s*, C(6)); 145.51 (*s*, C(4,8)); 136.07 (*d* + *d*, $^2J(1,3a) = 10.0$, $^2J(2,3a) = 4.0$, C(3a,8a)); 132.31 (*d*, $^2J(3a,2) = 4.0$, C(2)); 126.93 (*s*, C(5,7)); 155.95 (*d* + *s*, ratio 1:1, $^2J(3a,1) = 10.1$, C(1,3)); 28.39 (*s*, *Me*–C(6)); 25.01 (*s*, *Me*–C(4,8)); for isotopic shifts of [1,3a-$^{13}C_2$]-**20**, [2,3a-$^{13}C_2$]-**20**, and [1,3-$^{13}C_2$]-**20**, see *Table 1*. EI-MS: 172.2 (26.5, $[M + 2]^+$), 171.2 (22,7, $[M + 1]^+$), 170.2 (100, M^+), 157 (16, $[(M + 2) - Me]^+$), 156.0 (13, $[(M + 1) - Me]^+$), 155.1 (58, $[M - Me]^+$), 154 (13), 152 (14), 141 (8), 130 (8), 129 (12), 128 (17), 115 (14).

1.10.1. *Pyrolysis of* cis- *and* trans-**22** *and Formation of* **20**. When the reactions were performed under identical conditions with pure non-labelled *cis*-**22** (2.34 g) [21], a maximum yield of 5% of **20** was obtained. On the other hand, when pure non-labelled *trans*-**22** (2.34 g) [22] was the starting material, a maximum yield of only 1% of **20** could be realized.

2. Synthesis of the 1:1:1:1:1 Mixture of 1,4,6,8-Tetramethyl[1,3-$^{13}C_2$]-, -[1,3a-$^{13}C_2$]-, -[2,3a-$^{13}C_2$]-, -[2,8a-$^{13}C_2$]-, and -[3,8a-$^{13}C_2$]azulene ([1,3-$^{13}C_2$]-5, [1,3a-$^{13}C_2$]-5, [2,3a-$^{13}C_2$]-5, [2,8a-$^{13}C_2$]-5, and [3,8a-$^{13}C_2$]-5). – 2.1. *Formylation of the 2:2:1 Mixture [1,3a-$^{13}C_2$]-***20**/*[2,3a-$^{13}C_2$]-***20**/*[1,3-$^{13}C_2$]-***20**. The *Vilsmeier* reagent was prepared from freshly distilled DMF (0.4 ml, 5.2 mmol) and $POCl_3$ (0.14 g, 0.9 mmol) at 0°. The reagent was added with a syringe to a soln. of [$^{13}C_2$]-**20** (0.100 g, 0.59 mmol) in DMF (3 ml). The blue color of the soln. turned at once to red-brown. After 15 min stirring at 25°, the mixture was poured onto ice (10 g) and basified with 2N NaOH. The red oil was extracted with $CHCl_3$ (3 × 15 ml). The combined $CHCl_3$ phases were washed (3 × 15 ml H_2O) and dried ($MgSO_4$). The solvent was removed (r.e.) and the residue dried *in vacuo* (20 h at 0.04 Torr). The red carbaldehyde (0.104 g, 90%; *cf.* [9]) was reduced without further characterization.

2.2. *Reduction of 4,6,8-Trimethyl[$^{13}C_2$]azulene-1-carbaldehyde*. $NaBH_4$ (0.0064 g, 1.7 mmol) was suspended in diethyleneglycol dimethyl ether (diglyme; 1 ml), and solns. of the aldehyde (0.104 g, 0.52 mmol) in diglyme/Et_2O 1:1 (4 ml) as well as of $BF_3 \cdot OEt_2$ in Et_2O (2 ml) were simultaneously added through syringes within 20 min at 25°. The red color of the soln. of the aldehyde in diglyme turned at once to blue. The reduction was finished after 2 h stirring at r.t. (TLC (Et_2O/hexane 9:1; silica gel): R_f (aldehyde) 0.3 (red spot), R_f (**5**) 0.7 (blue spot)). The mixture was poured under cooling to a 1:1 mixture of Et_2O/H_2O (40 ml). The aq. phase was additionally extracted with Et_2O (3 × 20 ml). The combined Et_2O phases were washed with sat. NaCl soln. and dried ($MgSO_4$). The blue oil of [$^{13}C_2$]-**5** was, after the removal of Et_2O (r.e.), dried *in vacuo* (20 h at 0.04 Torr) to give 0.087 g (90%). ^{1}H-NMR ($CDCl_3$, 300 MHz; *cf. Table 2*): 7.44 (*d*, $^3J(2,3) = 3.9$, H–C(2)); 7.25 (*d*, $^3J(3,2) = 3.9$, H–C(3)); 6.85 (*s*, H–C(5,7)); 3.00 (*s*, Me–C(6)); 2.88 (*s*, Me–C(8)); 2.82 (*s*, Me–C(4)); 2.55 (*s*, Me–C(1)). ^{13}C-Satellite signals were not clearly recognizable. ^{13}C-NMR ($CDCl_3$; 150 MHz, ^{1}H-decoupled; *cf. Table 2* and *Fig. 2*): 147.01 (*s*, C(8)); 145.69 (*s*, C(6)); 144.86 (*s*, C(4)); 136.72 (*d* + *d*, $^2J(1,3a) = 10.7$, $^2J(2,3a) = 3.6$, C(3a)); 136.52 (*d* + *d*, $^2J(8a,2) = 5,7$, $^2J(3a,2) = 3.6$, C(2)); 132.92 (*d* + *d*, $^2J(3,8a) = 9.1$, $^2J(2,8a) = 5.7$, C(8a)); 127.67 (*s*, C(7)); 126.78 (*d* + *d*, $^2J(3,1) = 1.3$, $^2J(3a,1) = 10.7$, C(1)); 125.58 (*s*, C(5)); 114.64 (*d* + *d*, $^2J(1,3) = 1.2$, $^2J(8a,3) = 9.1$, C(3)); 28.36 (*s*, *Me*–C(6)); 27.56 (*s*, *Me*–C(8)); 25.34 (*s*, *Me*–C(4)); 19.67 (*s*, *Me*–C(1)); for isotopic shifts in [1,3-$^{13}C_2$]-**5**, [1,3a-$^{13}C_2$]-**5**, [2,3a-$^{13}C_2$]-**5**, [2,8a-$^{13}C_2$]-**5**, and [3a,8a-$^{13}C_2$]-**5**, see *Table 2*. EI-MS: 186.1 (16.5, $[M + 2]^+$), 185.1 (23, $[M + 1]^+$), 184.1 (100, M^+), 171.0 (18, $[M + 2 - Me]^+$), 170.0 (38, $[M + 1 - Me]^+$), 169.1 (89, $[M - Me]^+$), 167 (15), 166 (6), 165 (16), 157 (4), 156 (6), 155 (27), 154 (20), 153 (30), 152 (25), 143 (12), 142 (8), 141 (17), 130 (6), 129 (19), 128 (26), 127 (8), 116 (3), 115 (17). ^{13}C-NMR ($CDCl_3$; 150 MHz, ^{1}H-coupled) of non-labelled **5**: see *Table 2*.

3. Thermal Reaction of the 1:1:1:1:1 Mixture [1,3-$^{13}C_2$]-5/[1,3a-$^{13}C_2$]-5/[2,3a-$^{13}C_2$]-5/[2,8a-$^{13}C_2$]-5/[3,8a-$^{13}C_2$]-5 with Dimethyl Acetylenedicarboxylate (ADM) (*cf.* [9]). The isotopically isomeric mixture of [$^{13}C_2$]-**5** (0.087 g, 0.47 mmol) and ADM (0.25 ml; 1.91 mmol) were heated at 200° for 2 h under N_2 in tetralin (5 ml). The tetralin was removed by bulb-to-bulb distillation (50°/0.004 Torr). The black-blue residue was separated twice on a prep. TLC plate (20 × 20 cm) on silica gel with Et_2O/hexane 1:1. Three zones were isolated. The first one (orange; R_f 0.5) represented the heptalene-4,5-dicarboxylate **6b** (0.029 g, 19%), the second one (yellow; R_f 0.4) the heptalene-1,2-dicarboxylate **6a** (0.034 g, 22%), and the third one (blue; R_f 0.3) the azulene-1,2-dicarboxylate **7** (0.028 g, 18%). Compound **6a** was recrystallized from Et_2O/hexane and yielded pure yelow crystals (0.018 g). ^{1}H-NMR ($CDCl_3$; 300 MHz; *cf. Table 3* and [9]): 7.53 (*dq*-like, $^3J(4,3) = 5.9$, $^5J(Me–C(5),3) = 0.9$, H–C(3)); 6.28 (*dq*, $^3J(3,4) = 5.9$, $^4J(Me–C(5),4) = 1.4$, H–C(4)); 6.15 (br. *s*, H–C(7)); 6.02 (*quint.* like, $^4J(7,9) \approx {}^4J(Me–C(10),9) \approx 1.1$, H–C(9)); 3.71 (*s*, MeOCO–C(2)); 3.70 (*s*, MeOCO–C(1)); 2.05 (*d*, $^4J(9, Me–C(10)) = 1.2$, Me–C(10)); 2.01 (*t*-like, $^4J(4, Me–C(5)) \approx {}^5J(3, Me–C(5))$, $\Sigma\, {}^4J + {}^5J = 2.3$, Me–C(5)); 1.97

(*d*, ^4J(7, Me–C(8)) = 1.3, Me–C(8)); 1.75 (*s*, Me–C(6)). ^{13}C-Satellite signals could not be recognized unequivocally. ^{13}C-NMR ($CDCl_3$; 150 MHz, ^{1}H-decoupled; *cf. Table 3* and *Fig. 3* as well as [28]): 167.75 (C(1)); 167.55 (C(2)); 145.64 (C(6)); 143.12 (C(5)); 139.45 (C(10)); 139.18 (C(3)); 131.31 (C(2)); 130.46 (C(10a)); 130.43 (C(5a)); 130.21 (C(7)); 129.13 (C(9)); 125.95 (C(4)); 125.49 (C(8)); 122.32 (C(1)); 52.03 (*Me*OCO–C(1)); 51.90 (*Me*OCO–C(2)); 25.07 (*Me*–C(8)); 23.48 (*Me*–C(5)); 22.03 (*Me*–C(10)); 18.35 (*Me*–C(6)). The *s* of C(3), C(4), C(5), C(5a), and C(10a) showed enhanced intensities in comparison to the other *s* or comparable C-atoms (see also *Fig. 3*). EI-MS: 328.3 (18.6, $[M + 2]^{+\cdot}$), 327.3 (25.9, $[M + 1]^{+\cdot}$) 326.3 (100, $M^{+\cdot}$), 313.3 (6, $[(M + 2) - Me]^+$), 312.3 (8, $[(M + 1) - Me]^+$), 311.3 (27.7, $[M - Me]^+$), 281 (11, $[(M + 2) - Me - MeOH]^+$), 280 (13, $[(M + 1) - Me - MeOH]^+$), 279 (37, $[M - Me–MeOH]^+$), 269 (7, $[(M + 2) - MeOCO]^+$), 268 (8, $[M + 1) - MeOCO]^+$), 267 (28, $[M - MeOCO]^+$), 255 (12), 254 (27), 253 (15), 252 (28), 251 (18), 237 (16, $[(M + 2) - MeOCO - MeOH]^+$), 236 (16, $[(M + 1) - MeOCO - MeOH]^+$), 236 (13, $[(M + 1) - MeOCO - MeOH]^+$), 235 (29, $[M - MeOCO - MeOH]^+$, 228 (27, $[M - MeC{\equiv}CCOOMe]^+$), 209 (19, $[(M + 2) - MeOCO - MeOH - CO]^+$), 208 (28, $[(M + 1) - MeOCO - MeOH - CO]^+$), 207 (38, $[M - MeOCO - MeOH - CO]^+$), 197 (17), 196 (23), 195 (23), 194 (23), 193 (49) 192 (38), 191 (34), 189 (29), 186 (8, $[(M + 2) - ADM]^{+\cdot}$), 185 (11, $[(M + 1) - ADM]^{+\cdot}$), 184 (51, $[M - ADM]^{+\cdot}$), 180 (16), 179 (20), 178 (43), 169 (16), 168 (16), 167 (16), 166 (18), 165 (48).

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